Pan African Conference & Summit

IYCr 2014 Africa

UNIVERSITY OF THE FREE STATE
UNIVERSITEIT VAN DIE VRYSTAAT
YUNIVESITHI YA FREISTATA
UFS·UV
NATURAL AND AGRICULTURAL SCIENCES
NATUUR- EN LANDBOUWETENSKAPPE
CHEMISTRY
CHEMIE

science & technology
Department:
Science and Technology
REPUBLIC OF SOUTH AFRICA

2014
international year of crystallography
United Nations Educational, Scientific and Cultural Organization
International Union of Crystallography
Partners for the International Year of Crystallography 2014

IUCr

Book of Abstracts

12-17 October 2014

Bloemfontein, South Africa

Pan African and South African Meeting of the International Year of Crystallography (IYCr2014)

IYCr2014 Africa

CONFERENCE HANDBOOK

Programme – Information – Abstracts – Delegates

Website: www.ufs.ac.za/IYCr2014Africa

Table of contents

Programme

Programme

12-15 October 2014: IYCr2014Africa Conference

Sunday	**12 October**				**Title**
	12:00	17:30	Registration	Bains Game Lodge	
Session 1			**Opening**	**Bains Game Lodge**	
	17:30	18:15		Opening	
	18:15	20:15		Mixer and Dinner	
Monday	**13 October**				**Title**
Breakfast	07:00	07:45	Breakfast		
Session 2		**Chair:**	**A Roodt**	**UFS**	
	08:00	08:40	KN1	L Barbour (US)	Establishing crystallography at the Univ. of Stellenbosch
	08.40	09:00	Y1	D Haynes (US)	Towards functional materials from multi-component Xtals
	09:00	09:30	KN2	D Billing (Wits)	Powder XRD in South Africa
	09:30	09:50	Y2	M Fernandez (Wits)	Opportunities for young Crystallographer at Wits & in SA
	09:50	10:20	KN3	A Thalal (UCA)	Crystallography In Morocco
Tea	10:20	11:00	Tea		
Session 3		**Chair:**	**D Billing**	**WITS**	
	11:00	11:30	KN4	S Bourne (UCT)	Adventures in Chemical Crystallography
	11:30	11:50	Y3	A Brink (UFS)	Crystallography in South Africa: thoughts from the young
	11:50	12:20	KN5	J v Rooyen (UCT)	From humble beginnings (Electron Microscopy)
	12:20	12:40	FPY1	4x Flash Posters	Young Scientists (4+1min each)
Lunch	12:45	14:00	Lunch		
Session 4		**Chair:**	**A Thalal**	**UCA, Morocco**	
	14:00	14:30	KN6	J Ngoune (Dschang)	New 3D Coord Polymer Based on the Cu3(1,2,3-
	14:30	15:00	KN7	M Tredoux (UFS)	Mineralogy: Nanoparticles in Geology
	15:00	15:30	KN8	H Boughzala (TEMU)	Crystallography in Tunisia: history and future
Tea	15:30	16:00	Tea		
Session 5		**Chair:**	**J Conradie**	**UFS**	
	16:00	16:30	KN9	Z Yav (UKin, DRC)	Crystallography in the D. R. Congo
	16:30	16:45	Y4	B Kennedy (UFS)	Identifying Minerals in Nanoparticles
	16:45	17:05	Y5	S Kimani (UCT)	Biological Crystallography in Chemistry and More
	17:05	17:25	Y6	C Oliver (UCT)	Challenges for a young crystallographer at UCT
	17:30	17:40	FPY2	3x Flash Posters	Young Scientists (4+1min each)
	17:40	18:30	**POSTER SESSION 1**		
Dinner	19:00		Dinner		
Tuesday	**14 October**				
Breakfast	07:00	07:45	Breakfast		
Session 6		**Chair:**	**WD Schubert**	**UP**	
	08:15	09:00	KN10	C Esterhuysen (US)	Building Crystallography at US as female scientist
	09:00	09:20	KN11	O Munro (UKZN)	History and Current Status of XRD Science in UKZN
	09:20	09:50	Y7	B Omondi (UKZN)	Challenges for a young Crystallographer at UJ/ UKZN
	09:50	10:20	KN12	HG Visser (UFS)	History of Crystallography at UFS: Past, Present, Future
	10:20	10:30	FPY3	2x Flash Posters	Young Scientists (4+1min each)
Tea	10:30	11:00	Tea		

Session 7		**Chair:**	**D Visser**	**UFS**	
	11:00	11:20	Y8	P Mangwala (UKin)	Structure Elucidation of Physalins Isolated from Physalis
	11:20	11:50	KN13	E du Plessis (Sasol)	XRD in Industry: applications at SASOL
	11:50	12:10	Y9	R Forbes (Sasol)	Young Scientist's perspective of XRD at Sasol
	12:10	12:40	KN14	M Lee (NMMU)	Electron microscopy: at the Atomic level
	12:40	13:00	I1	D Levendis (Wits)	High Pressure Crystallography (WITS)
Lunch	13:00	14:15	Lunch		
Session 8		**Chair:**	**J Dillen**	**US**	
	14:15	14:45	KN15	A Venter (NECSA)	Neutron Diffraction in South Africa
	14:45	15:20	KN16	P Comba (Heidelberg)	Structure and Function: From Crystallography to ...
	15:20	15:45	FPY4	3x Flash Posters	Young Scientists (4+1min each)
Tea	15:45	17:15	**Tea and POSTER SESSION 2**		
	17:15	**18:00**	**AGM (Chair: C Esterhuysen) Meeting of the SA Crystallographic Society**		
Dinner	19:00		Dinner		
Wednesday	**15 October**			**Title**	
Breakfast	07:00	07:45	Breakfast		
Session 10		**Chair:**	**H Boughzala**	**TEMU, Tunisia**	
	08:15	08:45	KN17	T Kroon (UFS)	Crystallography and Physics in the South African context
	08:45	09:15	KN18	WD Schubert (UP)	Biological XRD at UP (SA)
	09:15	09:45	I2	M Ntwaeaborwa (UFS)	SAASta/ NRF: Nanomaterials programme
	09:45	10:00	FPY5	3x Flash Posters	Young Scientists (4+1min each)
Tea	10:00	10:30	Tea		
Session 11		**Chair:**	**Levendis**	**Wits**	
	10:30	11:00	S1	JCA Boeyens (UP)	Establishing Crystallography at the CSIR and WITS
	11:00	11:30	S2	LR Nassimbeni (UCT)	Crystallography at the University of Cape Town
	11:30	12:00	ARoodt	Closing	
Lunch	12:00	13:30	Lunch		

Legend / Notes:

1. KNx = 30 min. Keynote & Yx = 15 min. Young Scientist lectures; across Africa.
2. FPYx = 4+1 min. poster flash presentations (3 slides per person); Young Scientists.
3. 2 x Poster Sessions: Monday and Tuesday afternoon.
4. 1 x Round Table panel discussion (Tuesday 17:15)
5. S1, S2: 2 x Presentations by South African legends: Boeyens & Nassimbeni (Wednesday Session 11)
6. South African Crystallographic Society: Annual General Meeting (Tuesday afternoon 17:15)

15-17 October 2014: IYCr2014Africa Summit

Wednesday	**15 October**			**Affiliation**	**Details**
	12:00	14:00	Arrival & Registration: CR Swart		UFS Campus, Bloemfontein
Session S1		**Chair:**	**A Roodt**	**UFS**	**Opening of Summit**
	14:00	15:30	Rectorate (UFS); T Auf der Heyde (SA DST); S Garcia-Granda (IUCr Exec Comm); G Pillay (SA NRF); JP Ngome Abiaga (UNESCO); M Zema (IYCr2014 of IUCr); A Roodt (ECA)		
Tea	15:30	16:15	Tea		
Session S2		**Chair:**	**M Zema**	**Pavia / IUCr**	
	16:15	16:45	SK1	S Garcia-Granda (Spain)	History of Crystallography
	16:45	17:00	FPY6	3x Flash Posters	Young Scientists (4+1min each)
	17:00	18:00	**POSTER SESSION 3**		
Dinner	19:00		Dinner		
Thursday	**16 October**			**Affiliation**	**Details**
Breakfast	07:00	07:45	Breakfast		
Session S3		**Chair:**	**S Garcia-Granda**	**Oviedo / IUCr**	
	08:15	09:00	SK2	P Kanyankogote (DRC)	Crystallography/ Science in DRC & Central Africa
	09:00	09:30	SK3	A Thalal (Morocco) & H Bougzala (Tunisia)	Overview: Crystallography/ Science in Arabic Africa
	09:30	10:00	SK4	P Steynberg (Sasol)	Crystallography/ Science in Industry
Tea	10:00	10:30	Tea		
Session S4		**Chairs:**	**C Esterhuysen & A Roodt**		**IYCr2014:**
	10:30	11:00	SK5	M Zema (IUCr; Italy)	Activities of IYCr2014
	11.00	11.20	SK6	Ngome-Abiaga (Unesco)	UNESCO initiatives in Africa
	11:25	12:45	**PANEL DISCUSSION 1**		'Current state of Crystallography / Science in Africa': (UFS SENATE HALL)

PANEL DISCUSSION 1: 'Current state of Crystallography / Science in Africa': (UFS SENATE HALL)

Some questions for PANEL:	**Panel:**	**Young Scientists:**
1. What is the current state? 2. What has Morocco & Tunisia done differently? 3. How was current activity in Francophore countries started? 4. Is it important for Industry? 5. Is it important for Suppliers of Equipment? 6. What has South Africa done differently?	Auf der Heyde (SA DST); Kanyankogote (DRC); Zema (IUCr); Pillay (SA NRF); Nyanganyura (NRF SAASta); Steynberg (Sasol); Venter (NECSA); Ngome-Abiaga (UNESCO); Taylor (UFS); Antalis (Bruker); Thalal (Morocco); Garcia–Granda (Spain)	Haynes (US; SA); Gitari (Kenia); Mangwala (DRC); Muller (Namibia); Simon (Nigeria); Traore (Mali); Dina (Madagascar); Brink (UFS)

Lunch	13:00	14:00	Lunch		
Session S5		**Chair:**	**J Venter**	**UFS**	Expanding Crystallography in Africa
	14:00	14:20	SI1	V Smith (US; SA)	TBA
	14:20	14:40	SI2	P Gitari (Kenia)	Establishing Crystallography & Nanotechnology in Kenya
	14:40	15:00	SI3	T Muller (Namibia)	XRD & kinetics: nitrosyl, cyanide & acetonitrile complexes
Tea	15:00	15:30	Tea		
Session S6		**Chair:**	**M Ntwaeaborwa**	**UFS**	
	15:30	16:00	SI4	M Zamxaka (SAASTA)	SAASTA's role in advancement of Science in SA
	16:00	16:15	SI5	R Dina (Madagascar)	Piezoelectric materials from Madagascar by XRD
	16:15	16:45	SI6	P Mensah (UFS)	Some perspectives from Science in Ghana
	16:45	17:00	FPY7	6x5min Posters	Young Scientists (4+1min each)
	17:10	18:15	**POSTER SESSION 4**		
Dinner	19:00			Dinner	
Friday	**17 October**			**Affiliation**	**Details**
Breakfast	07:00	07:45	Breakfast		
Session S7		**Chair:**	**TBA**	**UFS**	
	08:15	08:50	SK7	J Bradley (WITS)	Crystallography for All
	08:50	09:15	SK8	P Antalis (Bruker)	From Supplier to Open Labs in Africa
	09:15	09:35	SI7	D Billing (WITS)	Publishing in IUCr Journals
	09:35	10:00	SI8	D Nyanganyura	ICSU Africa: Action Plan and Science Activities
Tea	10:00	10:30	Tea		
Session S8		**Chair:**	**A Roodt & JP Ngome-Abiaga**		**PANEL DISCUSSION 2**
	10:30	11:30			

PANEL DISCUSSION 2: Way forward for crystallography/ Science in Africa: (**UFS SENATE HALL**)

Core questions for PANEL/Actions	**Panel:**	**Young Scientists:**
1. Modalities for setting up schemes for Regional Cooperation 2. Setting up of a regional fund for increasing human mobility 3. Regional training centre(s) of crystallography 4. Role of synchrotron /neutron in crystallography 5. Can UNESCO and IUCr help 6. Formation of **AfCA**	Ngome Abiaga (UNESCO); Bougzala (Tunisia); Taylor (UFS); Schubert (UP; SA); Kanyankogote (DRC); Zema (IUCr); Ngoune (Cameroon); SAASTa (NRF); Mensah (UFS)	Brink (UFS); Aziz (Sudan); Pretorius (UFS); Nibret (Ethiopia); Laza (Madagascar); Gitari (Kenia); Bungu (UFS & Cameroon); Muswema (DRC); Venter (UFS)

Session S9		**Chair:**	**A Roodt**	**UFS**	
	11:30	12:15	A Roodt	UFS	Conclusion / Declaration/ Formation AfCA
Lunch	12:20	14:00	Lunch		Depart

Legend / Notes:

1. SKx = 30 min. Keynote lectures; topical / international / across Africa.
2. YYx = 15 min. Young Scientist lectures, AND SIx = 5 x 10 min. Young scientists: Society and Future
3. 2 x Poster Sessions: Wednesday and Thursday afternoon.
4. 1 x Round Table panel discussion (Thursday 10:30)
5. Declaration / formation of AfCA

Welcome

Pan African and South African Meeting of the International Year of Crystallography: IYCr2014Africa

Bloemfontein, South Africa, 12-17 October 2014

Dear Delegate,

I would like to welcome you on behalf of the president of the IUCr, Prof Marvin L. Hackert, Dr Maciej Nalecz from UNESCO (Director: Natural Sciences Sector: Division of Science Policy and Capacity Building), the European Crystallographic Association (ECA) and the University of the Free State's Department of Chemistry, to the 'Pan African and South African Meeting of the International Year of Crystallography: IYCr2014Africa', which has the ambitious theme of: 'Crystallography as vehicle to promote science in Africa and beyond'.

As you know by now, 2014 has been declared by the United Nations as the International Year of Crystallography. As part of the celebrations, three world summit meetings are also held during 2014, i.e. in Karachi (Pakistan), Campinas (Brazil) and indeed, here in Bloemfontein (South Africa).

The meeting here in Bloemfontein consists of a 2.5-day Conference (12-15 October), followed by a 2-day Summit (15-17 October).

At the Conference, we will discuss and showcase the current state of crystallography in Africa, as presented in keynote lectures and presentations by young scientists in particular from the English, French and Arab speaking African regions.

At the Summit, we will focus on how we might use crystallography as vehicle to expand science in Africa and need the inputs from established and young scientists, but also policy makers.

I would like to acknowledge the efforts from everyone who made this event possible and the support from our sponsors, in particular that from the South African Government's Department of Science and Technology (DST) and the continuous support from Dr Thomas Auf der Heyde, acting Director General, as well as the International Union of Crystallography.

I further would also like to acknowledge the enthusiasm, efforts and time spent, of the immediate past president of the IUCr, Prof Gautam Desiraju, and in particular the immediate past vice-president Prof Claude Lecomte, for making this event a reality.

Thank you for visiting us. Enjoy the hospitality of Bloemfontein and the University of the Free State, and the science presented here; and please pro-actively help to continue the strategies initiated.

And come back soon.

Kin

An
President: EUROPEAN CRYSTALLOGRAPHIC ASSOCIATION
Chair: IYCr2014Africa

United Nations
Educational, Scientific and
Cultural Organization

Organisation
des Nations Unies
pour l'éducation,
la science et la culture

Organización
de las Naciones Unidas
para la Educación,
la Ciencia y la Cultura

Организация
Объединенных Наций по
вопросам образования,
науки и культуры

منظمة الأمم المتحدة
للتربية والعلم والثقافة

联合国教育、
科学及文化组织

Natural Sciences Sector
Division of Science Policy and Capacity-Building

Dear Sir/Madam

On behalf of UNESCO and the International Union of Crystallography (IUCr), it is my pleasure to invite you to take part in the Pan-African Summit meeting entitled “Crystallography as vehicle to promote Science in Africa and beyond” which will be held at the Department of Chemistry of the University of the Free State, Bloemfontein, South Africa, from 15 to 17 October 2014.

This summit celebrates the United Nations International Year of Crystallography 2014 (IYCr2014) and is one of three Regional Summit Meetings that have been planned for this year by the International Union of Crystallography and UNESCO, the lead custodians for IYCr2014.

The meeting will serve as a platform wherein science policy makers, prominent scientists, leading academics from top universities, Ministers of Science and Technology as well as representation from the industry sector will be brought together and put in a position to explore and debate potential ways to promote education and research in crystallography, and its links to other sciences, fostering at the same time international collaboration among African States and scientists worldwide.

The arena and the environment provided will represent the perfect place to shed light to new agreements, discuss issues and challenges faced by researchers, creating at the same time synergy among high officials in the interest of the African continent and the entire world.

The event will also offer a unique opportunity to increase the understanding of the general public and of decision-makers of the role of crystallography as a discipline of science that is crucial for modern advances in the life sciences, chemistry and physics, and as a factor that will contribute significantly to addressing the post-2015 development agenda issues related to food security, safe drinking water, healthcare and renewable energy among others.

For all the aforementioned reasons we do believe your presence will be of utmost importance, and therefore would like to reaffirm our invitation to take part at this Regional Summit Meeting.

In anticipation of your positive response please accept, Sir/Madam, the assurances of my highest consideration.

Yours sincerely,

Maciej Nalecz
Director

1 rue Miollis, 75352
Paris Cedex 15, France
Tel: +33 (0)1 45 68 39 30
Email: M.Nalecz@unesco.org

Sponsors

The organisers would like to express their sincere gratitude to the following organisation / groups for sponsoring IYCr2014Africa:

- International Union of Crystallography (IUCr)
- European Crystallographic Association (ECA)
- United Nations Educational, Scientific and Cultural Organization (UNESCO)
- South African Department of Science and Technology (SA DST)
- University of the Free State Chemistry (UFS Chemistry)
- Bruker
- DECTRIS
- Cambridge Crystallographic Data Centre
- National Research Foundation – South African Agency for Science and Technology Advancement
- Hydrogen South Africa

Organising Committee

Andreas Roodt (Chair)	University of the Free State, South Africa	roodta@ufs.ac.za	General & Programme
Marietjie Schutte-Smith	University of the Free State, South Africa	chemar@ufs.ac.za	Secretary
Truidie Venter	University of the Free State, South Africa	entergjs@ufs.ac.za	Abstracts & Webpage

General Information

IYCr2014Africa will be held at the Main Campus of the University of the Free State in Bloemfontein, South Africa, which is also known as the City of Roses and is situated in the centre of South Africa. The scientific programme will be presented at the C.R. Swart building on the University campus, whereas breakfast and dinner will be served at the venue of accommodation, Bains Game Lodge.

Date	Time	Venue	Activity
Sunday 12 Oct	12:00-17:30	Bains Game Lodge	Registration
	18:00	Bains Game Lodge	Opening
Monday 13 Oct	08:00-17:40	CR Swart Auditorium	Sessions 1-5
	17:40-18:30	CR Swart Balcony	Poster Session 1
Tuesday 14 Oct	08:15-15:45	CR Swart Auditorium	Sessions 6-8
	15:45-17:15	CR Swart Balcony	Poster Session 2
	17:15-18:00	CR Swart Auditorium	AGM: S.A. Cryst. Soc.
Wednesday 15 Oct	08:15-11:30	CR Swart Auditorium	Sessions 10-11
	11:30-12:00	CR Swart Auditorium	Closing of Conference
	12:00-14:00	CR Swart Auditorium	Registration for Summit
	14:00-16:45	CR Swart Auditorium	Opening of Summit, Sessions S1-S2
	16:45-18:00	CR Swart Balcony	Poster Session 3
Thursday 16 Oct	08:15-17:00	CR Swart Auditorium	Sessions S3-S6
	11:25-12:45	CR Swart Senate Hall	Panel Discussion 1
	17:10-18:15	CR Swart Balcony	Poster Session 4
Friday 17 Oct	08:15-12:15	CR Swart Auditorium	Sessions S7-S9
	10:30-11:30	CR Swart Senate Hall	Panel Discussion 2
	11:30	CR Swart Auditorium	Conclusion

- **Registration** for the Conference and Summit will take place at the helpdesk in the foyer of Bains Game Lodge on Sunday 12 October from 12:00. Additional registration opportunity for registration for only the Summit will be available at the CR Swart building on the UFS campus on Wednesday 15 October between 12:00 and 14:00.
- **Transport** between Bains Game Lodge and the UFS campus will be provided daily for the duration of the Conference and Summit. In addition, shuttle services between the Bloemfontein International airport and Bains Game Lodge will be provided.
- **Breakfast** is available at Bains Game Lodge between 07:00 and 07:45 every morning for the duration of the Conference and Summit.
- **Tea** and other refreshments will be served twice daily,
- **Lunch** will be served between approximately 12:30 and 14:00 daily in the CR Swart foyer.
- **Dinner** will be served daily at 19:00 at Bains Game Lodge.
- **Stationary** is provided in the delegate conference package.
- **Security** – Please note that neither the Organising Committee, the University of the Free State nor Bains Game Lodge can be held responsible for any loss of personal belongings. If necessary, lock up valuable items when not in use in the resort’s safe and otherwise keep cell phones, laptops, etc. in your possession.

Presentations

Oral Presentations:

- All presentations will be presented in the CR Swart Auditorium.
- **Technical help** – Loganathan Nagarajan (Naga), Pennie Mokolokolo and Paul Bungu are in charge of technical issues relating to projection equipment, computers and other presentation variables during the conference. PowerPoint presentations should by uploaded the day before your scheduled presentation to ensure that as few as possible technical problems are encountered.
- **Order of presentations** – Times allocated for presentations are given in the scientific programme. In the interest of smooth running of the conference, fairness to fellow speakers and respect for the audience, we appeal to all our speakers to ensure that their presentations fit into the required time slot. Please comclude your presentation as soon as possible after the signal.

Poster Presentations:

- All posters should be put up before the end of the lunch hour on Monday 13 October. Material needed to affix posters to poster boards will be provided.
- Four poster sessions will be held:
    - Monday 13 October, 17:40-18:30
    - Tuesday 14 October, 15:45-17:15
    - Wednesday 15 October, 17:00-18:00
    - Thursday 16 October, 17:10-18:15

KN1

Establishing crystallography at the University of Stellenbosch

Len Barbour

[a] Department of Chemistry and Polymer Science, University of Stellenbosch, Stellenbosch 7600, E-mail: ljb@sun.ac.za

Keywords: history, porous materials, advice.

The presentation will deal with the presenter's own experiences with regard to establishing a laboratory for the study of crystalline materials at the University of Stellenbosch. It will be subdivided into three parts (i) Short History – the presenter's academic background and the unlikely story of how he ended up in Stellenbosch; (ii) a brief summary of the presenter's research in South Africa – dealing with porous materials and other solid-state concepts and (iii) hints and suggestions to establish similar thrusts elsewhere in Africa (particularly South Africa).

KN2

Powder XRD in South Africa

Dave Billing

Department of Chemistry, University of Witwatersrand, Johannesburg, South Africa. Email: dave.billing@wits.ac.za.

KN3

Crystallography in Morocco

Abdelmalek Thalal [a], *Moha Berraho* [a], *Ahmed Benharref* [a], *Lahcen El Ammari* [b] *and Driss Zakaria* [c]
[a] Cadi Ayyad University, Marrakech, Morocco, [b] Mohamed V University, Rabat, Morocco, [c] Chouaïb Doukkali University, El Jadida, Morocco.

Keywords: Teaching, Research, Instrumentation, Organization.

In Morocco a major effort was made during the last decade to develop and promote science education and scientific research in general, especially crystallography. Analysis and characterization centers have been established at several universities to optimize equipment and create synergy between researchers [1].

Morocco has a notable scientific and human potential in this field. About more than 400 researchers have direct or indirect connections with crystallography. They use the X-ray, the scanning electron microscopy and transmission electron microscopy as means of investigation equipment. Researchers are working in physics, chemistry, geology and biology laboratories in universities, engineering colleges and other institutes of technology [2].

Crystallography is taught from the second academic year. Students receive, each year, basic knowledge in crystallography; large number of them is graduated in physics or chemistry.

Significant number continues their postgraduate studies in Master's and PhD in the areas using crystallography [3].

Research in crystallography covers a broad spectrum of activity, particularly in materials science and inorganic chemistry. Over the last years, crystallography begins to attract researchers working in the field of organic chemistry, biochemistry and medicinal chemistry. Moreover, recently crystallography becomes an important part of research on the art and cultural heritage [2].

In 2002, Moroccan crystallographers gathered to found the Moroccan Association of crystallography. This association is a network for all its adherents; it contributes to the effort of equipment and maintenance, organizes schools and conferences and provides to the Moroccan universities the main scientific journals in crystallography. It also contributes to the training of young researchers, both in theoretical and practical crystallography and the crystallographic software.

Moroccan Crystallographic Association is member of the European Crystallographic Association since 2002, and recently member of the IUCr . It participates actively to the program “Crystallography in Africa” launched by the IUCr.

Moroccan Crystallographic Association, which spearheaded the project of the IYCr2014, has celebrated the International Year of Crystallography by organizing the first African School of crystallography, three open labs for to French speaking Africans, contests of crystallization in school and several large public conferences.

---

[1] Ministry of Higher Education, Scientific Research http://www.enssup.gov.ma

[2] Sources: archive Moroccan universities http://www.maroc-adresses.com/

[3] Moroccan Institute for Scientific and Technical Information http://toubkal.imist.ma

KN4

Adventures in Chemical Crystallography: from Inclusion Compounds to MOFs

Susan A. Bourne

Department of Chemistry, University of Cape Town, Rondebosch 7701, E-mail: susan.bourne@uct.ac.za

Keywords: metal-organic framework, solvatochromism, thermochromism.

This presentation will take the form of a perspective view of the presenter's personal journey in chemical crystallography.

From early work applying physical chemical techniques to organic inclusion compounds, through the early years of crystal engineering, work in our laboratory has focused on correlating solid state structures with physical properties or reactivity.

Current research projects fall into two broad areas, and aspects of each will be presented:

1) Crystal engineering of dyanamic metal-organic frameworks (MOFs).

We have undertaken work on the production, characterisation and utilisation of metal-organic networks and frameworks with the focus on molecular storage or sensing functionalities. Examples of recent work include carboxylate-MOFs which are capable of releasing and resorbing guest molecules without loss of structural integrity - although this is accompanied by loss and regain of crystallinity in a "breathing" mechanism. [1] Using aromatic pyridylcarboxylates as bridging ligands, we have reported the formation of a new class of thermo- and solvatochromic MOFs [2]. Since some of these MOFs are capable of releasing and resorbing guest molecules from vapour or liquid, without loss of crystallinity, we have exploited them as chemo-selective sensors and molecular sponges for the sorption of a range of alcohols [3,4].

2) Supramolecular modification of pharmaceutically and agrochemically active compounds.

Apart from the inherent usefulness of co-crystallisation as a means of testing the robustness of supramolecular synthons, co-crystals are also of interest to the pharmaceutical industry. Solid active pharmaceutical ingredients (APIs) can suffer from poor solubility and bioavailability and often have the potential for crystallising in different solid forms (polymorphism). By using crystal engineering principles to make co-crystals and salts with the API and a GRAS (generally regarded as safe) component, it may be possible to improve solubility and stability as well as to reduce the likelihood of polymorphic behaviour of the API [5].

---

[1] Davies, K; Bourne, S.A.; Oliver, C.L. *Cryst Growth Des*, 2012, **12**, 1999.

[2] Mehlana, G; Bourne, S.A..; Ramon, G. *Dalton Trans*, 2012, **41**, 4224.

[3] Mehlana, G.; Ramon, G.; Bourne, S.A. *Z Kristallogr.*, 2013, **228**, 318.

[4] Mehlana, G.; Ramon, G.; Bourne, *CrystEngComm*, 2013, **15**, 9521.

[5] Li, J; Bourne, S.A.; de Villiers, M.M.; Crider, M.; Caira, M.R. *Crystal Growth Des*. 2011, **11**, 4950.

KN5

From humble beginnings

Jason van Rooyen, Brandon Weber and Trevor Sewell
Structural Biology Research Unit, Division of Medical Biochemistry, Institute of Infectious Diseases and Molecular Medicine, University of Cape Town, E-mail: trevor.sewell@uct.ac.za .

Keywords: Electron microscopy, X-ray crystallography, Structural Biology, South African History.

The literature is devoid of evidence that a single three dimensional structure of a protein was determined experimentally by South Africans, working in South Africa, during the twentieth century. A great deal changed in 2003 with the publication of the first crystal structure [1] of an angiotensin converting enzyme domain and later that year of the first nitrilase structure solved by three-dimensional electron microscopy [2]. The structures were determined by groups at the University of Cape Town that had the benefit of Wellcome Trust funding and close ties with structural biology groups in the UK.

By the time these two papers were published efforts were underway to create a sustainable structural biology infrastructure in South Africa. The discipline requires not only a continual stream of new recruits that have an understanding of biology, physics chemistry, mathematics and computing but also physical infrastructure for protein production and crystallization in addition to specialized X-ray diffractometers and electron microscopes. It was necessary to build both the educational and the research infrastructure in a risk-averse, underfunded environment. The programme nevertheless gathered momentum and has been formalized in three structures that are only now taking shape: The Department of Computational and Molecular Medicine, The Structural Biology Research Unit (SBRU) and the Centre for Imaging and Analysis (CIA). The Department will offer a BSc Med. (Hons.)(Structural Biology) degree from 2015 and has already had considerable experience in supervising Structural Biology degrees at MSc and PhD level. The Unit will provide the research infrastructure for projects. It will develop research questions, apply for funding and assist with projects at all levels. The Centre will contain equipment and technical infrastructure including crystallization facilities, cryo-electron microscopes, computing facilities and an X-ray diffractometer as well as the expertise to use these resources. The SBRU and CIA will maintain international relationships that will continue to give researchers at UCT (and indeed all of South Africa) access to synchrotron beamlines and higher performance electron microscopes than are available locally.

Much of the effort of the UCT groups has been aimed ultimately at drug discovery, in particular, inhibitors of angiotensin converting enzyme that enable side-effect free regulation of blood pressure. Another branch of the work has been directed at understanding the mechanism, specificity and thermostability of members of the nitrilase superfamily of enzymes that are commonly used industrially as well as, in some cases, being potential drug targets. The work has resulted in 70 deposits of co-ordinates in the Protein Data Bank [3].

---

[1] Natesh, R; Schwager, SLU; Sturrock, ED; et al. *Nature*, 2003, **421**, 551-554.

[2] Sewell, BT; Berman, MN; Meyers, PR; et al. *Structure*, 2003, **11**, 1413-1422.

[3] Protein Data Bank Entries: 1o8a, 1o86, 1uze, 1uzf, 2c6n, 2ive, 2ivd, 2iux, 2iul, 2c6f, 2oc2, 3bkl, 3bkk, 3l3n, 2x96, 2x97, 2x8z, 2x90, 2x91, 2x92, 2x93, 2x94, 2x95, 2x8y, 2xhm, 3nxq, 2xyd, 2xy9, 3zq2, 2ybm, 4apj, 4aph, 4asr,4asq, 4aa1, 4aa2, 4bxk, 4cab, 4ca7, 4ca6, 4ca5, 4cr2, 4c2n, 4c20, 4c2p, 4c2q, 4c2r, 4bzr, 4bzs, 2plq, 2dpp, 2r6k, 3c9k, 3hkx, 3hht, 3ktl, 3hgj,3hf3,3o6x, 4ewl, 4lf0, 4k2f, 4gyn, 4gyl, 4izs, 4izt, 4izu, 4izv,4izw

KN6

New 3D Coordination Polymer Based on the $Cu_3(1,2,3\text{-}BTC)_2\cdot 3H_2O$ and a N-donor Ligand

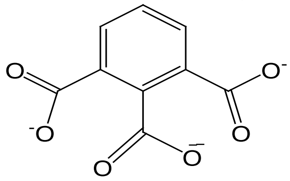
J. Ngoune[a], *J. Nenwa* [b], *N. Mascioccgi* [c], *A.S. Fontsa B,*[d] *T. J. Matemb Ma Ntep, T.R. Fomuta,*[a]
O. N. Ngnabeuya,[a] *C. Pettinari* [e]

[a]Department of Chemistry, The University of Dschang, (Cameroon); E-mail: jeangoune@yahoo.com. [b] Department of Inorganic Chemistry, The University of Yaounde I, (Cameroon); [c]Dipartimento di Scienze Chimiche e Ambientali, Università dell'Insubria, (Como, Italy); Ecole Normale Supérieure, The University of Yaounde I, (Cameroon); [e]Department of Chemical Sciences, The University of Camerino, (Italy)

Keywords: Copper, synthesis, coordination polymer and magnetism.

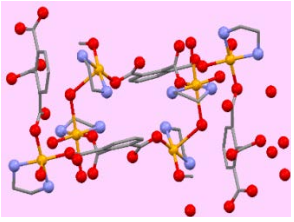
Metal-Organic Frameworks or coordination polymer(MOFs/CP) often obtained by (self)-assembling of oligonuclear metal clusters (the so-called Secondary Building Units or SBUs) are the subjects of an increasing number of studies due to their interesting properties and promising applications in numerous important fields, such as gas storage, molecular recognition, catalysis, etc. [1] An interesting class of polynucleating ligands, appropriate to drive the self-assembly of MOFs, is represented by N-donor units containing two moieties interconnected by various spacers, which can afford different lengths, linear or non-linear geometries and conformationally rigid or flexible molecular skeletons having an infinite one-(1D), two-(2D) or three-(3D) dimensional framework or periodic nets.[2] Yaghi *et al*. have successfully developed porous materials (such as metal carboxylate) with controllable shape and size of the cavities.[3] Some of these metal carboxylates appeared to have unusual magnetic properties [4] while some other exhibited high efficiency for gas absorption such as dihydrogen, dinitrogen etc.

On this basis, we have decided to synthesize and characterize new MOFs/CP by treating the simple unit copper 1,2,3-benzenetricarboxylate-water (1/3) or $Cu_3(1,2,3\text{-}BTC)_2.3H_2O$ with a N-donor containing ligand: ethylenediammine (en). In the resulting compound $\{[Cu_3(en)_3(OH_2)_3(\mu_3\text{-}1,2,3\text{-}BTC)_2(\mu\text{-}OH_2)].3H_2O\}_\infty$ 2, the ligand ***en*** sandwiches the centre metal which are alternatively bridged by $1,2,3\text{-}BTC^{3-}$ moieties and H_2O molecules.



Benzene-1,2,3-tricarboxylate
(1,2,3-BTC)

(1)



(2)

This compound which exhibits a magnetic susceptibility of 3.21BM, was completely characterized and its X-ray structural determinations revealed infinite waved channels. The synthesis and structural characterization of this coordination polymer will be discussed.

[1] a) M. Eddaudi, J. Kim, N. Rosi, D. Vodak, J. Watcher, M. O'Keeffe, O.M. Yaghi, *Science*, 295, 469 (**2002**); b) S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem. Int. Ed*. 43, 2334 (**2004**); c) S. Kitagawa, K. Uemura, *Chem. Soc. Rev*. 34, 109 (**2005**)

[2] a) O.M. Yaghi, M. O'Keeffe, M.G. Kanatzidis, *J. Solid State Chem*. 152, 1 (**2000**); b) C. Di Nicola, F. Garau, M. F. C. Guedes da Silva, J. Ngoune, L. Pandolfo, C. Pettinari, A.J.L. Pombeiro, 4th EuChems Conference on Nitrogen Ligands, Garmisch-Partenkirchen (Germany) (**2008**) and references therein cited.

[3] a) H. Furukawa, J. Kim, K.E. Plass, O.M. Yaghi, *J. Am. Chem. Soc*. 128, 8398 (**2006**); b) J.L.C. Rowsell, O.M. Yaghi, *J. Am. Chem. Soc*. 128, 1304 (**2006**); Z. Ni, A. Yassar, T. Antoun, O.M. Yaghi, *J. Am. Chem. Soc*. 127, 12752 (**2005**)

[4] a) B. Moulton, A. Mondal, M.J. Zaworotko, *Chem. Commun*., 863 (**2001**), b) B. Moulton, M.W. Bradner Abourahma, J. Lu, J.G. McManus, M.J. Zaworotko, *Chem. Commun*., 1342 (**2003**), c) B. Moulton, J. Lu, R. Hajndl, S. Hariharan, J.G. McManus, M.J. Zaworotko, *Angew. Chem., Int. Ed*. 41, 2821 (**2002**)

KN7

Mineralogy: nano-particles in geology.

Marian Tredoux
Department of Geology, University of the Free State, Bloemfontein 9300, South Africa, mtredoux@ufs.ac.za.

Keywords: mineralogy, South African minerals, nanoparticles.

The International Association of Mineralogy (IMA) keeps a list of all known mineralsa nd adjudicates claims about new minerals. The critical criterion for a new mineral is that it should represent a natural occurrence of (i) a distinct chemistry with (ii) a crystallographic arrangement that is not shared by any other naturally-occurring material. The first new South African mineral to be described, in 1788 [1], was prehnite (ideal formula: $Ca_2Al[Si_3AlO_{10}](OH)_2$), which has an orthorhombic crystal structure. Subsequently, 68 more new minerals from South African rocks have joined the IMA list, the most recent being the triclinic Sr-Ca hydro-silicate cairncrossite [2], (ideal formula: $Sr_2Ca_7[Si_4O_{10}]_4(OH)_2{\cdot}15H_2O$). A set of Ni-Sb-As phases has recently been documented for the first time in a rare Ni-oxide rock type from Barberton [3], and only sound crystallographic information is lacking before these can be registered as new minerals.

When it comes to the platinum-group element (PGE) minerals, the days of macroscopic specimens are long gone; all PGM mineralogy and crystallography are done with X-ray microscopes and probes. A lively debate has opened about whether PGM formation is mediated primarily by crystallo-chemical associations, as predicted by the 'rules' of the great geochemist Victor Goldschmidt, or whether nano-particles, e.g. clusters, might be responsible for a more physical mechanism.

Results from a recent experimental study [4] will be reported. The evidence is strong that the PGE atoms arrange into clusters (<100nm longest diameter), and later nano-particles, with non-metals like As, at concentrations well below what it required for the actual PGMs to form. Fast Fourier transforms (FFT) of transmission electron microscope images indicate that both nano-crystals of sperrylite ($PtAs_2$), as well as hexagonal Pt-As platelets with thckness 1-2 nm, occur (see figure 1). These are accompanied by more globular non-crystalline clusters of Pt-Fe-As.

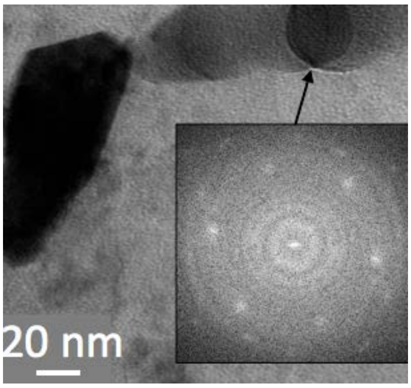


Figure 1: PGE nano-phases in an experimental sulphide melt. The crystalline phase is sperrylite. The FFT inset of the globules show the pattern of the host sulphide indicating that the globules themselves are non-crystalline.

---

[1] .Cairncross, B; *Field guide to the rocks and minerals of southern Africa*, 2004, Struik, Cape Town.

[2] Giester, G., et al.; *Cairncrossite, IMA 2013-012*, 2013 Min. Mag., **77**, 2695-2709.

[3] Tredoux et al.; *Phases in the Ni-Sb-As system which occur in the Bon Accord oxide body, Barberton greenstone belt, South Africa*, 2014, Min. Mag. (in press).

[4] Helmy et al.; *Noble metal nanoclusters and nanoparticles precede mineral formation in magmatic*

KN8

Crystallography in Tunisia history and future

Habib Boughzala
Université El Manar. Faculté des Sciences de Tunis. Laboratoire de Cristallochimie et Matériaux
E-mail : habib.boughzala@ipein.rnu.tn

The first laboratory of crystallography in Tunisia was created in 1979 in the Faculty of Science of Tunis by Pr. Tahar Jouini. In the 90th many other labs were created in Sfax, Monastir, Bizerte, etc… with modest diffraction equipment working on several fields apatite, cements, zeolites, phosphates, arsenates, hybrids, organics, organometallics, etc…

In 1993 a Nonius CAD4 diffractometer was installed in our lab (still working!!!). More later (2008), a Bruker D8 Advance is diffracting powder in the same lab with the powerful TOPAS Rietveld investigation tool as well as ICSD, CCDC (WEBCSD) and PDF2 databases licenses.

Actually, one of our main crystallographic investigations is on the Metal Organic Frameworks (MOFs) for hydrogen storage, greenhouse gas capture, drugs field, catalysis, energy storage, etc... In particular, in the photonics field, self-organized metal halide organic-inorganic hybrids exhibit confined excitons in one- two- or three- dimensional secondary building unit (SBU) network with corner, edge, face or mixed mode sharing topology. Generally, the HUMO-LUMO energy gaps of the organic part are higher than that of the inorganic moiety. Therefore, the electronic structures of these compounds can be regarded as a self-organized multiple quantum-dot -well or bulk structures. The high contrast in dielectric constants between the organic and inorganic parts strengthens the interaction between an electron and a hole in a stable exciton with a strong binding energy that can be set free as photoluminescence emission at room temperature.

Nowadays, more than 100 confirmed Tunisian crystallographers are distributed in a dozen of labs and struggling along a total absence of political will to promote science and particularly purchase new (or used) diffraction hardware. The access to the European diffraction facilities (Ex: ESRF, PSI) is becoming more and more difficult. Only shy partnership programs between Tunisian and foreign labs can give some satisfaction to young Tunisian researchers.

The crystallography blooming in Tunisia cannot happen without the NGO help, crystallographic associations contribution (IUCr particularly) and the hardware manufactures assistance.

KN9

Crystallographic in the D.R. Congo

Zéphirin Gushimana Yav
Department of Chemistry at the University of Kinshasa, B.P. 190 Kinshasa XI, D. R. Congo.
Email: zephirin.yav@unikin.ac.cd.

We have formed a friendly connection with the Cambridge Crystallographic Data Centre (CCDC) in Cambridge, United Kingdom. Contacts with the CCDC date back to 2007/8, when a Cambridge Strctural Database (CSD) System licence was granted to my laboratory as part of collaboration with Professor Luc Van Meervelt at Kath. Univ. Leuven, Belgium. In 2012, the CCDC's Director Colin Groom and Juliette Pradon spent a week at the Univesity of Kinshasa as part of a three years long, British Council/UK, financed Science Training Laboratory project delivering a series of seminars and workshops on the use of CSD System to an audience consisting of academic staff and other researchers.

2013, the CCDC was delighted to be entering into a research collaboration with me in the area of structural chemistry. To lay the groundwork for research projects, which have just commenced, CCDC staff members Juliette Pradon and Pater Galek spent week at the University of Kinshasa in June 2013, delivering several talks and workshops about the CSD System, as well as running an electronic structure therory workshop where the interface to MOPAC in Mercury was used to probe molecular geometries, energies of interactions, and the Jahn-Teller effect. In July 2014, the CCDC's Director Colin Groom and Juliette Pradon, spent anathor week at the University of Kinshasa delivering courses and workshops on "Using the CSD for drug discovery".

The research projects are dealing with investigations on the hydrogen and sigma-hole bonds involving chalcogen elements using the CSD System and computational methods. One of them consists of a comparative study of the interaction geometries and energies of hydrogen bonds to traditional acceptors with those to functional groups involving the element selenium. Another work is on the use of the CSD and QM calculations to investigate sigma-hole and H-bond interactions made by selenium and possibly tellurium. These two research projects are financially sponsored by the CCDC and are based at the Chemistry Department of the University of Kinshasa, to include several visits to the CCDC in Cambridge.

We are expecting these research projects will help to show how the CSD System can be used in the developing world to do valuable, publishable, cutting-edge research at minimal cost and to enable the understanding of structural chemistry. Another interesting and efficient upgrade could be a grant to the Department of Chemistry at the University of Kinshasa, expected from the IUCr to allowing the purchase of a single crystal diffractomer.

KN10

Building Crystallography at the University of Stellenbosch as a female scientist

Catharine Esterhuysen

Department of Chemistry and Polymer Science, University of Stellenbosch, Matieland, Stellenbosch, 7602, South Africa,
E-mail: ce@sun.ac.za.

Keywords: gender issues.

Although it is well-known that crystallography is a field that has had a relatively large number of female scientists in comparison to other scientific disciplines, women are nevertheless still under-represented [1]. In this presentation I will start by giving a brief introduction to my scientific background and research field within crystallography, with reference to the role that my gender has played on shaping my scientific career. I will then share my experiences as a woman in the field of crystallography, from my context as an academic at the University of Stellenbosch, and give my perspective on how women could be supported and empowered within the crystallographic community.

---

[1] Francl, M. *Nature Chem.*, 2014, **6**, 842–844.

KN11

The History and Current Status of X-ray Diffraction Science in KwaZulu-Natal

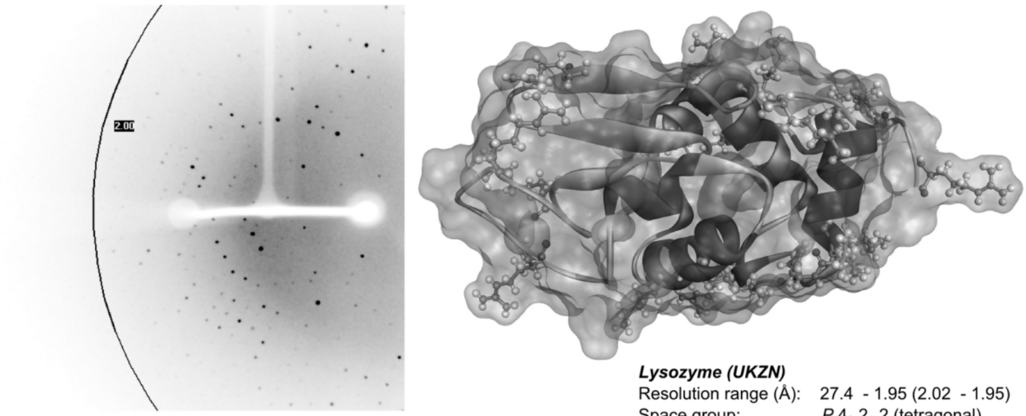
Orde Q. Munro
School of Chemistry & Physics, University of KwaZulu-Natal, Private Bag X01, Scottsville 3209, South Africa;
E-mail: munroo@ukzn.ac.za

Keywords: crystallography, diffractometer.

The lecture will be descriptive and divided into three sections, commencing with an account of the history of X-ray crystallography in KwaZulu-Natal, primarily in academia. The current focus of the majority of the research in crystallography in the province, and thus the lecture, is on single-crystal X-ray diffraction, though mention of the increasingly important role of powder diffraction work being done particularly within the scope of materials science research will be made.

The second focus of the lecture will be to highlight some X-ray crystallographic work that has recently been done at UKZN and UNIZUL; this will include work from a range of researchers and will include some non-routine work done in Pietermaritzburg.

The final part of the lecture will be presentation of one or two ideas that could have merit for growing the number of crystallography researchers in Africa.



Example diffraction frame (Cu Kα radiation) for a lysozyme crystal (*ca.* 2.0 Å resolution). Instrument: Bruker Apex II Duo, IuS source, Quazar optics, 4 min exposure.

Lysozyme (UKZN)

Resolution range (Å):	27.4 - 1.95 (2.02 - 1.95)
Space group:	$P\,4_3\,2_1\,2$ (tetragonal)
Unit cell:	77.508 77.508 37.615
R-factor:	0.1906

Figure 1: Crystal structure of lysozyme (a typical macromolecular test crystal) determined with an in-house diffractometer at UKZN. The structure was solved by isomorphous replacement and represents the transition from small-molecule crystallography to macromolecular crystallography that is possible when the facilities exist to grow protein crystals and to measure their diffraction with an appropriate instrument. The structure was refined with open-source software (PHENIX and COOT) and rendered with free visualization software (PYMOL and Discovery Studio Visualizer).

KN12

The History of Crystallography at the UFS: Past, Present and Future.

Hendrik G. Visser
Department of Chemistry, University of the Free State, Bloemfontein, South Africa E-mail: visserhgt@ufs.ac.za.

Keywords: crystallography, teaching, research.

A brief history of crystallography at the UFS is presented. Key aspects with regards to teaching young scientists are highlighted. During the last few years, single crystal X-ray crystallography served a dual purpose at the UFS. It is a major driving factor in all Inorganic Chemistry research. Highlights of this include research in industrial reaction mechanisms and radiopharmacology research and will be illustrated briefly.

Another purpose of crystallography is directly related to teaching young scientists the basics of preparing research documents in the form of short reports It is reported that South African students perform very poorly in terms of literacy and ability to read and write. This lack of ability to write, directly translates to the quality of the scientist and who eventually needs to write up his or her own research [1] and naturally affects the quality of the research. We have been able to address this by having students publish several short papers (crystal structure reports) in journals with a crystallographic influence, e.g. *Acta E* and *Zeithschrift*.

---

[1] Baruthram, S. *South African Journal of Education.*,2012, **32**, 205-214.

KN13

Crystallography at Sasol

Esna du Plessis
Sasol Technology (Pty) Ltd, Sasolburg, 1947, South Africa, E-mail: esna.duplessis@sasol.com.

Keywords: Sasol, crystallography, catalyst, Fischer Tropsch synthesis.

Sasol is an international integrated energy and chemical company that develops and commercializes chemical technologies. There is a growing need in the world for a secure supply of energy and chemicals. Sasol's experience and understanding of Fischer Tropsch synthesis provides us with a unique value proposition and enables us to expand nationally and internationally.

Sasol is one of the world's largest producers of synthetic fuels. We mine coal in South Africa and produce natural gas and condensate in Mozambique and Gabon. Sasol employs people not only in South Africa, but also in a number of African countries, for example Botswana, Zambia, Nigeria and Egypt. Sasol's recent financial results showcases our focus on sustainable value creation and our South African energy cluster listed a number of successes.

A substantial financial investment is made to build stakeholder relationships, such as Sasol sponsorships for the South African national women's football team, the Sasol league and the South African Paralympics team. Our investment at eleven South African universities over a ten year period is done to support the development of world-class scientists and chemical, mechanical, electrical and control engineers.

Sasol has a number of proprietary technologies and the commercial processes require quality control, legal and product specifications and therefore chemical analyses. In Analytics we strive to provide world-class catalyst characterization to support our Coal-To-Liquids (CTL), Gas-To-Liquids (GTL) and new catalyst development partners. A fundamental understanding of a Fischer Tropsch catalyst's life-cycle is required, from production to activation and the de-activation mechanisms thereof [1]. Understanding the crystalline phase and catalyst activity relation is important and crystallography plays an important role in this characterization process.

Powder X-ray diffraction, vibrational spectroscopy, Mössbauer absorption spectroscopy, magnetic measurements and electron microscopy are some of the analytical techniques for catalyst characterization. A few examples where these techniques were used will be discussed: the determination of the γ-alumina crystal structures from a powder [2-4], analysis of a wax coated catalyst and *in situ* powder X-ray diffraction to determine the crystalline phases formed during reduction of a model alumina supported cobalt catalyst [5].

---

[1] van de Loosdrecht, J.; et al, Fischer–Tropsch Synthesis: Catalysts and Chemistry. In: J. Reedijk and K. Poeppelmeier, ed. *Comprehensive Inorganic Chemistry* II, Vol 7, Oxford: Elsevier; 2013, 525-557.

[2] Wefers K.; Misra, C.; *Oxides and hydroxides of aluminium*, ALCOA Laboratories, Pennsylvania, USA, 1987, 20.

[3] Kim, H.; Kosuda, K.M.; Van Duyne, R.P.; Stair, P.C. *Chem. Soc. Rev.*, 2010, **39**, 4820-4844.

[4] Smrčok, Ĺ.; Langer, V.; Křesťan, J. *Acta Cryst.*, 2006, **C62**, i83-i84.

[5] du Plessis, H.E.; Forbes, R.P.; Barnard, W.; Erasmus, W.J.; Steuwer, A. *Physical Chemistry Chemical Physics*, 2013, 11640-11645.

KN14

Electron crystallography: At the atomic scale

Mike Lee, Jan Neethling, Jaco Olivier, Arno Janse van Vuuren, William Goosen and Jacques O'Connell[a]

[a] Centre for High Resolution Transmission Electron Microscopy, Physics Department, Nelson Mandela Metropolitan University, Port Elizabeth 6031, South Africa, michael.lee@nmmu.ac.za

Keywords: electron, diffraction, imaging, SEM, HRTEM.

Since the introduction of the first commercial transmission electron microscope (TEM) in 1938 and the scanning electron microscope (SEM) in 1965, electron microscopy has made a tremendous impact on our fundamental understanding of the microstructure of materials down to the atomic level. Recent advances in electron microscopy with the introduction of the aberration corrected (Cs-corrected) TEMs have allowed scientists to investigate the crystalline nature of nanoparticles and crystal lattice defects at the atomic level.

The installation of the first double Cs corrected JEOL ARM 200F TEM in Africa, for the Centre for High Resolution Transmission Electron Microscopy (CHRTEM) at NMMU in 2011, has provided the scientific community in South Africa with a world class EM facility. In this paper, we will firstly describe the CHRTEM microscope facility with respect to the applications of electron crystallography for the understanding of material properties. These applications will include the techniques of EBSD and TKD (using Kikuchi diffraction) in the SEM for the orientation mapping of polycrystalline materials on the micrometer scale. The general applications of TEM in material science will be described at the nanometer scale and followed by the application of atomic resolution in the HRTEM at the picometer scale. A number of examples which represent some of the work carried out at the CHRTEM will be presented which will include the observation, at atomic resolution, of a single dislocation loop in a GaAs lattice as shown in figure 1 below. In this case the regular lattice structure (pairs of Ga and As atoms showing white contrast) has clearly been disturbed by the lattice defect.

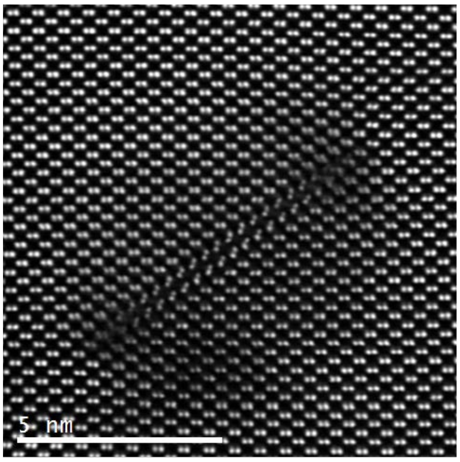


Figure 1: High resolution HAADF STEM image of a dislocation loop in neutron irradiated GaAs.

KN15

Neutron Diffraction contributing to science in South Africa and beyond

Andrew Venter

Research and Development Division, Necsa Limited, Pretoria, South Africa.. Email: amventer@necsa.co.za

Neutron diffraction elucidates the atomic and molecular structure of materials in a different, but highly complementary way to conventional X-ray diffraction. Notwithstanding the abundant availability of X-ray diffraction instruments in South Africa, many problems exist in materials research that cannot be comprehensively studied. For example, most modern energy applications are based on light elements (hydrogen, lithium, sodium, oxygen), whose investigation by conventional (laboratory) or synchrotron-based methods are quite challenging and in many cases inconclusive.

The interactions of neutrons with matter are fundamentally different to X-rays, rendering them an excellent tool, often having no alternative. This includes the characterization of complex systems such as containing light elements, especially in the presence of heavy ones, or distinguishing between elements that are chemically similar such as the transition metal series. Neutrons furthermore have a magnetic moment that can directly sense magnetic interactions. In addition the high penetration depths of thermal neutrons along with their low energy make them ideally suited for non-destructive in-situ, in-operando and depth-resolved studies. The combination of either nearly neutron-transparent, or nearly fully neutron-absorbing materials, makes the use of complicated sample environment (temperature, pressure, electric and magnetic fields, gas atmosphere, tension etc.) possible. The superior penetrating capability of thermal neutrons enables accurate and non-destructive studies of residual (and applied) stresses in components by direct probing at the microstructural level, as well as determination of the bulk texture (crystallite orientation).

In this talk I shall describe the basic properties of neutrons and their interaction with matter that enables gathering of information that is not only complementary to that attained with X-rays, but that are also quite unique in many cases. At Necsa (South African Nuclear Energy Corporation), two modern neutron diffractometers, complemented with in-situ sample environments, are now available as User Facilities within the National System of Innovation in support of the South African research community.

KN16

Structure and Function in Chemistry – From Crystallography to Modeling, Spectroscopy and Reactivity.

Peter Comba
Department of Inorganic Chemistry, University Heidelberg, 69120 Heidelberg, Germany,
E-mail: peter.comba@aci.uni-heidelberg.de.

Keywords: crystallography, molecular modeling, spectroscopy, reactivity, structure, function.

The discovery of novel transition metal complexes with exciting properties is often to a large extent based on serendipity and on a careful observation and interpretation of experimental data (i.e. crystal structures and spectroscopy) with classical models, including ligand field theory, molecular mechanics and quantum chemistry. On the emerging basis of a thorough understanding of the new structures and their influence on the properties (thermodynamics, reactivities, spectroscopy) these compounds may then be further optimized for specific applications. The lecture will discuss the basis for this approach together with a few recent examples.

KN17

Crystallography and Physics in the South African context

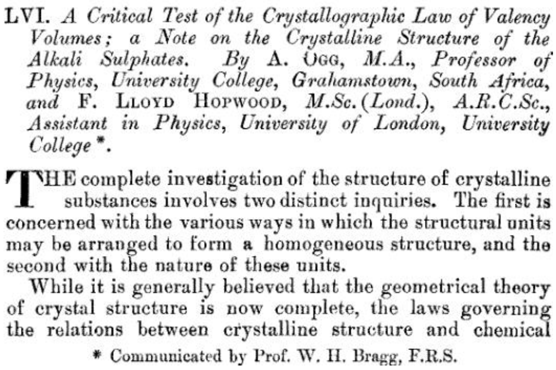
R.E. Kroon and H.C. Swart
Department of Physics, University of the Free State, Bloemfontein, South Africa 9300, E-mail: KroonRE@ufs.ac.za.

Keywords: X-ray diffraction, low energy electron diffraction, surface structure, high resolution transmission electron microscopy, texturing, crystallite size, residual strain, nanoscience.

Although the macroscopic properties of crystals were well established, the microscopic picture of the nature and spacing of the repeating units was still unclear when Laue made the suggestion in 1912 that crystals may act as three dimensional diffraction gratings for X-rays. This was soon confirmed by Friedrich and Knipping and quickly led to the technique of X-ray diffraction which is still so heavily relied on today.

This was about the same time that the first physics departments in South Africa became active in research. Alexander Ogg became chair of Physics at the newly established Rhodes University College in 1905. He published on the crystalline structure of the alkali sulphates in 1916 (figure 1), communicating his paper via W.H. Bragg. After three years at what would become Wits University, Ogg moved to the University of Cape Town in 1920 where the work and his correspondence with W.H. Bragg continued. Although Ogg later became distracted by geomagnetism, in the early 1920's he and R.W. James (working in W.L. Bragg's laboratory) had both published on the structure of antimony and bismuth; James came to South Africa in 1937 to succeed Ogg and re-established the work on X-ray crystallography. The first structure reported was that of 4,4'-dinitrodiphenyl by J.N. van Niekerk in 1943. He went on to establish the X-ray crystallography division of the National Physical Laboratory at the CSIR. In the 1960's at this laboratory, E.G. Boonstra later refined and modified the same structure. He went on to became head of UFS Physics in 1968 where he established X-ray diffraction research.

An interesting addition to X-ray diffraction was the discovery of electron diffraction by Davisson and Germer in 1927, which led to a demand of transmission electron microscopes as well as X-ray diffraction apparatus. Applications in the physics setting included plastic deformation of metals and dislocation theory, as well as epitaxial crystal growth. The surface structure of iron was of interest due to its use for catalysis in the Fisher-Tropsch process and this led to work with surface sensitive low-energy electron diffraction. Routine applications of X-ray diffraction in the materials setting include phase analysis, texturing, alloying and the estimation of residual strain and crystallite size (the latter being particularly important in nanoscience). Examples of such applications will be given. The recent installation of an atomic resolution transmission electron microscope at NMMU under J.H. Neethling represents a mile-stone since it allows direct visualization of the crystal structure. Future prospects for X-ray crystallography include the current initiative to establish a synchrotron X-ray source in South Africa.



LVI. *A Critical Test of the Crystallographic Law of Valency Volumes; a Note on the Crystalline Structure of the Alkali Sulphates. By* A. OGG, *M.A., Professor of Physics, University College, Grahamstown, South Africa, and* F. LLOYD HOPWOOD, *M.Sc. (Lond.), A.R.C.Sc., Assistant in Physics, University of London, University College**.

THE complete investigation of the structure of crystalline substances involves two distinct inquiries. The first is concerned with the various ways in which the structural units may be arranged to form a homogeneous structure, and the second with the nature of these units.

While it is generally believed that the geometrical theory of crystal structure is now complete, the laws governing the relations between crystalline structure and chemical

* Communicated by Prof. W. H. Bragg, F.R.S.

Figure 1: An early South African paper from 1916 on the application of X-ray diffraction to crystal structure determination (A. Ogg and F. Lloyd Hopwood, Philosophical Magazine Series 6, 1916, volume 32, issue 191, paper LVI, pages 518-525).

KN18

Structural Biology of Infectious Diseases at the University of Pretoria.

Wolf-Dieter Schubert[a]

[a] Department of Biochemistry, University of Pretoria, Pretoria, South Africa 0002, E-mail: wolf-dieter.schubert@up.ac.za

Keywords: macromolecular crystallography, communicable diseases, molecular basis of disease

The application of crystallography to biological systems has infused and revolutionized all aspects of molecular biology by providing a fundamental understanding of structural principles of the molecules involved. Starting with the first model of DNA by Watson and Crick and the first crystal structures of hemoglobin and myoglobin in the late 1950's, the description of hundreds of enzymes to large molecular machines such as ribosomes and viruses, comprising millions of atoms, macromolecular crystallography has elucidated how these complicated systems work down to individual atoms. Many of these achievements have been acknowledged at the highest levels by the awarding of Nobel prizes and many other accolades, underscoring their importance to human understanding of the biosphere and hence the world we live in.

Macromolecular crystallography as one technique in the field of structural biology was initially highly specialized and required expertise in numerous fields such as molecular biology, physics, mathematics, chemistry, computer science and computer graphics. As a result it flourished in developed countries with accessible infrastructure but languished in developing countries due to the lack of such infrastructure, the perceived expense and inferred non-essential elitism. This applies to South Africa and all other African countries. In South Africa Structural Biology was only truly established after the year 2000 with a few groups actively involved across the country.

The history of macromolecular crystallography at the University of Pretoria only extends back to July 2013 with my appointment in the department of biochemistry, though some attempts at protein crystallization and structure modeling had been undertaken before. The research group plus equipment moved to Pretoria in January 2014 and is hence still in its infancy. It, however, goes back to 2005, when my research group "Molecular Host-Pathogen Interactions" was established at the Helmholtz-Centre for Infection Research, Braunschweig, Germany, which in 2009 relocated to the University of the Western Cape, before moving to Pretoria in 2013/4.

At the University of Pretoria our main emphasis involves investigating proteins associated with infectious diseases and primarily bacterial diseases. Organisms that we are currently working on include *Mycobacterium tuberculosis*, the causative agent of tuberculosis, enterotoxigenic *Escherichia coli* (ETEC) causing dysentery mostly in small children, *Listeria monocytogenes*, a food-borne pathogen leading to blood poisoning, meningitis and miscarriages of unborn babies, as well as *Legionella pneumophila*, the cause of Legionnaires' disease. Our studies include structural analysis, biophysical investigation of protein-protein interactions of bacterial virulence factors with host proteins, as well as cell-based infection studies.

This talk will highlight the type of work in structural biology that is achievable in a third-world country – to the benefit of the South African, African and potentially global population.

I1

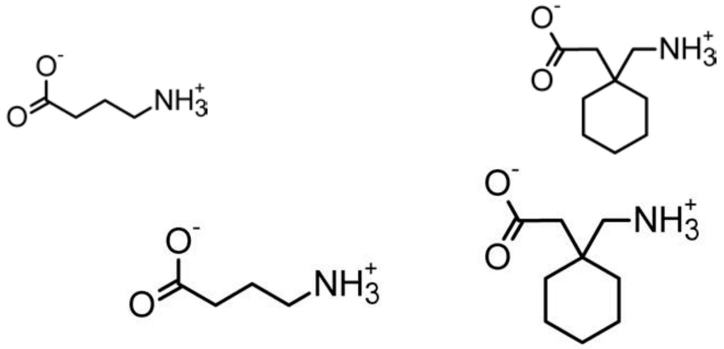
Polymorphs under Pressure: the case of GABA and Gabapentin

Demetrius Levendis [a] *and Francesca P. A. Fabbiani* [b]

[a] Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Johannesburg, South Africa, e-mail: Demetrius.levendis@wits.ac.za, [b] Universität Göttingen, Germany. e-mail: ffabbia@gwdg.de

Keywords: high-pressure crystallization, GABA, gabapentin, pharmaceutical hydrates.

The application of high pressure is a powerful method for exploring the polymorphic behaviour of molecular compounds. Depending on the melting point and solubility, single crystal and powder samples can be studied by direct compression, in situ crystal growth from the melt and in situ recrystallisation from solution.



GABA gabapentin

By virtue of their conformational flexibility and known polymorphism, γ-amino butyric acid (GABA) and the neuroepileptic drug, gabapentin, are small molecules ideally suited for high pressure polymorphism investigations. This paper reports our results on the discovery of the ambient pressure and temperature polymorphs of gabapentin and the exploration of the high-pressure polymorphism and solvate formation of GABA and gabapentin. The latter were obtained by in situ high-pressure crystallization using a diamond anvil cell (DAC) at the Universität Göttingen, Germany, in collaboration with Francesca Fabbiani.[1]

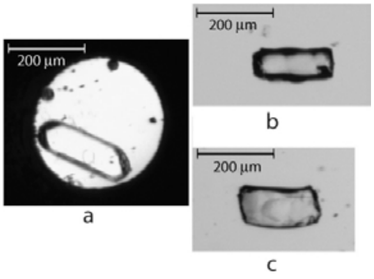


Fig. 1 Optical images of GABA monohydrate (a) at 0.44 GPa in the DAC and (b and c) recovered to ambient temperature.

Similar studies are now being planned at the Jan Boeyens Structural Chemistry Laboratory, University of the Witwatersrand, where the equipment for high pressure diffraction studies has recently been acquired.

---

[1] Fabbiani, FPA, Buth, G, Levendis, DC and Cruz-Cabeza A.J, *Chem. Commun.*, 2014, **50**, 1817-1819. "Pharmaceutical hydrates under ambient conditions from high-pressure seeds: a case study of GABA monohydrate."

I2

Nanostructured Materials Characterization by X-ray Diffraction

Martin Ntwaeaborwa

Department of Physics, University of the Free State, Bloemfontein, South Africa, ZA9300, E-mail: ntwaeab@ufs.ac.za.

Keywords: Nanomaterials, X-ray diffraction, crystalline structure.

Today, nanostructured materials have been the main focus area of engineering and research worldwide. Today, nanomaterials have many uses in applications such as drug delivery, medical imaging, theft prevention, information display, solar cells, and water treatment. The development of these new materials very much depends on the understanding of their fundamental properties including structure, particle morphology and optical properties, among other things. X-ray diffraction (XRD) is an important characterization technique to determine the crystal structure of these materials. Furthermore, the XRD data can be used to determine the crystallite size, particle size distribution and defects. We have used the XRD technique to investigate the crystalline structure of nanomaterials in powder and thin film forms. The crystalline structure of these materials will be discussed. In addition, the role the South African Nanotechnology Public Engagement Programme (NPEP) in disseminating information to enlighten the South African public about nanotechnology will be presented.

S1

Establishing Crystallography at the CSIR and WITS

Jan Boeyens

Centre for the Advancement of Scholarship, University of Pretoria

In the official history of the CSIR (D.G. Kingwill: CSIR. The first forty years) it is claimed (page 139) that:

> In the application of X-ray diffraction techniques, Dr J.N. van Niekerk was one of the first scientists in the world to characterize metal to metal bonds in transition metal acetates, which led to a new understanding of paramagnetism.

Unfortunately, not a word of this is true. Ludwig Schöning determined the crystal structure of copper acetate. Copper is not a transition element and although the molecule has the same symmetry as that of chromium acetate, it has no metal-metal bond. What it has to do with paramagnetism only Kingwill knows.

I also worked in the Chemical Physics Group of the NPRL/NCRL and we produced some compotent work, without being world leaders. The most famous (judged by internet response) crystallographic work from that period is the analysis of the crystal structure of the mineral iscorite. The story behind that is also more like a comedy of errors than cutting-edge research. It only became known twenty years on when the same mineral was identified in moon rocks.

I fear that talking about the history of X-ray crystallography produces more apocryphal stories of the same type. Apparently even Max von Laue did not understand the first diffraction pattern credited to him. I recommend that this forum concentrate less on the past and instead consider if crystallography in its present form still has a useful scientific role in science. To my mind it could easily collapse into another routine analytical technique, unless some fundamental questions are being asked about the true nature of molecular and crystal structure and the periodicity of matter.

I am a bit vague about what happens elsewhere in the country, but I am pleased to note that at Wits, in the group with which I was associated until fifteen years ago, some serious consideration is given to precisely such fundamental issues.

S2

Crystallography at the University of Cape Town

Luigi R Nassimbeni
Centre for Supramolecular Chemistry Research, Department of Chemistry, University of Cape Town, Rondebosch 7701, South Africa; Email: luigi.nassimbeni@uct.ac.za

Keywords: UCT crystallography, host-guest chemistry.

Professor Andre Roodt suggested that my lecture should outline the historical contribution that the University of Cape Town has made in the field of X-ray crystallography, followed by my personal research and ending with suggestions regarding the contributions that can be made by other countries in Africa.

X-Ray crystallography was started in South Africa by Professor R. W. James, who headed the Department of Physics at UCT. He was an outstanding scholar and teacher, who trained the next generation of leaders in the field, including two Nobel laureates. This tradition was continued in the Department of Physics by Professor Walter Schaffer and Dr. Dirk Feil.

In 1966, the discipline moved to the Department of Chemistry at UCT and was headed by Luigi Nassimbeni, who trained many post-graduate students, some of whom have distinguished themselves in research and academia. Among these are Guy Orpen, Michael Thackeray, Mino Caira, Leonard Barbour and Susan Bourne.

Professor Nassimbeni’s current research is in the field of inclusion chemistry. He founded the Centre for Supramolecular Chemistry in 1997 and he has concentrated on the correlation of the macroproperties of host-guest systems with their structure. The most recent work deals with the mechanism of enantiomeric resolution of chiral racemic compounds. This will be illustrated by appropriate examples.

The lecture will close with some appropriate suggestions for crystallography-based research in other parts of our continent.

SK1

(One Short) History of Crystallography (and Diffraction)

Santiago Garcia-Granda

Department of Physical and Analytical Chemistry, University of Oviedo-CINN, 33006-Oviedo, Spain,
E-mail: sgg@uniovi.es. International Union of Crystallography.

Keywords: Crystallography, Diffraction, Gypsum, Sunstone, XFEL, Nobel laureates.

In the framework of the activities of the International Year of Crystallography (IYCr), under the auspices of the International Union of Crystallography (IUCr) and United Nations Educational, Scientific and Cultural Organization (UNESCO), the *Pan African and South African Meeting of the International Year of Crystallography (IYCr2014) - IYCr2014 Africa* is organized. The aim of these activities will persuade to inspire young people by illustrating the universality of science and foster international collaboration among scientists worldwide, with especial attention to North–South contributions.

The International Year of Crystallography 2014 (IYCr2014) commemorates not only the centennial of X-ray diffraction, which allowed the detailed study of crystalline material, but also the 400th anniversary of Kepler's observation in 1611 of the symmetrical form of ice crystals, which began the wider study of the role of symmetry in matter. IYCr-2014 also celebrates 50th anniversary of the Dorothy Hodgkin's Nobel Prize in Chemistry.

Crystallography has achieved the category of mature science in close connection to Crystal Growth and Diffraction playing nowadays a fundamental role in the development of Physics, Chemistry, Materials Sciences and Technology or Life Sciences. A simple analysis of the impact of crystallography in our daily lives shows how it underpins most technological developments in our modern society. Promoting education and research in crystallography, and its links to other sciences, is still a major issue and, therefore, the IUCr provides support by gathering scientist worldwide to introduce crystallography to young African generations, in this international year, and for the future.

In this particular talk we shall quickly review the history of crystallography and diffraction [1] and give the first flavor on the Crystal-Radiation relationship by reviewing the milestones and the most relevant challenges for crystallography in the future. Introducing some basic ideas, generated by many eminent crystallographers, several distinguished with the Nobel Prize. Many of these concepts are deep and complex theories that will be sketched with the aim of stimulate the interest and promote new generations of African young crystallographers.

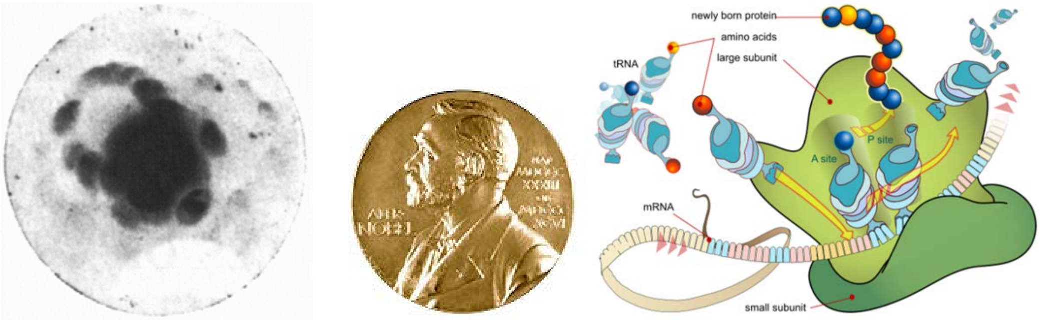


Figure 1: From "beerstein" pattern to structure and function of Ribosome

---

[1] P.P. Ewald (editor and author), 50 years of X-ray diffraction (International Union of Crystallography, Utrecht 1962) (Reprinted in pdf format for the IUCr XVIII Congress, Glasgow, Scotland, 1962, 1999 International Union of Crystallography)

SK2

Crystallography / Science in DRC & Central Africa

P Kanyankogote
Laboratory of Soil Science, Faculty of Science, University of Kinshasa, Democratic Republic of Congo.

SK3

Overview: Crystallography/ Science in Arabic Africa

A Thalal [a] and H. Boughzala [b]

[a] Cadi Ayyad University, Marrakech, Morocco, [b] Université El Manar. Faculté des Sciences de Tunis. Laboratoire de Cristallochimie et Matériaux

SK4

Crystallography/Science in Industry.

Petrie Steynberg

[a] Group Technology, 1 Klasie Havenga Street, 1947, PO Box 1, Sasolburg, 1947, www.sasol.com.

Keywords: Crystallography, Science, Industry.

A strategic view will be provided on the relevance of science and crystallography in industry, specifically the petro-chemical industry in South Africa.

SK5

IYCr2014: its achievements and legacy

Michele Zema
International Union of Crystallography, Chester, UK.

Following a proposal from Morocco, in July 2012 the UN General Assembly adopted the resolution 66/284 and proclaimed 2014 as the International Year of Crystallography (IYCr2014). IYCr2014 commemorates the centennial of the birth of X-ray crystallography, thanks to the works of Max von Laue, who was awarded the Nobel Prize in Physics in 1914, and William Henry and William Lawrence Bragg, who were awarded the same prize in 1915. IYCr2014 also falls on the 50th anniversary of the Nobel Prize in Chemistry awarded to Dorothy Hodgkin for her determinations by X-ray techniques of the structures of penicillin and vitamin B12. IYCr2014 is the well-deserved celebration of the many successes and advances that crystallography allowed to almost all branches of science (e.g., chemistry, biology, physics, pharmaceuticals and medicine, mineralogy, materials science, mathematics, cultural heritage and art sciences, and all related technologies), as well as a new starting point, the birth of the second century of modern crystallography, with new challenges and frontiers to be explored. Understanding the structure of matter has transformed industries and created new frontiers, from the design of new medicines and materials to assessing the mineral content of Mars.

The future global economy will be determined by progress in cutting-edge fields. However, the playing field is not level in crystallography. Therefore, the IUCr and UNESCO have set up a programme of initiatives for IYCr2014 aimed at improving public awareness of the field, boost access to instrumentation and high-level research, nurture "home-grown" crystallographers in developing nations, and increase international collaborations for the benefit of future generations.

The IUCr-UNESCO OpenLab is a network of operational crystallographic laboratories, organized in partnership with industry, and are enabling students in far-flung lands to have hands-on training in modern techniques and expose them to cutting-edge research in the field. OpenLabs have already been implemented in Pakistan, Argentina, Morocco, Ghana, Cambodia, Uruguay, Indonesia, Turkey and others are scheduled in Algeria and Hong Kong by the end of the year.

The Summit meetings are intended to bring together scientists from countries in three widely separated parts of the world, using a common crystallographic theme. The Pan African and South African Summit meeting on "Crystallography as vehicle to promote Science in Africa and beyond" is indeed the third of the series, following the South Asian summit (Karachi, Pakistan, 28-30 April) and the Latin American one (Campinas, Brazil, 22-24 September). These meetings, attended by scientists from academia and industry and by science administrators, focus on high-level science, and also highlight the difficulties and problems of conducting competitive scientific research in different parts of the developing world.

A worldwide crystal-growing competition aims at attracting and inspiring youngsters, showing them that science – and especially crystallography – is also fun!

The outcomes of these actions and of the many initiatives organized at the regional, national or local levels, as well as their follow-up the will be shown and discussed.

SK6

UNESCO initiatives in Africa

J.P. Ngome-Abiaga
United Nations Educational, Scientific and Cultural Organization, Paris, France. Email: jj.ngome-abiaga@unesco.org.

SK7

Crystallography for All

Basson R, Bell B, Bradley JD, Lycoudi M and Roberg CH
RADMASTE, Wits School of Education, University of the Witwatersrand, Johannesburg, South Africa
E-mail: john.bradley@wits.ac.za.

Keywords: metal-organic framework, solvatochromism, thermochromism.

Crystals have a natural, wide appeal, yet they have been little exploited in programmes designed to stimulate interest in science. The IYCr2014 has created an opportunity to explore this potential both in South Africa and elsewhere.

In response to a request from the Department of Science and Technology (DST), our group has developed a set of four activities designed for use within the context of Science Centres around South Africa. Our design principles were cost-effectiveness, simplicity and links to school curriculum topics. The activities cover crystal growing, crystals and amorphous solids, modeling of crystals, and diffraction. The Crystallography Kit prepared for this project includes all equipment, chemicals, samples and Facilitator's Guide and worksheets, to deal with groups of 40-50 learners, teachers or general public.

Fifty of the Crystallography Kits were supplied to DST and 10 of these were delivered to Bloemfontein for National Science Week. We have also used the Kit in the context of National Science Week at Orange Farm near Johannesburg, where the impact on learners was very strong.

Figure 1: The Facilitator's Crystallography Kit

Figure 2: Learners encounter crystals at Orange Farm, Johannesburg – choosing a seed crystal (left); crystal-growing (centre); observing crystals with a hand-held microscope (right)

In other countries there has been a strong emphasis on crystal growing through competitions to grow the best/biggest crystal. We have sought to dig deeper into crystallography and to link more overtly with the avowed aim of the IUCr, which emphasises X-ray crystallography. We would welcome suggestions for improvement.

Crystals not only attract interest, but they are as common an object as water: there can be few people in the World who do not have daily contact with sugar and salt as well as water! Thus every country shares a common experience of crystals; crystallography is for all and could form the basis for a new programme to stimulate science awareness and interest.

SK8

Bruker proudly joins IYCr activities

Pari Antalis[a], *Martin Adam*[b] *and Eric Hovestreydt*[b]
[a] Bruker South Africa (Pty) Ltd., 65 Homestead Ave, Johannesburg, 2021, South Africa, Pari.Antalis@bruker.com
[b] Bruker AXS GmbH, Östl. Rheinbr:uckenstr. 49, 76187 Karlsruhe, Germany

Keywords: IYCr2104, Open Lab, travelling lab, Bruker

As one of the world's leading analytical instrumentation companies, Bruker enthusiastically supports the IYCr activities to increase public awareness of the science of crystallography through supporting meetings and conferences. Furthermore, we are organizing workshops and user meetings to inspire new blood as well as old hands.

Young Crystallographers' activities

In a number of countries very active groups of young crystallographers have formed or are forming because of IYCr activities. Bruker is supporting these activities by providing sponsorship and contributing with lectures or training at the events organized, e.g. in France, Germany and the United Kingdom.

OpenLab Initiative

To further increase knowledge about crystallography the IYCr has started the OpenLab initiative. This initiative is strongly influenced by the IUCr activities to propagate crystallography in the developing regions. Bruker customers will open their laboratory, equipped with our state-of-art instruments. At these sites workshops and hands-on experiments for students and young professors will be on the agenda. Bruker facilitated contacts between the customers and the IYCr and will provide application support wherever required.

An instrument travelling all year

As an additional, strong support of the IUCr's idea of bringing crystallography to countries with no or a very small installed base, Bruker is providing free-of-charge instrumentation temporarily to a number of sites through-out the entire year.

Promoting interdisciplinarity

We are convinced that the combined efforts of the global crystallographic community will demonstrate the importance of crystallography in most technological developments and increase interest in our interdisciplinary method.

SI1

Topic to be announced

V Smith
University of Stellenbosch, Stellenbosch, South Africa.

SI2

Establishing Crystallography and Nanotechnology in Kenya

Patricia W. Gitari and Abiy Yenesew
Department of Chemistry, College of Biological and Physical Sciences, University of Nairobi, Nairobi, Kenya, E-mail: patricia.gitari@uonbi.ac.ke

Keywords: Nanotechnology, Kenya, Vision 2030, xanthones.

The competitive edge of any developing nation lies heavily in its investment in technology. With the enactment of Science, Technology and Innovation Act 2012, the Government of Kenya has committed to a substantial increase in funding of science, technology, innovation with the intention of industrialising the country in line with Kenya Vision 2030. The Kenya *Vision 2030* is the country's current strategy in development which covers the period 2008 to 2030. In this regard, a nanotechnology policy has been developed for the purpose of promoting frameworks for the safe exploitation of nanotechnology. With regard to crystallography, academic institutions currently rely on private research centres or collaboration with overseas research groups.

The successful determination of the structure of a xanthone was possible through collaboration with an European research group. As part of on-going program in search for new bioactive natural compounds from Eastern African plants of the Asphodelaceae family, two new natural products and six known compounds were isolated.[1] Based on HR-EIMS, UV-VIS and NMR spectroscopic evidence the compound was characterized as 8- hydroxy-6-methylxanthone-1-carboxylic acid (**Fig. 1**).

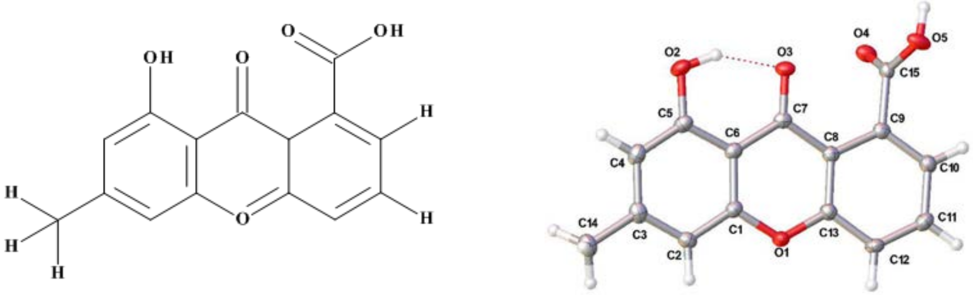


Fig 1. 8-hydroxy-6-methylxanthone-1-carboxylic acid

This is the first report on the occurrence of this compound in nature having previously been reported as a synthetic intermediate.[1] The structure of the compound was used as a reference to propose the revision of the structures of six seco-anthraquinones into xanthones.

Finally, to address the challenges encountered in scientific research, East Africa needs to develop the basic infrastructure, training and knowledge bases that can act as a spring board to propel the new revolution in application and utilization of nanotechnology and crystallography.

---

[1] Abdissa, N, Heydenreich, M, Midiwo, J.O, Ndakala, A, Majer, Z, Neumann, B, Stammler, H-G, Sewald, N, Yenesew, A. *Phytochem. Lett.*, 2014, **9,** 67-73.

[2] Kudav, N.A, Trivedi, B.K, Kulkarni, A.B. *Indian J. Chem*., 1976, 336-338.

SI3

Crystallographic and kinetic investigation of nitrosyl, cyanide and acetonitrile complexes of Rh(I)/(III)

T.J. Muller[a], *H.G. Visser*[b] *and A. Roodt*[b]
[a] Langher Heinrich Uranium, Einstein str 3981 B, Ext 10, New Industrial Area, Swakopmund, Namibia. E-mail: Muller.Theunis@gmail.com. [b] Department of Chemistry, University of the Free State, Nelson Mandela Avenue, Bloemfontein, 9300, South Africa

Keywords: rhodium; nitrosyl; cyanide; electronic parameters; steric parameters.

The reactivity of Rh(I) is well known and has been studied intensely in the last couple of decades while little is known about the reactivity of Rh(III) phosphine complexes. The complexes studied were those of the general form [$Rh(PX_3)_2(NO)(Cl)_2$], [$Rh(PX_3)_2(CO)(CN)$] and [$Rh(PX_3)_2(Cl)_3(CH_3CN)$], where PX_3= aryl. The steric and electronic parameters of the phosphine ligand may be tuned by varyingsubstituents on the phosphorous(III) coordinating atom.One aim of this study was to investigate the affinity of the rhodium metal centre for the phosphine by tuning the electronic and steric properties thereof. The solution state behaviour of these complexes were investigated by following the formation and reactivity of different monodentateentering ligands. The different complexes were successfully characterised by IR, NMR and X-Ray crystallography. IR data of the NO, CO and CN stretching frequencies of the different complexes allowed a comparison of the electronic properties of the different phosphine ligands. The first-order coupling constants from the NMR data also correlate well with the Rh-P bond length from the crystal structures [1]. The difference in electronic and steric properties of the different phosphine ligandswere further correlated with the NO bond angle and the Cl-Rh-Cl bond angles. The reactivity of Rh(III) complexes were also evaluated with respect to differences in steric and electronic properties. This presentation thus deals with an overall correlation of the complexes' spectroscopic, solid state and kinetic reactivities, which will be discussed in detail.

Also a brief discussion on the current state of crystallography in Namibia and the way forward from the perspective of a young scientist.

---

[1] Roodt, A., Visser, H.G. & Brink, A. (2011) *Crystallography Reviews*. **17**, 4, 241-280.

SI4

The role played by SAASTA in the advancement of science, technology, engineering, mathematics and innovation in South Africa

Mthuthuzeli Zamxaka
National Research Foundation, PO Box 1758, Pretoria 0001, South Africa. Email: info@saasta.ac.za

The South African Agency for Science and Technology Advancement (SAASTA), a business unit of the National Research Foundation (NRF), aims to advance awareness, appreciation of and engagement with science, technology, engineering, mathematics and innovation in South Africa. The bedrock of SAASTA's success to advancing a culture of engagement with science in South Africa lies in its synergistic approach. Therefore all SAASTA initiatives fall under three key strategic areas:

- Science Education: through which we build up the supply of tomorrow's scientists, engineers and innovators.
- Science Awareness: through which we engage the public with the phenomena of science, engineering and technology; and
- Science Communication: through which we share science and technology achievements and building up their appreciation of the benefits of science.

This synergistic approach ensures that the system is fed with a health supply of learners whose interest in SET is guided by equally passionate educators; growing the awareness and wonder of science through exploration, exhibition and actual experience and; good science communication which lies in providing credible and accurate information that is accessible to all South African communities.

Housed within SAASTA's science communication unit are three Department of Science and Technology (DST) funded programmes, namely the Public Understanding of Biotechnology (PUB); Nanotechnology Public Engagement Programme (NPEP) and the Hydrogen South Africa Public Awareness and Demonstration and Demonstration Platform (HYSA PADEP). The aim of the PUB programme is to promote a clear, balanced understanding of the potential of biotechnology and to ensure broad public awareness; dialogue and debate about biotechnology and its current and potential applications. The main aim of NPEP programme is to promote public understanding of nanoscience and nanotechnology and promote engagement with this new emerging scientific discipline. The NPEP was born out of the government's National Nanotechnology Strategy (NNS). HYSA PADP aims to create broad awareness, visibility and acceptance amongst the public, stakeholders, entrepreneurs and key decision makers in South Africa about the benefits and challenges of using Hydrogen and Fuel Cell Technology in the alternative energy industry. These platforms further aim to introduce these fields of expertise to the youth of South Africa in order to stimulate an interest in the field by showcasing cutting-edge research and profiling current and future careers this sector has on offer.

SI5

Piezoelectric materials from Madagascar by XRD

R Dina

SI6

Some perspectives from Science in Ghana

P Mensah
University of the Free State, Bloemfontein, South Africa. Email: MensahPDNA@ufs.ac.za

Y1

Towards functional materials from multi-component crystals

Delia A. Haynes
Department of Chemistry and Polymer Science, University of Stellenbosch, P. Bag X1, Matieland 7602,
E-mail: dhaynes@sun.ac.za

Keywords: multi-component crystals, dithiadiazolyl radicals, porous organic salts.

Multi-component crystals, which include both salts and co-crystals, have received much attention in the crystal engineering community due to the advantages they offer in terms of flexibility and ability to alter physical properties without changing molecular structure. In this presentation, our efforts to use multi-component crystals to develop materials with interesting physical properties will be described. The focus is on two systems: co-crystals of dithiadiazolyl radicals, and porous organic salts.

The 1,2,3,5-dithiadiazolyl radicals (hereafter DTDA) are of considerable interest due to their potential as building blocks for organic magnetic or conducting materials. These radicals frequently dimerise in the solid state, rendering them diamagnetic. [1] We have recently begun investigating the potential of co-crystallisation as a means of overcoming dimerisation in DTDA radicals *via* the introduction of a strong supramolecular synthon on the co-crystal former. The synthesis and crystal structure of two DTDA-DTDA co-crystals, [PhCNSSN][C_6F_5CNSSN] and [PhCNSSN][C_5F_4NCNSSN], have been reported. [2] The structures of these materials, as well as routes to obtain them, will be presented. Attempts to obtain further co-crystals with both radical and non-radical co-crystal formers will also be described.

Porous organic salts offer several advantages over metal-organic frameworks and covalent organic frameworks: for example these materials can be dissolved and re-assembled from solution. [3] We have investigated the use of the pamoate ion in the design of porous organic salts, and the interesting properties of several salts will be presented. [4] Recent results involving a series of zwitterionic building blocks [5] will also be discussed.

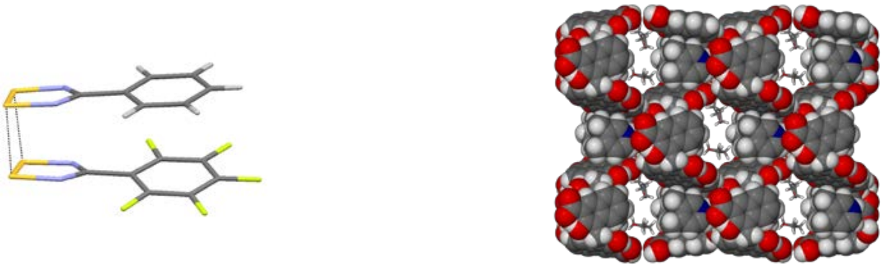


Figure 1: A DTDA-DTDA co-crystal (left) and a porous pamoate salt (right)

---

[1] see D. A. Haynes, *CrystEngComm*, 2011, **13**, 4793-4805 and references therein.

[2] C. Alan, D. A. Haynes, C. M. Pask, and J. M. Rawson, *CrystEngComm*, 2009, **11**, 2048-2050; S. W. Robinson, D. A. Haynes and J. M. Rawson, *CrystEngComm*, 2013, **15**, 10205-10211.

[3] N. B.McKeown, *J. Mater. Chem.*, 2010, 20, 10588–10597; J. R. Holst, A. Trewin and A. I. Cooper, *Nat. Chem.*, 2010, 2, 915–920.

[4] H. Wahl, D. A. Haynes and T. le Roex, *Chem. Commun.*, 2012, **48, 1775-1777.**

[5] L. Loots, D. A. Haynes and T. Le Roex, *New Journal of Chemistry*, 2014, **38**, 2778-2786.

Y2

Opportunities for Young Crystallographers at Wits & in South Africa.

Manuel A. Fernandes

Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Private Bag 3, 2050 Johannesburg, South Africa. Manuel.Fernandes@wits.ac.za.

Keywords: careers in crystallography, alternative career pathways, strategies for building a career in science.

Advances in the field of crystallography have over the last 100 years allowed scientists to examine and understand the world around us at the atomic level. In addition, the availability of powerful computers and more advanced X-ray diffraction equipment have allowed crystallographers to attempt more ambitious projects over time. Single crystal structures that were once difficult and time consuming to carry out have now become routine; so much so that the crystal structure of the final product in a synthesis study is starting to become a basic experimental requirement for the acceptance of a paper in a high impact journal. There is also currently a major drive towards materials chemistry where samples are usually studied in powder form, creating a demand for crystallographers with skills in the collection and complete analysis of X-ray powder diffraction patterns. In addition, the range of phenomena being studied by means of diffraction – both single crystal and powder using X-rays, neutrons or electron beams - is increasing all the time requiring crystallographers to develop new skill sets all the time. These factors have created a demand for skilled crystallographers in academia and in industry worldwide.

This talk will focus on the types of crystallography related research projects that have been or are currently being carried out at the University of the Witwatersrand, and the skill sets that are typically developed during a postgraduate degree involving crystallography. The career paths of past members of the School of Chemistry who have further pursued a career in crystallography after the completion of their postgraduate degree will be highlighted. International sites where jobs in crystallography are advertised will also be indicated. However, the skills obtained as a crystallographer allows a specialist in this field to pursue other careers should they need or want to. Examples of past members who have chosen to pursue other career paths will be presented together with reasons as to why they did so.

Y3

Crystallography in South Africa: thoughts from the young.

Alice Brink
Department of Chemistry, University of Free State, Bloemfontein 9300, South Africa, E-mail: brinka@ufs.ac.za

Keywords: rhenium tricarbonyl, catalysis, crystallography viewpoints.

This talk addresses concerns of young crystallographers in the 21st century, both in South Africa and abroad. Topics such as grant making, external pressures of funding agencies and teaching load of young faculty are a few subjects which young scientists believe should be re-evaluated by policy makers. Current grant and policy committees carefully attempt to establish the future of research based on their wide experience. They may however be unaware of the challenges facing researchers who have recently started their careers. Young researchers have been raised in different times, have grown from different soils than those whose careers have already been established and will face different world challenges. Valuable insight into future strategies can be provided by them as they better foresee the challenges which lie ahead of them. The best policies may well be established by combining these various strengths: the wisdom and experience of the Established with the viewpoints and dreams of the Young.

This presentation will concentrate on conveying the thoughts and ideas of the young scientist and the challenges which are faced not only in Southern Africa but in other developing and developed countries. A brief description of the discussion behind the UNESCO Declaration of Young Talented Crystallographers of the World as well as current research trends occurring at the Free State University will be mentioned.

Y4

Identifying Minerals in Nanoparticles.

Bianca Kennedy[a], *Marian Tredoux*[a] , *Chris Ballhaus*[b], *Gideon Steyl*[c] *and Lisa Coetsee-Hugo*[d]

[a] Department of Geology, University of the Free State, Bloemfontein, South Africa, E-mail: kennedybia@gmail.com
[b] Steinmann Institute, University of Bonn, Bonn, Germany, [c] Department of Chemistry, University of the Free State, Bloemfontein, South Africa, [d] Department of Physics, University of the Free State, Bloemfontein, South Africa.

Keywords: PGE, Bushveld complex, nano structures, experimental petrology.

In the study by Kennedy (2014), which was conducted to determine the behaviour of platinum-group elements (PGE: Ru, Rh, Pd, Os, Ir and Pt) on a nano-level in a magma chamber various nano-entities were measured. Although the results seemed in line with the so-called ‘cluster model’, suggested by Tredoux et al. (1995), direct comparison was difficult as there existed no reference set or criteria against which to classify the nano- entities. How are nano entities grouped, and can they be classified as different phases?

Synthetic sulphide melts, based the Cu-Ni-S±PGE rich sulphide portion of a magmatic system, and run at controlled temperature and oxygen fugacity, was used to mimic the conditions for possible formation of PGE nano-phases. Experiments were prepared using the dry powder silica tube technique. Powders consisted of a base mixture of S, Cu and Fe doped with variable concentrations of Pt, Pd or Ru and a chalcogene ligand (As). Samples were cooled at different rates (chilled or annealed) to monitor the influence of environmental changes on possible nano-phase formation.

Primary and secondary nano- entities were measured in the samples, using semi-quantitative scanning Auger microscopy (SAM). Results showed that the type of nano- entities that formed were functions of i) of the concentration of As and ii) the allowed cooling time. The structures formed irrelevant of the PGE concentration. A classification scheme was set-up for the nano-entities (<100nm), based on the physical and chemical characteristics of clusters, nano- crystals, -minerals and –particles. The classification scheme was primarily used to distinguish possible PGE-clusters from the other nano-entities.

Potential PGE-clusters (10-100nm) were distinguished from the other identified nano-structures, which were re-classified as possible nano-crystals, or –minerals as shown in the classification scheme. Nano- minerals and -crystals were limited to major sulphide mineral phases of the system such as pyrrhotite (Fe-S) and Fe-Cu sulphides, and exhibited angular to crystal-like features. Possible PGE-clusters showed more rounded habits.

---

[1] Kennedy, B. 2014, Investigation of the possibility of platinum-group element clusters in magmatic systems, using synthetic sulphide melts, Unpublished Master Thesis, University of the Free State.

[2] Tredoux, M., Lindsay, N.M., Davies, G. and McDonald, I., 1995, The fractionation of platinum-group elements in magmatic systems, with the suggestion of a novel casual mechanism, South African Journal of Geology, **98**, 157-167.

Y5

Structural Studies on the catalytic mechanism of amidases.

Serah Kimani[a,b] *and Trevor Sewell*[a,c]

[a] Clinical Laboratory Sciences department, University of Cape Town, Rondebosch 7700, South Africa, [b] Molecular and Cell Biology department, University of Cape Town, Rondebosch 7700, South Africa, [c] Electron Microscope Unit, University of Cape Town, Rondebosch 7700, South Africa, E-mail: swkimani@gmail.com

Nitrilase superfamily amidases are thiol enzymes that catalyze the conversion of amides to their corresponding acids and ammonia. A conserved Cys, Glu and Lys (CEK) catalytic triad has been identified in these enzymes [1], and catalysis shown to follow a ‘ping pong bi bi’ mechanism [2] in which the substrate forms a thioester with the catalytic cysteine. A ‘second’, structurally conserved active site glutamate has been found to be essential for activity in amidases [3], but its role in catalysis has not been elucidated in detail. Our work is focused on understanding the mechanism of amidases, by elucidating the role of catalytic residues.

The four catalytic residues (C165, E61, E139 and K131) were mutated individually in the model amidase from *Nesterenkonia* species (NitN) [4]. The mutants were reacted with a range of short aliphatic amide substrates and the resultant proteins characterized by mass spectrometry and X-ray crystallography.

Mutation of the two catalytic glutamates and the lysine resulted in unstable mutants that were inactive, highlighting the importance of these residues in maintaining the protein fold and for enzymatic activity. Mass spectrometry showed that thioester acyl-enzyme intermediates could be trapped by mutating the ‘first’ glutamate (E61). In addition, incubation of the glutamate mutants with amide substrates resulted in two types of unexpected reactions: An S_N2 substitution reaction leading to the displacement of the fluorine in fluoroacetamide was observed with the E61Q/L mutants, while Michael addition of acrylamide at the catalytic cysteine was observed with the mutants of both glutamate residues (E61Q/L and E139Q). These artifactual reactions not only emphasize the role that the two glutamates play in positioning the substrates but also demonstrate that the ‘first’ glutamate is not always necessary to catalyze nucleophilic attack by the cysteine. Mutation of K131 to a glutamine resulted in covalently modified protein that had a possible adipamide thioester intermediate trapped in the active site, suggesting a component of general acid catalysis. These results support a Cys, Glu, Glu and Lys (CEEK) catalytic tetrad in which the two glutamates and the lysine function as a modular assembly.

---

[1] Pace, H. C. and Brenner, C., Genome Biol. **2**, REVIEWS0001 (2001).

[2] Maestracci, M., Thiery, A., Arnaud, A. and Galzy, P., *Agricultural and Biological Chemistry* **50**, 2237 (1986).

[3] Soriano-Maldonado, P., Martinez-Gomez, A.I., Ndujar-Sanchez, M., Neira, J. L., Clemente-Jimenez, J. M., Las Heras-Vazquez, F. J., Rodriguez-Vico, F. and Martinez-Rodriguez, S., *Appl. Environ. Microbiol.* **77**, 5761 (2011).

[4] Nel, A. J., Tuffin, I. M., Sewell, B. T. and Cowan, D. A., *Applied and Environ. Microbiol.* **77**, 3696 (2011).

Y6

Challenges for a young crystallographer at the University of Cape Town

Clive L. Oliver
Centre for Supramolecular Chemistry Research, Department of Chemistry, University of Cape Town, 7701, South Africa,
E-mail: clive.oliver@uct.ac.za

Keywords: metal-organic frameworks, large supramolecular assemblies, research independence.

Dr Clive Oliver trained in solid-state supramolecular Chemistry at the University of Cape Town (UCT) under the supervision of Professors Mino Caira and Susan Bourne. His PhD thesis was on the solid-state characterisation of the bronchodilator tulobuterol in terms of its polymorphism, cyclodextrin inclusion and salt formation. During his postdoctoral research, under the supervision of Prof. Len Barbour (University of Stellenbosch), he concentrated on solid-state gas sorption studies of porous systems as well as the crystal engineering of large supramolecular assemblies. He is an academic member of staff within the Department of Chemistry at UCT and is one of four academics that manage the Centre for Supramolecular Chemistry Research, a UCT-accredited research centre.

Currently, his research interests combine his doctoral and postdoctoral studies which he entitles “Crystal engineering of porous materials and large supramolecular assemblies”. On the side of porous materials his research investigates metal-organic frameworks (MOFs) and purely organic systems which may have applications in liquid and gas sorption. The MOF research concentrates on mixed ligands in attempt to vary pore directional features independently, thus allowing for further tailoring of properties. Some success has been achieved with the construction of a cadmium-based MOF employing 1,3,5-benzenetricarboxylate and 1,2-bis(4-pyridyl)ethane as ligands (Figure 1).[1] Purely organic systems, such as beta- and gamma-cyclodextrin inclusion complexes, are also under investigation. Large supramolecular assemblies which enclose chemical space are quite rare in small-molecule, synthetic, supramolecular chemistry. In this regard, systems based on *p*-sulfanotocalix[4]arene and *C*-methylcalix[4]resorcinarene are being investigated. It is envisaged that these assemblies may have future applications as drug carriers or in catalysis.

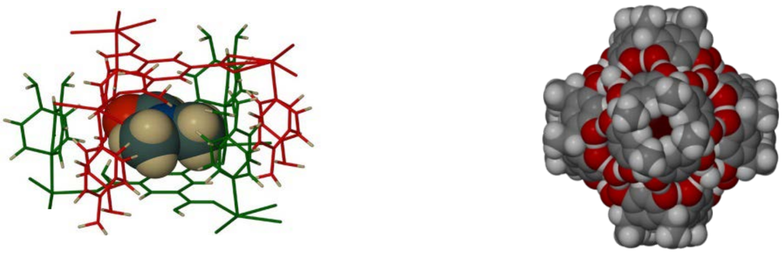


Figure 1: Cavity (occupied by a *N*,*N′*-dimethylformamide molecule) formed by a 2-fold interpenetrated MOF (left) and a giant supramolecular assembly consisting of 6 *C*-methylcalix[4]resorcinarene molecules (right)

Dr Oliver has benefitted from joining a well-estabished supramolecular Chemistry research thrust at the University of Cape Town where resources are pooled. The main challenge for a young crystallographer within this group is to establish an independent reputation. The lecture will share some of these attempts to establish a unique identity within a group of such well-respected researchers.

---

[1] A. Husain, M. Ellwart, S. A. Bourne, L. Öhrström and C. L. Oliver, *Crystal Growth and Design*, **2013**, 13, 1526−1534.

Challenges for a young Crystallographer at UJ and UKZN

Bernard Omondi
School of Chemistry and Physics, University of KwaZulu-Natal, Westville, Durban, South Africa 4000.
E-mail: owaga@ukzn.ac.za.

Keywords: UJ, UKZN, Silver(I) phosphine complexes and coordination polymers, formamidines.

This paper aims at giving a very brief outline of my the very initial contacts with crystallography at the University of the Witwatersrand during my postgraduate studies (Honours, MSc and PhD), followed by brief history of the two Universities I have worked at as a crystallographer, University of Johannesburg (UJ) where I began as a postdoctoral fellow and later on as an Instrument Scientist, the University of KwaZulu-Natal (UKZN) where am currently holding a position as a lecturer with added responsibilities of looking after the single crystal diffractometer at the Westville Campus. The talk also will address the 'bits and pieces' of research I have been involved in from my postgraduate years to the present. Some of the highlights will include a bit of work from my postgraduate years, some work done while at UJ and some of the work I am currently involved with.

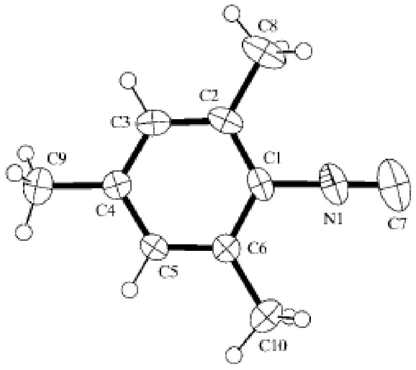


Figure 1: One of my very first crystal structures [1].

---

[1] Fernandes, MA., Layh, M. and Omondi, B, *Acta Cryst*, 2002, C**58**, o384—o385.

Y8

Structure Elucidation of Two Physalins Isolated from *Physalis angulata L.* (Solanaceae).

Peter Mangwala Kimpende,[a,d] *Mariano Lusakibanza,*[b,c] *Luc Angenot,*[b] *Gauthier Mesia,*[b] *Michel Fredich,*[b] *Luc Van Meervelt,*[d]

[a]Department of Chemistry, University of Kinshasa, B.P. 190 Kinshasa XI, D.R. Congo, [b]Laboratory of Pharmacognosy, University of Liège, 4000 Liège, Belgium, [c]University of Kinshasa, Faculty of Pharmaceutical Sciences, Kinshasa XI, D.R. Congo, [d]Chemistry Department, KU Leuven, Celestijnenlaan 200F, 3001 Heverlee, Belgium. E-mail: pmangwala@yahoo.fr, peter.mangwala@unikin.ac.cd

Keywords: antimalarial; physalin B; epoxyphysalin B ; *Physalis angulata L.*

The identification and the crystal structure determination of two steroids extracted from a medicinal plant named *Physalis angulata L.*, collected in the D.R. Congo and whose antimalarial activity is known [1-3], have been fully realized by the X-ray diffraction analysis. Whole plants were then dried at room temperature in the laboratory protected from sunlight. Crude extract, obtained by maceration of the powdered plants in CH_2Cl_2 at room temperature, was filtered and evaporated to dryness under reduced pressure at 40 °C. Two products, X and Y, were isolated by bio-guided fractionation of the extract using Si-60 open chromatography followed by preparative HPLC. The powders of both samples were separately dissolved in an acetone:DMSO mixture. Plate-like crystals, suitable for X-ray diffraction measurement, were obtained in DMSO after the slow evaporation. For the compound X, diffraction data were collected on a diffractometer equipped with a Bruker-AXS SMART 6000 CCD detector and integrated by the program SAINT. A multi-scan absorption was performed by the program SADABS. For the compound Y, diffraction data collected on a Supernova diffractometer were analyzed with CrysAlisPRO software, and an empirical absorption correction based on the crystal morphology was performed. The structures were, in both cases, solved by direct methods using the SHELXS program and refined according to the least-squares methods to R-values of 0.0490 for X and 0.0563 for Y. Both crystals belong to the monoclinic space group $P2_1$ and show disorder. The asymmetric unit of the compound X comprises two physalin B molecules, one acetone molecule, and one water molecule with occupancy 0.22. The asymmetric unit of Y consists of one acetone molecule and two disordered physalin molecules, each corresponding to co-physalin B–5ß,6ß-epoxyphysalin B with occupancies of 0.76 and 0.57 for physalin B and 0.24 and 0.43 for 5ß,6ß-epoxyphysalin B. In both crystal structures, the physalin molecules in the asymmetric unit are strongly hydrogen-bonded through two O–H···O contacts, leading to dimers, which are used as building blocks during the crystallization of both compounds.

---

[1] Ankrah, N.-A., Nyarko, A. K., Addo, P. G. A., Ofosuhene, M., Dzokoto, C., Marley, E., Addae, M. M. and Ekuban, F. A. (2003). *Phytother. Res.*, **17**, 697–701.

[2] Lusakibanza, M., Mesia, G., Tona, G., Karemere, S., Lukuka, A., Tits, M., Angenot, L., Frédérich, M. (2010). *J. Ethnopharmacol.*, **129**, 398-402.

[3] Sá, M.S., De Menezes, M.N., Krettli, A.U., Ribeiro, I.M., Tomassini, T.C.B., Ribeiro dos Santos, R., Walter F deAzevedo, Jr., Soares, M.B.P. (2011). *Journal of Natural Products **74***, 2269-2272.

Y9

Young Scientist's Perspective of XRD at Sasol

R Forbes
Sasol Technologies, Johannesburg, South Africa

P1

Modulated Luminescent Chemistry of *tris*-Quinoline-Trivalent Metals (Al, Ga and In) Specimens.

Orbett T. Alexander, Alice Brink and Hendrik G. Visser
Department of Chemistry, University of Free State, P.O. Box 339, Bloemfontein 9300, South Africa.
E-mail: orbettalexander@yahoo.com

Keywords: Gallium, Fluorescence, Quinolinol, Oleds.

This project entails further exploration of luminescent capabilities of quinolinol derivatives, as potential fluorophores, chelated to the aluminum family group (Al, Ga and In). Moreover, the study of emission wavelength shift thereof; vastly influenced by the functional groups carefully introduced to the ligand.

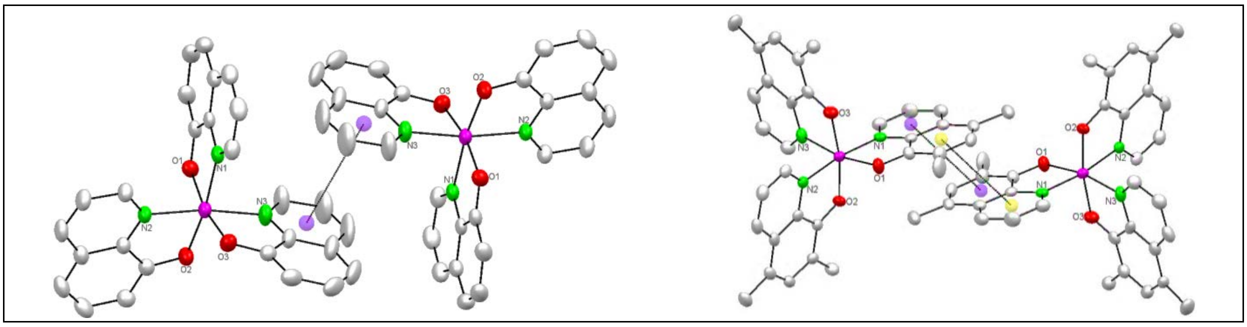


Figure 1: Schematic representation of Gallium species.

However, it is also concerned with understanding the solid and solution character of quinolinol derivatives as a ligand system coordinated to trivalent metal centers. These Metal-(quinoline)$_3$ entities, have known character of luminescent which was first discovered in 1987 by Tang and Van Slyke, using Aluminium as the metal center [1]. Their current applications consists amongst others, as the electroluminescent layer in the day-to-day manufacturing of the organic light emitting diodes (OLEDS). These metal coordinated quinolinol species have the potential application for consumer, industrial and medicinal use. They are used in the manufacturing of TV's, cell phones, computer monitors, watches, medicinal equipment, UPS's and also serve as potential anticancer agents to mention few [2-3]. Several interesting solid and solution state behaviour of the synthesized Metal-(quinoline)$_3$ complexes as determined by X-ray diffraction, NMR, UV/Vis spectroscopy as well as Fluorescence studies will be described. The potential fluorescence capability of these systems will be discussed as future "glow-in-the-dark" science.

---

[1] C.W. Tang, S.A. Van Slyke, Appl. Phys., 51, 913 (1987).

[2] http://www.emory.edu/BUSINESS/et/552fall2002/oled/applications.htm (Accessed 17-09-2014).

[3] A.A. Hummer, C. Bartel, V.B. Arion, M.A. Jakupec, W. Meyer-Klaucke, T. Geraki, P.D. Quinn, A. Mijovilovich, B.K.

[4] Keppler, A. Rompel, J. Med. Chem., 55, 5601 (2012).

P2

Structural Analysis of GH9 C1 Cellulase from a Compost Metagenomic Library

Valentine Anye [a] *and Wolf-Dieter Schubert* [b]

[a] Department Biotechnology, University of the Western Cape, Cape Town, South Africa 7535, E-mail: 2814902@myuwc.ac.za. [b] Department of Biochemistry, University of Pretoria, Pretoria 0002, South Africa.

Keywords: Crystallization, chromatography, GH9 Cellulases, structure modeling.

The rapid depletion of fossil fuel deposits and the deteriorating impact of fossil fuel combustion on the environment necessitate the exploration of cleaner and renewable energy sources like biofuels. Biofuels are energy sources derived from organic materials. Agricultural and forest residues rich in lignocellulose are attracting most attention as biomass for biofuel production. However, technologies to deconstruct lignocellulose to fermentable sugars are inefficient and costly. The use of biocatalyst, like cellulases, presents an alternative and cost effective route of lignocellulose deconstruction. Cellulases are enzymes that catalyse the hydrolysis of cellulose. Though considerable efforts have been made to study cellulases from microorganisms, cellulases to efficiently degrade cellulose have not been found. The metagenomic world seems to carry promising solutions to the industrial need of better cellulases. Metagenomics involves the direct analysis of DNA fragments from environmental samples for novel genes and gene products. This study was aimed at analysing the structure of GH9 C1 cellulase, the product of a novel cellulase gene isolated from straw based mushroom compost from Medallion mushroom farm, Stellenbosch, South Africa. The gene was cloned and expressed from a pET21a vector in *E. coli*. Using chromatographic methods, the protein was purified and characterized. The protein showed maximum activity between pH 5.5 and 7.0 with a pH optimum of 5.5 and a temperature optimum of 55°C. The enzyme showed low thermostability, relatively high specific enzyme activity and loses activity at low temperatures. The protein was crystallized by hanging and seating drop crystallization methods in reservoir solution made up of 15-30% (w/v) PEG 3350, 200 mM salt (any monovalent or divalent chloride) and 100 mM Tris-HCl pH 7.5-8.5. The protein crystals diffracted X-rays to 4 Å resolution with high crystal mosaicity (> 2°). The integrated dataset had very few fully recorded reflections and hence could not be used to build a 3D structure of the protein. The diffraction data showed that the crystals are monoclinic with a P2 space group. By homology modelling, GH9 C1 cellulase was shown to be a two modular protein with a smaller N-terminal Ig-like module linked to a larger catalytic module. The catalytic module conserved two calcium binding sites which potentially stabilize the active site conformation. Overall GH9 C1 cellulase is structurally similar to other GH9 cellulases, suggesting that its catalytic mechanism maybe conserved.

P3

Isomerization Behavior of Functionalized Tropolone in Oxidative Addition Processes.

Paul Severin Eselem Bungu[a], *Andreas Roodt* [a] *and Gideon Steyl*[b]
[a] Department of Chemistry, University of the Free State, Bloemfontein 9300, South Africa. E-mail: Bungueps@ufs.ac.za. [b] Golder Associates Pty. Ltd., Milton, Queensland, Australia 4064.

Keywords: Single crystals, rhodium, catalysis, spectroscopy.

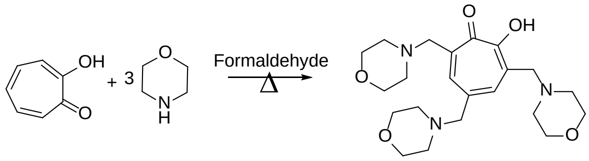
Crystal engineering is the planning and construction of the structure and properties of crystalline materials by designing molecular building blocks. [1] In this regard, tropolone (2-hydroxy-2,4,6-cloheptatrien-one) have been utilized as building blocks for the construction of liquid crystals and organogels.[2]

The growing application of rhodium(I) tropolonato tertiary aryl phosphine complexes toward oxidative addition as relevant to the Monsanto process, has also gained significant interest since the work done by Steyl et al. in the early 2000's.[3,4] The small bite (O-M-O) angle in tropolonato rhodium(I) complexes make them suitable to accommodate two phosphine/arsine ligands in the rhodium coordination sphere, hence forming a trigonal-bipyramidal geometry.[5] Moreover, tropolone ligands are symmetrical in nature; as a result, the isomerization of the oxidative addition products is assumed irrelevant as observed for other rhodium complexes,[6] thus, are considered good for catalyst design.

In this study, the effect of functionalized tropolone toward oxidative addition of methyl iodide to the rhodium (I) metal centre was investigated. The sterically hindered functionalized tropolone ligand was utilized to manipulate the rhodium metal centre.

To complete the coordination sphere of the rhodium (I) metal centre, tertiary aryl phosphine and carbonyls ligand moieties were used to design the precursors of the type ($[Rh(TropX_n)(CO)(PR_3)]$) (X = methylpiperidine, methyl(4-phenylpiperazine), R = tertiary aryl phosphine, and n = 2,3).

All materials and the resultant products were characterized in their solid state single crystal x-ray diffraction. Solution state characterization was obtained by multinuclear NMR, infrared and UV-Vis spectroscopy. These techniques were vital in the characterization of the intermediates species formed during the oxidative addition, hence were useful in proposing the mechanism and the rate law suitable for the reactions. The mechanism of action in the iodomethane oxidative addition will be discussed in detail in this presentation.



---

[1] (a) Steed, J. W; Atwood, J. *Supramol. Chem.* 2000, 389–462. (b) Matsumoto, A; Tanaka, T; Tsubouchi, T; Tashiro, K; Saragai, S; Nakamoto, S. *J. Am. Chem. Soc. Jpn*. 2002, **124**, 8891–8902.
[2](a) Kubo, K; Mori, A; Ujiie, S; Tschierske, C. *J. Oleo Sci.* 2004**, 53**, 575–579. (b) Kubo, K; Mori, A; Ujiie, S; Tschierske, C. *J. Oleo Sci*. 2005, **54**, 179–183.
[3] Steyl, G. *PhD Thesis: Experimatal and Theoretical Study on Tropolonato Complexes of Rhodium, Rand Afrucaans University, Johannesburg, South Africa*. 2004.
[4]Steyl, G. *M.Sc. Thesis, University of the Free State, Bloemfontein, South Africa*. 2000.
[5] Roodt, A; Otto, S;Steyl, G. *Coord. Chem. Rev*. 2003 **245**, 121–137.
[6]Aswegen, K. G; Leipolt, J.G; Potgieter, I.M; Lampbrecht, J.G; Roodt, A; van Zyl, G.J. *Trans. Met. Chem*. 1991,**16**, 369.

P4

X-ray Crystallographic and Computational chemistry study of selected molecular systems.

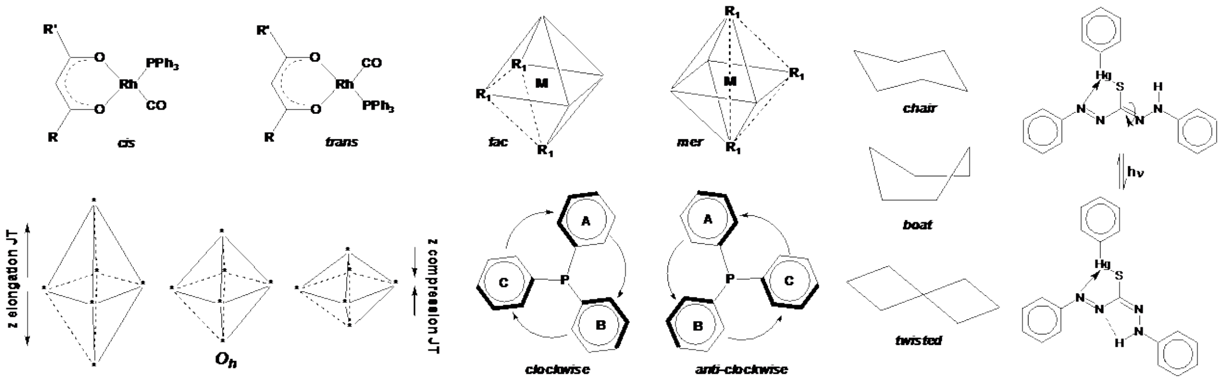
Jeanet Conradie

Department of Chemistry, University of the Free State, Bloemfontein 9300, South Africa.

Keywords: X-ray crystallography, DFT.

X-ray crystallography is an experimental tool used to determine the three-dimensional arrangement of atoms in a molecular system. However, it often is difficult or even impossible to obtain crystals to be studied experimentally. It also is not always clear why only specific isomers or conformers are isolated by experiment. In comparison, computational chemistry by means of density functional theory (DFT) calculations, is an effective tool to understand, predict and complement experimental results.

In this contribution, X-ray crystallographic as well as DFT results on selected molecular systems, will be compared and discussed. Questions such as the following will be investigated: What are the favoured conformations of metal-bound PPh_3 in tetrahedral, trigonal-bipyramidal, octahedral or square planar complexes [1,2]? What is the expected isomer to be isolated in different *fac* and *mer*; *trans* and *cis;* or *E* and *Z* crystal systems [3]? What is the lowest energy product obtained from the oxidative addition reaction of methyl iodide to model square planar rhodium complexes, which are used as catalyst precursors [4]? When the ground state structure of a photochromic complex is known, how can DFT be utilized to also predict the structure of the excited state [5]? How can DFT calculations predict the type of Jahn–Teller distortion, observed in octahedral complexes with doubly degenerate ground states [6]?



---

[1] Conradie, J. *Dalton Transactions*, 2012, **41**, 10633-10642.

[2] Stuurman, N.F; Muller, A; Conradie, J. *Inorganic Chimica Acta*, 2013, **395**, 237–244.

[3] Conradie, M.M; van Rooyen, P.H; Conradie, J. *Journal of Molecular Structure*, 2013, **1053**, 134-140.

[4] Conradie, M.M. and Conradie, J. *South African Journal of Chemistry*, 2008, **61**, 102-111.

[5] von Eschwege, K.G; Conradie, J; Swarts, J.C. *Journal of Physical Chemistry B*, 2008, **112**, 2211-2218.

[6] Freitag, R; Muller, T.J; Conradie, J. *Journal of Chemical Crystallography*, 2014, **44**, 352-359.

P5

Hydrogen bonding at C=Se acceptors in selenium compounds

Bibelayi Dikima[a], *Juliette Pradon*[b] , *Zephyrin G. Yav*[a] , *Frank H. Allen*[b] , *Peter T.A. Galek*[b] , *A. S. Lundemba*[a] *and Colin R. Groom*[b]

[a] Département de Chimie, Université de Kinshasa, B.P.190 Kinshasa XI, République Démocratique du Congo. E-mail: ddikima@gmail.com. [b] Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

Keywords: hydrogen bonding, C=Se acceptors.

Due to the importance of both inorganic and organic selenium, we are embarking on a series of studies of structural chemistry of small-molecule Se compounds, with an emphasis on their intermolecular interactions in crystal structures. The Cambridge Structural Database [1, 2] and Gaussian09 [3] form the principal information and computational resources for these surveys and, where appropriate, comparisons are made with the structural chemistry of analogous O- and S-containing compounds. At this stage, we report a general survey of Se in small-molecule crystal structures and examine the ability of Se to accept H-bonds in these compounds. This survey builds on earlier studies of the H-bonding abilities of the analogous C=O and C=S acceptors [4, 5].

---

[1] Allen, F. H. *Acta Cryst.*, 2002, **B58**, 380-388.

[2] Groom, C; Allen, F. H. *CSD System Software.*, 2014.

[3] Frisch, M. J. *et al. GAUSSIAN09.*, 2013, Revision D.01. Gaussian, Inc., Wallingford CT.

[4] Allen, F. H.; Bird, C. M.; Rowland, R. S. & Raithby, P. R. *Acta Cryst.*, 1997, **B53**, 696-701.

[5] Wood, P. A.; Pidcock, E; Allen, F. H. *Acta Cryst.*, 2008, **B64**, 491-496.

P6

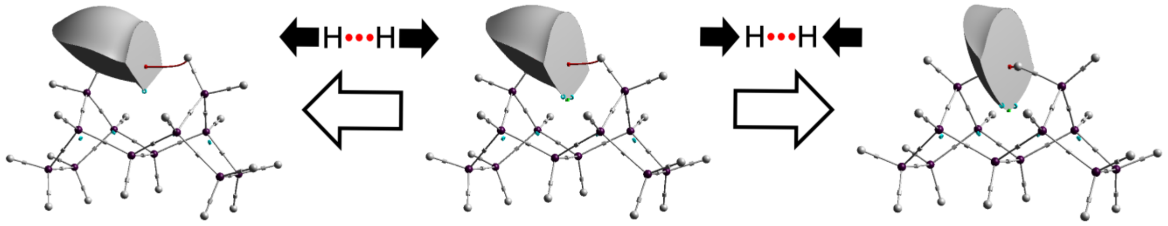
Atoms in Molecules. Beyond Electron Density: the Ehrenfest Force Field

Jan Dillen
Department of Chemistry and Polymer Science, Stellenbosch University, South Africa, JLMD@sun.ac.za

Keywords: quantum theory, AIM.

In the traditional Quantum Theory of Atoms in Molecules (AIM), [1] the partitioning of molecules into atoms is based on electron density, an observable quantity, using properties such as bond critical points and zero-flux surfaces as indicators. Recently, this method has come under severe criticism. [2-7]

In this work, an alternative partitioning scheme based on the Ehrenfest force density is presented, the latter being the force exerted on a point in the electron density by all the other particles in the molecule. In contrast to common quantum mechanical practice, Slater-type Orbitals (STO) are used instead of the ubiquitous Gaussian-type orbitals (GTO).



This study removes some, but not all controversial issues of the traditional AIM theory and shows that current and widely-spread basis sets based on GTO’s are useless to study the Ehrenfest Force, and that the few available (commercial) STO basis sets only perform marginally better.

---

[1] Bader, R.F.W. *Atoms in Molecules: A Quantum Theory*, 1990, Oxford, University Press, Oxford, UK..

[2] Fernández, I.; Frenking, G.; Uggerud, E. *Chem. Eur. J.* 2009, **15**, 2166–2175.

[3] van Zeist, W.J.; Bickelhaupt, F. M. *Chem. Eur. J.* 2010, **16**, 5538–5541.

[4] Fernández, I.; Frenking, G.; Uggerud, E. *Chem. Eur. J.* 2010, **16**, 5542–5543.

[5] J. Poater, M. Solà, F. M. Bickelhaupt, *Chem. Eur. J.* 2006, **12**, 2889 – 2895

[6] R.F.W. Bader, *Chem. Eur. J.* 2006, **12**, 2896 – 2901

[7] J. Poater, M. Solà, F. M. Bickelhaupt, *Chem. Eur. J.* 2006, **12**, 2902 – 2905

P7

Hydrate formation in pharmaceutically relevant salts

Bernard Dippenaar, *Catharine Esterhuysen and Delia Haynes*
Department of Chemistry, University of Stellenbosch, Stellenbosch, South Africa, E-mail: abdippenaar@sun.ac.za

Keywords: hydrate, hydrogen bond, pharmaceutically relevant salts, AIM, water activity.

The formation of hydrates are of particular interest in pharmaceutical studies as hydrates may exhibit properties such as improved stability, solubility, hygroscopicity, crystallinity and bioavailability as opposed to the dehydrated form[1]. Although factors that influence hydrate formation have been investigated[2], and crystallographic database studies assessing the probability of organic compounds or salts crystallising as hydrates have been carried out[3], the reasons for the propensity for certain compounds to form hydrates have not yet been identified. The role of the hydrogen bond in hydrate formation was specifically investigated in this study as it has been suggested that the absence of a hydrogen bond in hydrates is a very rare occurrence[4]. The strength of the hydrogen bond was investigated by performing geometry optimisations and intermolecular interaction energy calculations for various pharmaceutically relevant anionic groups. It was found that the polarity and electronegativity of each group will have a significant effect on the strength of the hydrogen bond, but only if sterics are not present. Furthermore the inductive effects from substitutions on an aromatic ring were investigated by adding electron-donating and electron-withdrawing groups on the ring and measuring the change in strength of the hydrogen bond, where the strength of the hydrogen bond increased if electron donating groups were placed at the ortho and para positions. This was confirmed by AIM analysis, which showed an increase in electron density at the hydrogen bond critical points when adding electron donating groups. Lastly the effect of water activity was investigated by performing a series of crystallisations in different solvent mixtures. The results showed that water activity has a significant effect on the propensity of compounds to form hydrates.

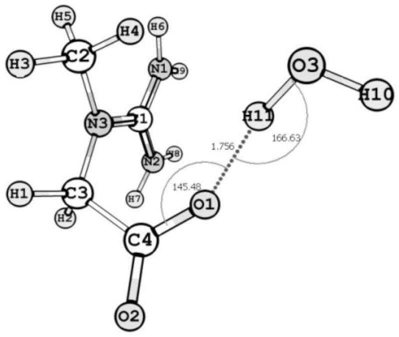


Figure 1: The hydrogen bond in N-carbamimidoyl-N-methylglycine

---

[1] Vippagunta, S R; Brittain, H G; Grant, D J W. *Adv. Drug Del. Rev.*, 2001, **48**, 3-26, R. R. vich R; Cooke M; Peterson M L. *J. Pharm. Sci.*, 2012, **101**, 4013–4017; Aaltonen J; M Alleso; Mirza M; Koradia V; Gordon K C; Rantanen J. *Eur. J. Pharm. Biopharm.*, 2009, **71** 23-37.

[2] Infantes L; Fabian L; Motherwell W D S. *CrystEngComm*, 2007, **9** 65-71; Briggs, N E B; Kennedy A R; Morrison C A. *Acta Crystallographica Section B*, 2012, **68** 453-464; Fabbiani, F P A et al. *CrystEngComm*, 2010, **12**, 2354-2360.

[3] Haynes D A; Jones W; Motherwell W D S. *CrystEngComm.*, 2005, **7** 342-345.

[4] Infantes L; Chisholm J; Motherwell W D S. *CrystEngComm*, 2003, **5**, 480–486.

P8

Coordination behaviour of biuret in different metal complexes

Mohammed Elmakki and Johan Venter
Department of Chemistry, University of the Free State, Bloemfontein, South Africa 9300, E-mail:elmakkim@ufs.ac.za

Keywords: Biuret, various configurations.

Biuret (Bu), $H_2N\text{-}CO\text{-}NH\text{-}CO\text{-}NH_2$ was first obtained by Wiedemann [1] in 1848 and has since become known as a good donor ligand. It forms coordinating complexes with bivalent transition metals and rare earth metals like Y^{3+}, Gd^{3+}, La^{3+} and Sm^{3+}. The biuret molecule can have various structural configurations when acting as a ligand. In low-pH or neutral conditions, biuret shows O, O'-bidentate coordination to metal cations, e.g. with zinc [2], copper [3] (Fig.1) and samarium [4] (Fig.2). When biuret is deprotonated in basic conditions, N, N'-bidentate coordination, e.g. with copper arise [5] (Fig.3). Biuret can also act as a mono-dentate ligand in *trans* conformation as seen in the cadmium complex in Fig.4 [6]. The molecular structure of a nickel biuret complex is shown in Fig.5 [7].

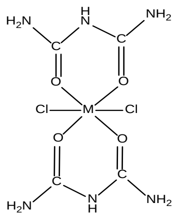


Fig.1. M = Cu^{2+}, Zn^{2+}

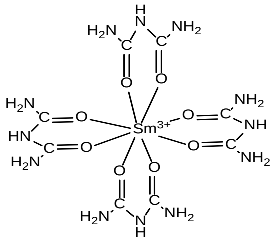


Fig.2. Tetrakis (biuret) samarium (III)

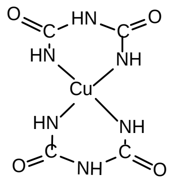


Fig.3. Copper biuret complex

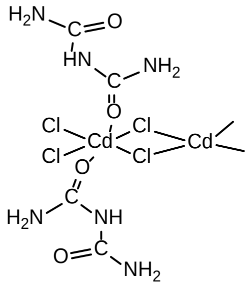


Fig.4. Cd biuret complex

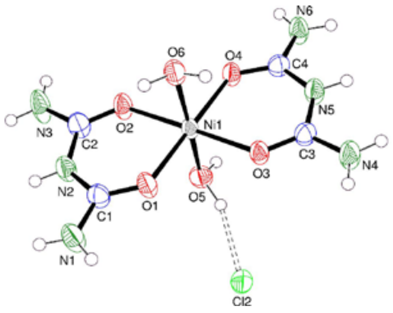


Fig.5. $[Ni(Bu)_2(H_2O)_2]Cl_2$

We are currently investigating biuret complexes with rhodium and other platinum group metals.

---

[1] Wiedemann, G, *Ann. Chem.*, **68**, 324-330 (1848).

[2] Nardelli, M., Fava, G, Giraldi, G., *Acta Cryst.*, **16**, 343-352 (1963).

[3] Freeman, H.C., Smith, J.E.W.L., *Acta Cryst.*, **20**,153-159 (1966).

[4] Haddad, S.F., *Acta Cryst.*, **C43**, 1882-1885 (1987).

[5] Aida, K., Musya, Y., Kinumaki, S., *Inorg. Chem.*, **2**, 1268-1269 (1963).

[6] Cavalca, L., Nardelli, M., Fava, G., *Acta Cryst.*, **13**, 594-600 (1960).

[7] Lawson, J., Harrison, W.T.A., *Acta Cryst.*, **E61**, m525-m527 (2005).

P9

Structural and catalytic evaluation of phosphorous containing complexes of rhodium and iridium for use in olefin hydroformylation

Ilana Engelbrecht, Hendrik G. Visser and Andreas Roodt
Department of Chemistry, University of the Free State, Bloemfontein, South Africa, 9300, E-mail: engelbrechti@ufs.ac.za.

Keywords: rhodium, iridium, catalysis, hydroformylation.

Globally there is a large push towards getting more favorable product outcomes and reaction conditions in catalytic design. Hydroformylation is one of the largest and most important homogeneous catalyzed industrial processes for the production of aldehydes from alkenes. High selectivity for the desired isomer of the aldehyde can be kinetically manipulated by variation of the ligands and process conditions [1]. In rhodium systems, it is known that the presence of phosphine ligands give way to more active, highly selective catalysts, reacting under milder reaction conditions [2]. Iridium compounds are often used as model complexes since Ir(I) and Ir(III) complexes with similar ligand sets to those proposed in rhodium chemistry tend to behave in the same way.

The influence of a range of PNP (diphosphinoamine) ligands, with various substituents on the nitrogen atom (Figure 1a), was investigated on the hydroformylation of 1-octene using rhodium and iridium as metal centers. The steric bulk of the nitrogen atom was calculated through a newly introduced *Effective Tolman-based N-substituent steric parameter* ($\theta_{\text{N-sub}}$, Figure 1b) which is a modification of the Tolman Angle [3-4]. This parameter was calculated for the free ligands as well as for different metal complexes thereof and compared to catalytic data. A tendency is observed for increasing selectivity and activity with the increase in bulkiness around the nitrogen atom.

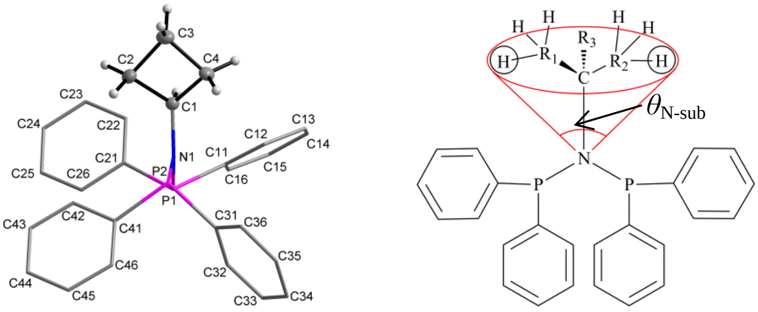


Figure 1: (a) DIAMOND representation of *N*,*N*-Bis(diphenyl-phosphanyl)cyclobutananime (b) Effective Tolman-based N-subtituent steric parameter ($\theta_{\text{N-sub}}$).

---

[1] Van Leeuwen P.W.N.M; *Homogeneous Catalysis: Understanding the Art*, 2004, Dordrecht: Kluwer Academic Publishers.

[2] Osborn, J.A; Wilkinson, G; Young, J.F. *Chem. Commun*., 1965, 17.

[3] Cloete, N.; Visser, H. G.; Engelbrecht, I.; Overett, M. J.; Gabrielli, W. F.; Roodt, A. Inorg. Chem. 2013, 52, 2268-2270.

[4] Tolman, C. A. *Chem. Rev*. 1977, **77**, 313-348.

P10

Negative thermal expansion facilitated by weak host-guest interactions

Emile R. Engel, Vincent J. Smith, Charl X. Bezuidenhout and Leonard J. Barbour
Department of Chemistry and Polymer Science, University of Stellenbosch, Stellenbosch 7600, South Africa,
E-mail: ere@sun.ac.za

Keywords: negative thermal expansion, inclusion compound, crown ether.

Reports of anomalous thermal expansion have become more frequent in recent years but are dominated by inorganic systems showing negative linear and volumetric thermal expansion. Typical examples include silicates and zirconium tungstenates that incorporate strong covalent bonds as well as MOF-5 and related IRMOFs constructed with metal-ligand coordination bonds.[1] Organic compounds displaying these properties are still relatively rare.

Several mechanisms resulting in negative thermal expansion have been described. Arguably the most important of these have involved bridging atoms and rigid unit vibrational modes; magnetostriction; and electronic effects.[2,3] Extremely large positive and negative thermal expansion for a dumbbell-shaped organic molecule was reported where the mechanism depended on a helical pattern of strong O-H•••O hydrogen bonds.[4] For a multi-component organic hydrate recently reported as undergoing negative linear thermal expansion, an extensive network of ionic and hydrogen bonds is present.[5]

In the present study an 18-crown-6 solvate was investigated by variable temperature single-crystal X-ray diffraction. Exceptionally large positive thermal expansion in two axial directions and negative thermal expansion along the third was confirmed (figure 1). This is a very rare observation for an organic inclusion compound. Furthermore, the mechanism of negative thermal expansion relies exclusively on weak electrostatic interactions.

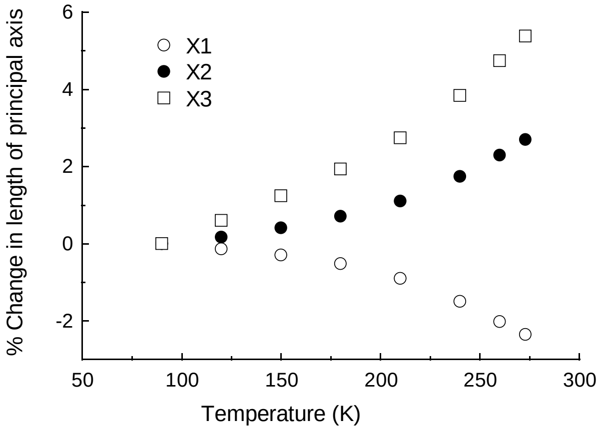


Figure 1: Percentage changes in principal axis lengths as a function of temperature.

---

[1] T.A. Mary, J.S.O. Evans, T. Vogt, A.W. Sleight, Science, 272 (1996) 90-92.

[2] G.D. Barrera, J.A.O. Bruno, T. H. K. Barron, N.L. Allan, J. Phys.: Condens. Matter, 17 (2005) R217-R252.

[3] W. Zhou, H. Wu, T. Yildirim, J.R. Simpson, A.R. Hight Walker, Phys. Rev. B, 78 (2008) 054114.

[4] D. Das, T. Jacobs, L.J. Barbour, Nature Mater., 9 (2010) 36-39.

[5] S. Bhattacharya, B.K. Saha, Cryst. Growth Des., 12 (2012) 4716-4719.

P11

Gallium(III) based Complexes as Models for Radiopharmaceuticals

M. Esterhuysen, H.G.Visser and A. Roodt
Department of Chemistry, University of the Free State, Bloemfontein 9300, South Africa.
E-mail: 2008005060@ufs4life.ac.za

Keywords: N,N'-tetradentate ligands, radiopharmaceuticals, cell toxicity, transferrin-gallium complex.

The majority of the radiopharmaceuticals produced to date (95%) are used for diagnostic purposes.[1] ^{99m}Tc is the isotope of choice for nuclear imaging, but other alternatives investigated includes the isotopes of gallium (^{67}Ga (used for SPECT) and ^{68}Ga (used for PET)), because of the similarity of the coordination chemistry of Tc and Ga.[2] Two *N,N'*-tetradentate ligands that can be coodinated to metals such as Ga(III) were synthesized and characterization of the ligands and the metal complexes were performed with X-ray crystallography, NMR, IR spectroscopy and elemental analysis.

The two compounds that were tested on oesophageal cancer cell lines showed promising results for inhibition of cell growth and further exploration of this possibility forms part of future work. Other metals, combined with the *N,N'*-tetradentate ligands, which can be investigated and characterized include gold, platinum, indium and aluminium.

Focusing on the biological interaction of compound A (*figure 1*), a cell toxicity test (MTT assay) was performed and results include the IC$_{50}$ dose with value of 2.285 indicating moderate toxicity in a biological system (*figure 2*). Gallium forms a transferrin-gallium complex that inhibits DNA synthesis by acting on ribonucleic reductase and the Ga uptake is selective for actively proliferating tumour cells.

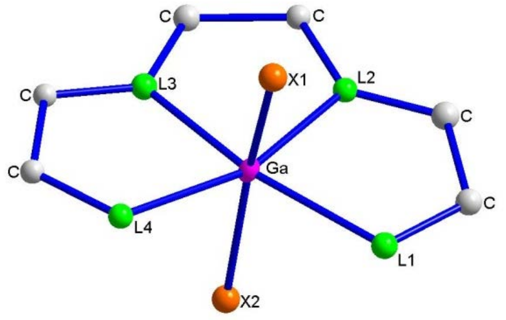


Figure 1: Graphical representation of compound A

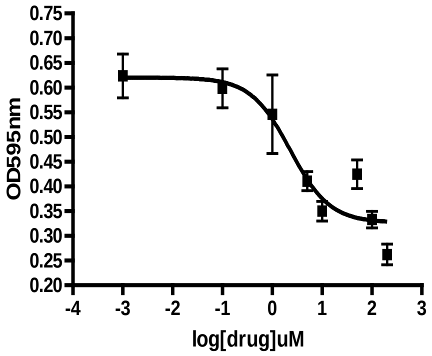


Figure 2: Results of MTT assay for compound A

---

[1] Zuchman, S. A., Freeman, G. M., Trouter, D. E., Volkert, W. A., Holmes, R. A., Van Derveer, D. G., Barfield, E. K., *Inorg. Chem.*, **20**, 2386, 1981.

[2] Bartholoma, M. D., Louie, A. S., Valliant, J. F. and Zubieta, J., *Chem. Rev.*, **110**, 2903-2920, 2010.

P12

Utilization of Computational chemistry and X-ray crystallography to study the Jahn-Teller distortion in Mn(dbm)$_3$.

Roxanne Freitag and Jeanet Conradie

Department of Chemistry, University of the Free State, Bloemfontein 9300, South Africa, E-mail:
roxannefreitag@gmail.com.

Keywords: Manganese, β-diketone, computational chemistry, Jahn-Teller distortion.

The Jahn-Teller distortion, physically observed as a geometric distortion of certain molecular systems to reduce its symmetry and energy, is typically observed among octahedral complexes where the two axial bonds are shorter or longer than the equatorial bonds. High-spin octahedral Mn(β-diketonato)$_3$ complexes undergo Jahn-Teller distortion due to the partially filled doubly degenerate (e_g) orbital [1][2]. Generally elongation Jahn-Teller distortion [3][4][5][6] was observed in the Mn(β-diketonato)$_3$ crystal structures, although compression Jahn-Teller distortion was also reported [7][8].

The Jahn-Teller distortion obtained in the crystal structure of Mn(PhCOCHCOPh)$_3$, measured at 100 K, will be presented and compared with previously published structures obtained at room temperature [5][6]. The experimental results will be complimented by density functional theory (DFT) calculated results to understand compression and elongation Jahn−Teller distortion in this Mn(PhCOCHCOPh)$_3$ structure.

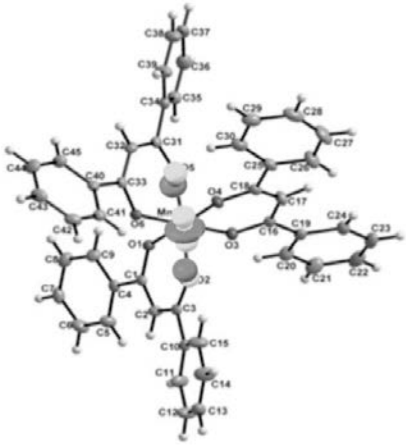


Figure 1: Crystal structure of Mn(PhCOCHCOPh)$_3$ with an overlay of the DFT calculated HOMO orbital (from the optimized geometry of the complex).

---

[1] Diaz-Acosta, I; Baker, J; Hinton, J.F; Puley, P. *Spectrochemica Acta Part A*, 2003, **59**, 363-377.

[2] Geremia, S; Demitri, N. *J. Chem. Educ.*, 2005, **82**, 460-465.

[3] Fackler, J.P; Avdeef, A. *Inorg. Chem.*, 1974, **13**, 1864–1875.

[4] Stults, R.B; Marianelli, R.S; Day, V.W. *Inorg. Chem.*, 1979, **18**, 1853–1858.

[5] Zaitseva, E.G; Baidina, I.A; Stabnikov, P.A; Borisov, S.V; Igumenov, I.K. Zh. Strukt. Khim. (Russ.) (J. Struct. Chem.), 1990, **31**, 184.

[6] Barra, A.L; Gatteschi, D; Sessoli, R; Abbati, G.L; Cornia, A; Fabretti, A.C; Uytterhoeven, M.G. Angew. Chem. Int. Ed.,1997, **36**, 2329.

[7] Magnus, P; Payne, A.H; Waring, M.J; Scott, D.A; Lynch, V. *Tetrahedron Lett.*, 2000, **41,** 9725.

[8] Frohlich, R; Milan, R; Yadava, S. *CCDC 692561*, **reference ACACMN24**, 2008.

P13

Proposal of a new supramolecular synthon: Gold(I) acting as a Lewis Base; an extensive theoretical investigation

Ferdi Groenewald[a], *Catharine Esterhuysen*[b] *and Jan Dillen*[a]

[a] Department of Chemistry and Polymer Science, Stellenbosch University, Private bag X1, Matieland, 7602, South Africa.

Keywords: Hydrogen Bonding, Halogen Bonding, Gold I, Synthon, Lewis Base.

The gold anion is known to form hydrogen bonds (H-Bonds) in the gas phase, as described in a short survey by Kryachko [1] in 2007. In this survey he lists H-Donors, HF, H_2O and NH_3, that have been shown to form H-Bonds. Furthermore, a more recent and extensive review about possible gold hydrogen bond formation has been published in Chem Soc Rev in 2013 [2]. The authors note that there are Au(I)···H contacts when the Cambridge Structural Database [3] is investigated. However, these contacts are a result of close-lying H-Bonds that are within the defined Au-H contact and are not a result of the formation of a Au(I)···H hydrogen bond. Also, some transition metals, when in a low oxidation state, are known to form H-Bonds as theoretically investigated by Alkorta and co-workers [4]. Interestingly, gold is one of the most electronegative metals [1], thus making it a candidate for possible H-Bond formation. In this regard it is interesting to note that very recently the first example of the Au(I)···H contact in a crystal structure was published by Koskinen and co-workers [5], where the Au(I) center forms an interaction with an aromatic hydrogen. The authors found the interaction energy to be weak, approximately 1.0 kcal/mol. Their results agree with our preliminary results. Since H-Bonding is known to be similar to halogen bonding, we are also investigating possible Au(I)···X interactions.

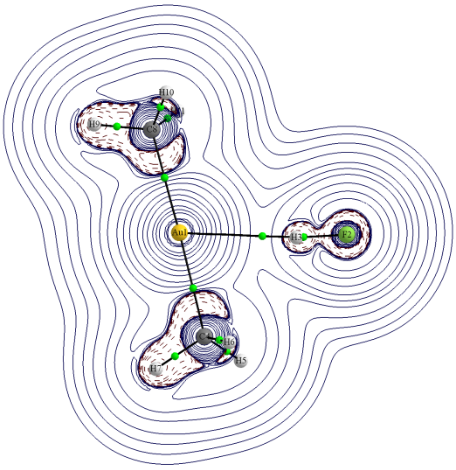


Figure 2 – $\Delta^2\rho$ of the electron density of the optimised structure $[H_3C\text{-}Au\text{-}CH_3]^-$ with HF at the MP2/aug-cc-pVTZ-pp level of theory.

---

[1] Kryachko, ES. *J. Mol. Struct.*, 2008, 880, 23-30.

[2] Schmidbaur, H; Raubenheimer, H G; Dobrzańska, L. *Chem. Soc. Rev.*, 2013, 43, 345-380.

[3] Allen, F H. *Acta Crystallogr.*, 2002, B58, 380-388.

[4] Alkorta, I; Rozas, I; Elguero, J. *J. Mol. Struct.* (*Theochem*), 2001, 537, 139-150.

[5] Koskinen, L; Jääskeläinen, S; Kalenius, E; Hirva, P; Haukka, M. *Cryst. Growth. Des.*, 2014, 14, 1989−1997.

P14

Synthesis of diphosphinoamine ligands (PNP) for hydroformylation reactions and their coordination with Pt and Pd.

Dumisani V Kama[a], *Hendrik G. Visser*[a] *and Alice Brink*[a]
[a] Department of Chemistry, University of the Free State, P.O. Box 399, Bloemfontein 9300, South Africa.
Email: kamadv@ufs.ac.za

Keywords: rhodium, platinum, palladium, catalysis.

Homogeneous catalysed hydroformylation is one of the largest aldehyde producing processes in the world, with over 12 million tons of hydroformylation products produced in 2012 [1-3] Synthesis of novel highly selective catalysts still poses a significant challenge to the field [4]. The first catalyst utilized for hydroformylation was $[CoH(CO)_4]$ [5] and in 1966, the petroleum company Shell discovered that substituting CO with a tertiary phosphine increased catalyst activity [6]. Current research is focused on increasing selectivity of the catalyst towards more valued linear products using phosphine ligands. To fully understand the mechanistic behavior of these catalysts, detailed evaluation of the coordination chemistry of the metal center and the coordinating ligands is needed. Determining the molecular structure of both the free ligand and the coordinated complex using different techniques such as Nuclear Magnetic Resonance (NMR), X-ray diffraction (XRD) and Infrared Spectroscopy (IR) can contribute greatly to this effect. We report here a range of systematically altered M – PNP (M = Pd, Pt) systems that offers an effective evaluation of the steric parameter of these PNP ligands. A preliminary hydroformylation reaction of 1-octene utilizing a Rh – PNP catalyst is also presented (**Figure 1**).

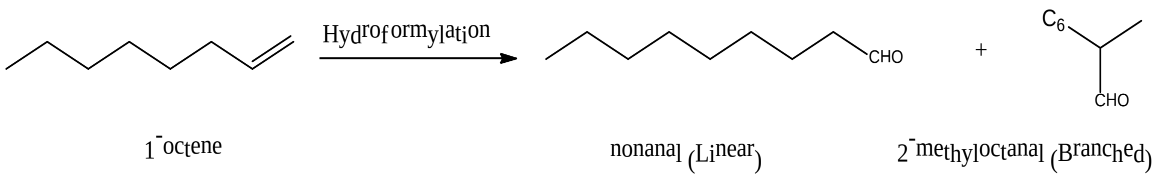


Figure 3 Schematic representation of a hydroformylation reaction of 1-octene, showing the formation of branched (2-methyloctanal) and a linear (nonanal) product [2].

---

[1] Van der Veen, L.A; Kamer, P.C.J; Van Leeuwen, P.W.N.M. *Angew. Chem. Int. Ed.*, 1999, **38**, 3.

[2] Erkey, C; Palo, D.R; Haji, S. *Fuel. Chem. Div. Prep.*, 2002, **47,** 144.

[3] Frey, G.D. *J. Organomet. Chem*., 2014, **754**, 5-7.

[4] Kumar, M,; Chaudhari, R.V; Subramaniam, B; Jackson, T.A. *Organometallics.*, 2014, **33**, 4183−4191.

[5] Haumann, M; Meijboom, R; Moss, J.R; Roodt, A., *Dalton Trans*., 2004, **11**, 1679-1686.

[6] Meijboom, R; Haumann, M; Roodt, A; Damoense, L. *Helv. Chim. Acta*., 2005, **88** , 676 -693.

P15

New approaches in tantalum and niobium separation.

R. Koen, H.G. Visser & A. Roodt
Department of Chemistry, University of the Free State, Bloemfontein, 9300, South Africa, E-mail: koenr@ufs.ac.za.

Keywords: Tantalum, niobium, separation, bidentate.

The separation of niobium and tantalum has always been a complicated process, particularly due to their near identical chemical properties. Niobium(V) and tantalum(V) are both hard metal centres and the halido species are known to readily hydrolyse.[1] The aim of this project is to find significant chemical and physical differences between complexes of tantalum and niobium which would allow the separation and purification of these metals. The ultimate goal of this approach is to find differences in coordination preferences of analogous tantalum and niobium complexes when using the same synthetic procedure. This is done with the aim of exploiting these differences in a separation process

In this present investigation of tantalum(V) and niobium(V) complexes, different bidentate ligands (*L,L'-Bid*$^{-}$) have been used in synthesis, in an attempt to study the variation in activity and selectivity of coordination of *L,L'-Bid*$^{-}$ to tantalum and niobium -halides, -methoxides. (*L,L'-BidH* = functionalized acetylacetone-, 8-hydroxyquinoline- and tropolone derivatives). Novel bidentate carbene ligands systems have also been synthesized and coordination of the systems to the metal centres will be discussed.

Moreover, single crystal X-ray diffraction was used to evaluate the characteristics of a range of ligands and complexes, and the results of the obtained structures will be discussed. Examples include mono- (halido and pseudo halido) and bidentate (including novel carbene systems), hard ligands with *O,O'*- and *N,O*- donor atoms.[2]

---

[1] Lambert, J.B.; *Kirk-Othmer Encyclopedia of Chemical Technology*. 2011, John Wiley & Sons, Inc., 1-23.

[2] S. Basson, *Transition Met. Chem.*, 1982, 7, 207-209.

P16

Synthesis, Spectral Characterization and Biological Evaluation of Cu(II) and Fe(III) Complexes of Acetaldehyde Thiosemicarbazone.

[a,b] *Kpomah, B.*, [b] *Egboh, S.H.O.* and [b] *Agbaire, P.O.*
[a] Chemistry Department, Delta State College Physical Education, Mosogar Nigeria, E-mail: tressurekpomah@yahoo.com.
[b] Chemistry Department, Delta State University, Abraka Nigeria.

Keywords: Cu(II) Complex, Fe(III) complex, acetaldehyde thiosemicarbazone, antibacterial activities.

Two new Cu(II) and Fe(III) complexes with acetaldehyde thiosemicarbazone (ADTSC) were synthesized from the Schiff base derived from thiosemicarbazide and acetaldehyde. The newly synthesized complexes have been characterized by elemental analysis, molar conductance, electronic spectra and infrared FT-IR. On the basis of these spectral data, the general formulas: Cu(ADTSC)2 (SO4)(H2O) and Fe(ADTSC)2Cl2 .3H2O and an octahedral geometry was proposed for the complexes. The ligand and its complexes have been screened for their antibacterial activities against Salmonella typhi, Shegella species, Escherichia coli, Klebsiella sp, Staph. aureus Pseudomonas, aeruginosa and Vibrio cholera. The results of these studies show the metal complexes displayed more antibacterial activities against most of the species as compared to the uncomplexed ligand. The minimum inhibitory concentrations (MICs) of the compounds were also determined by two fold serial dilution method, the results showed an MIC value in the range of 500-250 µg/ml for the free ligand and 250-62.50 µg/ml range for the complexes.

P17

A Platinum(II) Complex Bearing Δ^2-1,2,4-Triazoline Ligand: Combined X-ray and NMR Structural Studies

Andreii S. Kritchenkov,[a] *Stanislav I. Selivanov*,[a] *Nadezhda A. Bokach*,[a] *Andreas Roodt*,[b] *Carla Pretorius*,[b] *and Vadim Yu. Kukushkin*[a]

[a] Institute of Chemistry, Saint Petersburg State University, Saint Petersburg, Russian Federation, E-mail: platinist@mail.ru; [b] Department of Chemistry, University of the Free State, Bloemfontein, South Africa

Keywords: platinum complexes, triazolines, X-ray structure, solution structure, NMR.

The title compound was synthesized by previously unknown cycloaddition reaction between the platinum(II) complex *trans*-$[PtCl_4(EtCN)_2]$ and the azomethine imine, viz. *p*-$MeOC_6H_4CH{=}N^aNC(O)CH(NHC(O)C_6H_4Me\text{-}m)C^bH(C_6H_4Cl\text{-}p)^{(a\text{–}b)}$, followed by reduction of thus formed platinum(IV) species with the phosphorous ylide $Ph_3P{=}CHCO_2Et$. The platinum(II) complex was characterized in the solid state by single-crystal X-ray diffraction (XRD). In addition, solution structure of the complex was assessed by inspection of scalar and direct (through space) dipole–dipole interactions detected, respectively, in the COSY-90 and NOESY spectra. In the complex, the bicyclic Δ^2-1,2,4-triazoline and the EtCN ligands lie in the *trans*-position to each other. The Pt(1)–N(2) bond length [1.991(5) Å] is typical for (imine)Pt^{II} species [1]. The C=N bond distance (N2–C3 1.285(9) Å) is in the range that is characteristic of the C=N double bonds [1]. The substituents at the C(6) atom and at the C(7) atom of Δ^2-1,2,4-triazoline ring are located in the *trans*-position, while the substituents at the C(7) atom and at the C(1) atom adopt the equatorial positions.

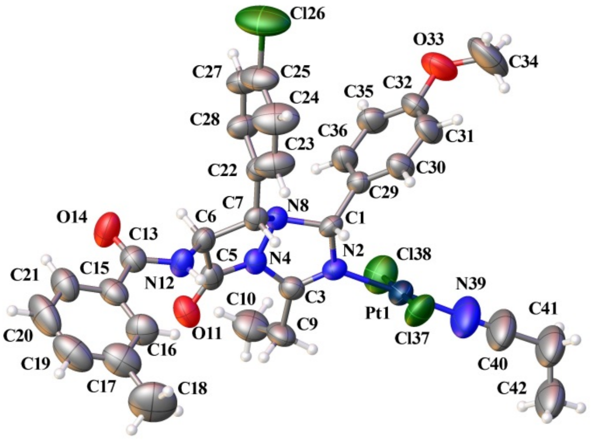


Figure 1. View of the title complex with the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

The quantitative evaluation of several pairs of interproton distances obtained by NMR (COSY-90 and NOESY experiments) and XRD agrees well with each other and with those obtained by MM+ calculation method.

---

[1] Allen, F.H., et al. *Perkin Transactions*, 1987, **12**, S1–S19.

Acknowledgements: Financial support from Russian Fund for Basic Research (grant 14-03-93959) and Russia/South Africa Research Cooperation Program (UID 92196) is gratefully acknowledged.

P18

Proposal for Thesis: Characterization of some natural phosphates in the soil of MADAGASCAR by X-ray diffraction method

Laza Andriamanantena, Mariette S. Razanajatovo and Claudine H.M. Rakotozafy
Laboratory of Solid state Physics and Experimental Physics (LSPEP), Department of Physics and Applications, University of Madagascar, Antananarivo 101. E-mail: lazatman@yahoo.fr.

Keywords: Phosphates, solid/liquid interface, hexagonal lattice, crystallographic parameters, ShelX.

Researches on minerals are essential for optimal use of Malagasy mining resources. This thesis related to the mineral phosphates, aims to introduce a long series of researches which use X-ray diffraction on local materials available in Madagascar.

Researches have demonstrate that there is a correlation between the supply function of the amount of phosphate ions which could be transferred by diffusion in the solid solution interface (as a result of the concentration gradient and time) and the variable (Fe + Al)*ox*, which characterize the iron and aluminum of poorly crystallized oxides which are capable to react with phosphate ions in solution. Some literatures [1] showed that the solubility of these phosphate varies according to the crystalline parameters **a** and **c** of the hexagonal lattice of the apatite.

On every mineral sample located in the interface solid/liquid, we expect to use firstly, the mono-crystal diffraction method, in order to fix its possible spatial group, and speculate on crystallographic parameters **a** and **c**. Secondly, we will use powder diffraction method for optimizing the calculus on **a** and **c**. For the computation, we will exploit two methods; one consists of solving the parameters by “hkl” files which is generated from diffraction data. While, in the second method we will index the powder diffraction data on the Bragg angle issued from the mono-crystal method, this computation method is commonly named Root Mean Square on $\sin\theta^2$. For the crystal resolution and refinement, we will use the SHELX software.

After the experiments, we will compare the data with the literature and classify the apatite, according to the structures and the crystalline parameters observed, and eventually we will highlight the existence of any “isotype” [2]. These results could help to inform more about the characteristics of mineral phosphates on the Madagascar Island, and could be used to determine the efficiency of the local natural phosphorus for solid/liquid interface applications like agriculture.

---

[1] Van Kauwenbergh and McClellan , *Efficiency of soil and fertilizer Phosphorus, characterization of Phosphate Rocks*, 1900, FAO.

[2] Emile Lucien R. R, *Contribution à l’étude des systems binaries MIPO3 – MII(PO3)2 , Structure cristallines de quelques monophosphates mixtes*; Université scientifique et médicale de Grenoble., 1972, **P. 25-97**.

P19

Novel Ruthenium(II/III) Complexes with Multidentate Schiff Base Chelates Containing Biologically Relevant Moieties.

Sanam Maikoo and Irvin Noel Booysen
[a] School of Chemistry and Physics, University of KwaZulu-Natal, Pietermaritzburg 3201, South Africa,
E-mail: smaikoo7@gmail.com.

Keywords: ruthenium, crystal structure, Schiff bases, benz(imidazole/othiazole).

There has been a growing interest in the development of new ruthenium metallopharmaceuticals due to the discovery of NAMI-A, *trans*-[$RuCl_4(DMSO)(Im)](ImH)$ {Im = imidazole}. NAMI-A has recently entered Phase II clinical trials due to its excellent metastatic cancer activity which is accompanied with fewer significant side effects than platinum-based metallopharmaceuticals [1]. Recent developments are geared towards the utilization of biocompatible ligands which may facilitate biodistribution and fine-tune solubility in the blood stream of the formulated ruthenium anticancer agents. This design approach has motivated us to explore the coordination behaviour of multidentate N-donor ligands incorporating various biologically active components (*viz.* uracil, antipyrine, chromone or benz(imidazole/othiazole) moieties) towards the diamagnetic ruthenium(II) core. Formulated compounds were characterized *via* various spectroscopic techniques and structural elucidations were confirmed using single X-ray analysis. Structural elucidations were complemented with electro-analytical, DFT and DNA interaction studies of selected complexes.

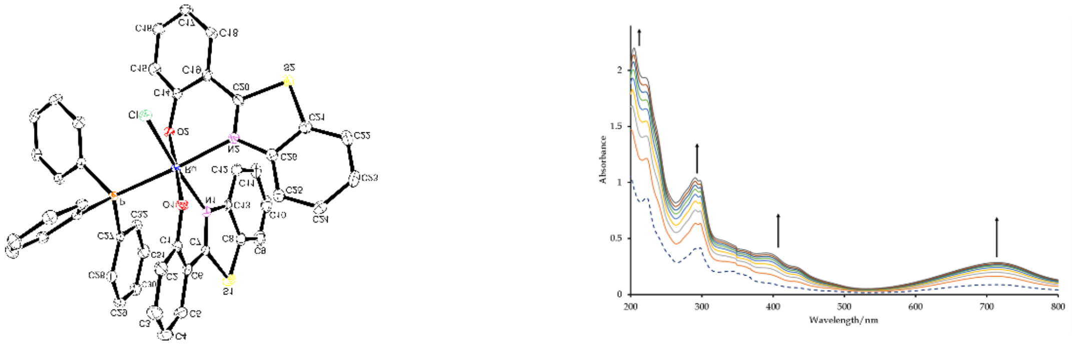


Figure 1: The ORTEP diagram of $[Ru^{II}Cl(Hobz)_2(PPh_3)]Cl$ (Hobz = 2-hydroxyphenylbenzimidazole) accompanied by its DNA titration spectral profile.

This study focused on the design, synthesis and characterization of novel ruthenium complexes with multidentate N-donor ligands. The metal centres of the formulated compounds were stabilized by various multidentate N-donor ligands which resulted in characteristic octahedral geometries. X-ray analysis of the complexes revealed that the mono-imine chelators coordinated to the *trans*-$[Ru^{II/III}(PPh_3)_2]$ core while the highly delocalized diimine and the '2+2' heterocyclic chelators replaced two bulky PPh_3 co-ligands of the metal precursor.

---

[1] Allesio, E., Mestroni, G., Bergamo, A., Savan, G. *Curr. Top. Med. Chem*., 2004, **4**, 1525.

P20

Structural characterization of EtpA and YghJ from Enterotoxigenic *Escherichia coli* (ETEC)

Lungelo Mandyoli[a], *Precious Motshwene*[a] *and Wolf-Dieter Schubert*[a]

[a] Structural Biology of Infectious Diseases, Department of Biochemistry, University of Pretoria, South Africa, E-mail: Lungelo.lungz@gmail.com

Keywords: ETEC, Crystallization, EtpA, YghJ.

Enterotoxigenic *Escherichia coli* (ETEC) are the most common bacterial pathogens causing diarrhoea in developing countries and in travellers to endemic countries. They cause hundreds of thousands of deaths, mostly in children. As part of its infection strategy, *ETEC* invades and colonize small intestinal epithelial cells where it secretes the heat-labile and/or the heat-stable enterotoxins inducing diarrhoea. The ability of ETEC to invade human epithelial cells is a hallmark of its pathogenicity controlled by a set of plasmid and chromosome encoded virulence factors. They include the plasmid encoded adhesin EtpA and the chromosome encoded metalloprotease, YghJ. In this study N-terminal EtpA (N-EtpA) and YghJ have been produced as His-tag fusion proteins in *E. coli* TOP10 cells and subsequently purified by metal affinity chromatography (MAC) using Ni-NTA column. Additional purification steps were conducted using size exclusion chromatography (SEC) on a Superdex 75 10/30 column. From the preliminary purification results it has been found that both N-EtpA and YghJ are stable under standard storage conditions, this enabled the first ever crystallization trials of these ETEC virulence proteins to be performed.

P21

β-diketone based ligands coordinated to Re(I) metal: structural and kinetic studies

Amanda-Lee Manicum, Marietjie Schutte-Smith, Hendrik Visser and Andreas Roodt
Department of Chemistry, University of the Free State, Bloemfontein 9300, South Africa. E-mail: volminkae@ufs.ac.za

Keywords: rhenium, radiopharmaceuticals, 2+1 mixed ligand approach.

The *fac*-$[M(CO)_3]^+$ (M = ^{99m}Tc(I) or Re(I)) core have interested a number of researchers over the last decade, mostly because it opens groundbreaking opportunities for new labeling methods as well as the development of novel diagnostic and therapeutic radiopharmaceuticals. [1] Alberto *et al*. has contributed significantly to the development of the tri-carbonyl core by being the first to report the one step synthesis of the air-stable *fac*-$[M(CO)_3(H_2O)_3]^+$ synthon. [2] The aqua ligands coordinated to the metal can effortlessly be replaced with a variety of ligands (monodentate, bidentate and tridentate) or ligand combinations (2 + 1 approach).

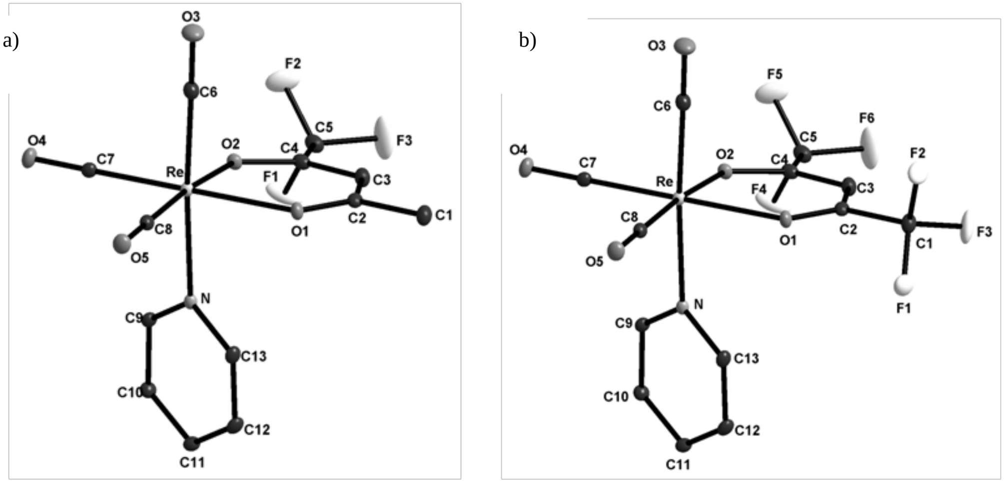


Fig 1: Graphical representations of *fac*-$[Re(CO)_3(Tfaa)Py]$ (a) and *fac*-$[Re(CO)_3(Hfaa)Py]$ (b), hydrogen atoms omitted for clarity.

Two new crystal structures are introduced and the need to explore the 2 + 1 mixed ligand approach on the *fac*-$[M(CO)_3(H_2O)_3]^+$ moiety serves as inspiration. The β-diketone ligands coordinated to the rhenium(I) metal centre are: 1,1,1-trifluoro-2,4-pentadione (Tfaa) and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (Hfaa). [3] The coordination of these acetylacetone-based ligands to the non-radioactive or natural rhenium can possibly provide a better understanding of the chemistry that would be found with the radioactive ^{99m}Tc and $^{186/188}$Re analogues. [4-5]

---

[1] M. Schutte, G. Kemp, H. G. Visser, A. Roodt, *Inorg. Chem*. **50** (2011) 12486.

[2] R. Schibli, R. Alberto, U. Abram, S. Abram, P. A. Schubiger, T. A. Kaden, *Inorg. Chem*. **37** (1998) 3509 - 3516.

[3] A. Manicum, M. Schutte-Smith, G. Kemp, H. G. Visser, *Polyhedron*, **85** (2015) 190.

[4] P. D. Benny, G. A. Fugate, A. O. Barden, J. E. Morley, E. Silva-Lopez, B. Twamley, *Inorg. Chem. Comm*. **47** (2008) 2240.

[5] M. Sagnou, C. Tsoukalas, C. Triantis, C. P. Raptopoulou, A. Terzis, I. Pirmettis, M. Pelecanou, M. Papadopoulos, *Inorg. Chim. Act*. **363** (2010) 1649.

P22

Elucidating the Role of Mycobacterium tuberculosis CarD and its Complex with RNA Polymerase in Mycobacterial Dormancy

Thuso Mapotsane and Wolf-Dieter Schubert

Structural Biology of Infectious Diseases, Department of Biochemistry, University of Pretoria

Tuberculosis (TB) is a major cause of human death globally – and especially so in Southern Africa. It is estimated that one third of world's population harbours Mycobacterium tuberculosis (Mtb) in a latent form which can be reactivated after sometime and cause active TB. It has been reported that CarD forms a complex with RNA polymerase in stress conditions. It is this physiological complex that causes Mtb to undergo dormancy. In dormant state, rRNA levels are down regulated to match the declining translational need of Mtb. This helps Mtb survive nutrient starvation, amino acid deprivation, phosphate deprivation, hypoxia and oxidative damage. Conventional antibiotics are not effective when Mtb is dormant as they exert their killing effects in actively growing bacteria. This has created an urgent need for new chemotherapeutic strategies. Structural studies of CarD/RNAP complex provide a promising avenue for TB drug design. A minimised RNAP β1m was used in this study.

P23

Synthesis and characterization of rhenium(I) tricarbonyl complexes with *N, O* ligands as potential radiopharmaceuticals.

Thabo D. Marake, *Alice Brink and Andreas Roodt*
Department of Chemistry, University of the Free State, Bloemfontein 9300, South Africa.
E-mail: maraketd@gmail.com.

Keywords: Rhenium(I) tricarbonyl complexes, radiopharmaceutical agents, Schiff-base ligands.

Tricarbonyl aqua complexes of the type *fac*-$[M(CO)_3(H_2O)_3]^+$ (M = Re(I), Tc(I)) have attracted much interest over the past decade as precursors for the development of new radiopharmaceutical agents [1-2]. These complexes consist of two important features which makes them very attractive in the design of pharmaceutical drugs. The *fac*-$[M(CO)_3]^+$ core [3] is generally known to be kinetically inert and stable towards dissociative ligand loss or associative substitution by other free ligands. The coordinated water molecules on the other hand, are relatively labile and can be substituted by a range of mono-, bi- and tridentate ligands. Nearly 80 % of diagnostic radiopharmaceuticals currently available in clinical nuclear medicine are labelled with ^{99m}Tc radionuclide because of its ideal nuclear properties [4]. The 6 h half-life is sufficiently long to synthesize the drug, collect useful images yet short enough to limit the radiation dose to the patient. The monochromatic 140 keV photons emitted by the radionuclide are readily collimated to give images of high spatial resolution. A few examples of well-established ^{99m}Tc labelled compounds in imaging include Cardiolite® (heart imaging) [5-6], Ceretec® (brain imaging) [7] and Technescan® (kidney and liver imaging) [8-9]. The similarity in the coordination chemistry of rhenium and technetium provides the opportunity to label biomolecules developed for technetium with rhenium. In this study, Schiff-base ligands were synthesized and systematically coordinated to the rhenium(I) centre. The choice of using Schiff-bases as our ligand system was prompted by their relative ease of formation and stability. However, the main reason for our particular interest in these N, O ligands is that they offer great versatility since the substituent on the nitrogen imine atom can easily be manipulated. Thus, the influence that the various substituents on the ligands have on the final complex is being investigated and described here.

---

[1] Alberto, R.; Schibli, R.; Abram, U.; Johannsen, B.; Pietzsch, H. J.; Schubiger, P. A. *J. Am. Chem. Soc.*, 1999, **25**, 6076-6077

[2] Waibel, R.; Alberto, R.; Willuda, J.; Finnern, R.; Schibli, R.; Stichelberger, A.; Egli, A.; Abram, U.; Mach, J. P.; Plueckthun, A.; Schubiger, P. A. *Nature Biotechnol.*, 1999, **17**, 897-901

[3] Alberto, R.; Schibli, R.; Waibel, R.; Abram, U.; Schubiger, P. A. *Coord. Chem. Rev.*, 1999, **190-192**, 901-919

[4] Liu, S. *Chem. Soc. Rev.*, 2004, **33**, 445-461

[5] Meggers, E. *Curr. Opin. Chem. Biol.*, 2007, **11**, 287-292

[6] Jones, A. G.; Abrams, M. J.; Davison, A.; Brodack, J. W.; Toothaker, A. K.; Adelstein, S. J.; Kassis, A. I. *Int. J. Nucl. Med. Biol.*, 1984, **11**, 225-234

[7] Leonard, J. P.; Novotnik, D. P.; Neirinckx, R. D. *J. Nucl. Med.*, 1986, **27**, 1819-1823

[8] Eshima, D.; Andrew, T. J.; Fritzberg, A. R.; Kasina, S.; Hansen, L.; Sorenson, J. F. *J. Nucl. Med.*, 1987, **28**, 1180-1186

[9] Eshima, D.; Fritzberg, A. R.; Taylor, A. *Semin. Nucl. Med.*, 1990, **20**, 28-40

P24

Manganese tricarbonyl as model radiopharmaceutical agents

Pennie P. Mokolokolo, Alice Brink and Deon Visser.

Department of Chemistry, University of the Free State, Bloemfontein, South Africa 9300,
E-mail: 2007102482@ufs4life.ac.za.

Keywords: Schiff base, manganese carbonyl, radiopharmaceutical.

The *fac*-$[M(CO)_3]^+$ (M=Tc, Re) core has garnered much interest due to its promising effects in the development of organometallic cores for labelling of biomolecules [1]. The low oxidation state of the metal carbonyl fragment is chemically inert and renders these types of complexes attractive to *in Vivo* application [2]. The monovalent tricarbonyl core allows a broader spectrum of donor and acceptor atoms to be coordinated. A large volume of research has been done on the tricarbonyl species of rhenium and technetium. Of particular interest in our research is the use of Schiff base ligands with the *fac*-$[M(CO)_3]^+$ (M=Tc, Re and Mn) . Schiff base ligands are easy to prepare, offer great stability to metal complexes, their chemical and electronic properties can be altered easily [3]. Manganese complexes with Schiff base chelating ligands show considerable promise as SOD mimics [4]. Carbonyl complexes of manganese are amongst the front runners in the development of carbonyl releasing molecules (CORMs) for therapeutic purposes [5].

Our study is concerned with the evaluation of the coordinative and kinetic properties of manganese tricarbonyl complexes coordinated with a variety of bi- and tridentate Schiff base ligands containing oxygen and nitrogen donor atoms, and their possible application in radiopharmaceutical design.

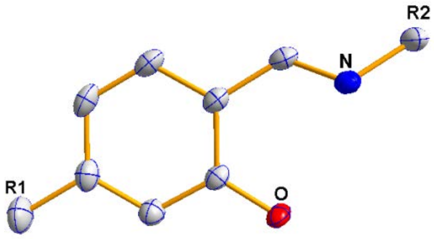


Figure 1 The substituted salicylidene backbone, where R_1 and R_2 represent a variety of substituents.

---

[1] Alberto, R; Schibli, R; Waibel; Abram, U; Schubiger, A.P, *Coord. Chem. Rev.*, 1999, **190-192**, 901-919.

[2] S. S; Jurisson and J. D. Lydon, *Chem. Rev.*, 1999**, 99**, 2205-2218.

[3] P. G Cozzi. *Chem. Soc. Rev.*, 2004, **33**, 410-421.

[4] Rimmer, R. D; Pierri A.E; Ford, P. C, *Coord. Chem. Rev.*, 2012, **256**, 1509–1519.

[5] Chen, H; Zhou, R. W; Ma, C. B; Hu, M.Q; Chen, C. N. *Chinese J. Struct. Chem.*, 2011**, (30)**, 158-163.

P25

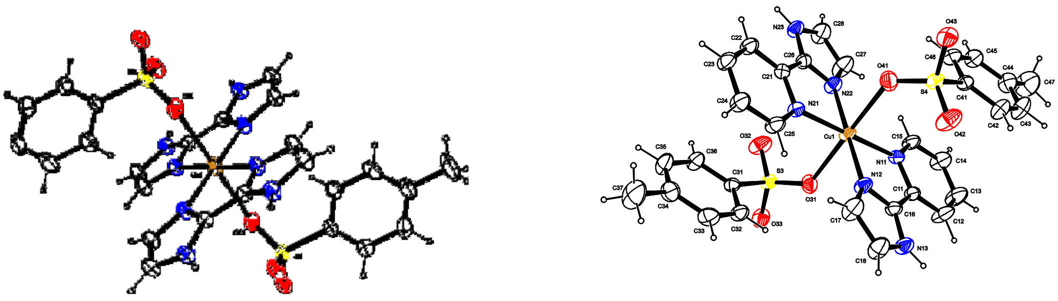
The coordination and extractive chemistry of the later divalent 3d transition metal ions with N,N'-donor imidazole-based ligands.

Pulleng Moleko, Eric Hosten, Richard Betz and Zenixole R. Tshentu

Department of Chemistry, Nelson Mandela Metropolitan University, Port Elizabeth, 6001, South Africa,
E-mail: moleko.puleng@gmail.com.

Keywords: 2,2'-pyridylimidazole, 2,2'-biimidazole, base metals, extractive and coordination chemistry.

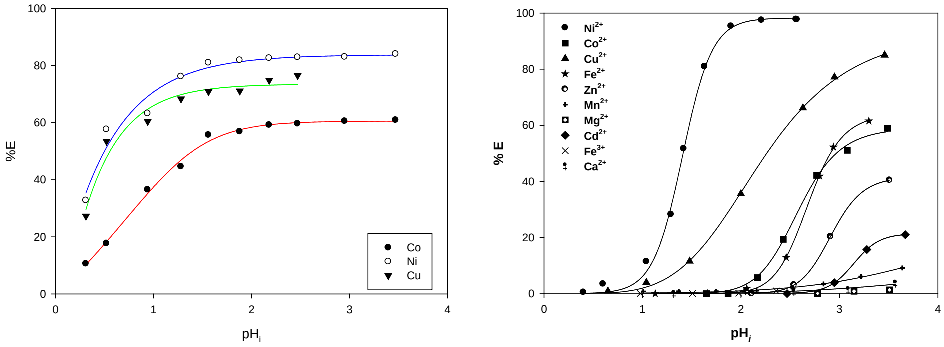
The application of bidentate N,N'-donor ligands, such as 2,2'-biimidazole (BIIM) and 2,2'-pyridylimidazole (PIM), in extractive chemistry of base metal ions in a sulfate/sulfonate medium is presented. The extraction patterns are explained from a coordination chemistry point of view using spectroscopic analysis and other analysis methods to diagnose the geometry of the complexes. The confirmation of the compounds formed in the complex equilibria were confirmed by single crystal X-ray crystallography. The crystal structures of the Jahn-Teller distorted $[Cu(BIIM)_2(RSO_3)_2]$ and $[Cu(PIM)_2(RSO_3)_2]$ complexes as well as the trigonal bipyrimidal $[Cu(PIM)_2(H_2O)](SO_4)$ complex were obtained (Figure 1). The UV–Vis solid reflectance spectra were used to characterize the geometry of the other compounds which could not be analysed by crystallography, and it seems that $[Ni(PIM)_2]SO_4{\cdot}yH_2O$ is a square planar complex. Copper(II) and cobalt(II) form *bis*-chelated aqua complexes with PIM as a ligand and with a non-coordinated sulfate ion as a counter-ion.



(a) (b)

Figure 1: The ORTEP diagram of (a) $[Cu(BIIM)_2(RSO_3)_2]$ and (b) $[Cu(PIM)_2(RSO_3)_2]$.

The extraction studies showed that the extraction patterns are influenced by stereochemical aspects, and the current drive is to design nickel(II)-specific extractants through stereochemical "tailor making". PIM (Figure 2b) showed selectivity for Ni(II) with the only interfering ion being Cu(II) in the pH range 1.2-1.8 [1] but BIIM lacks selectivity (Figure 2a).



(a) (b)

Figure 2: A plot of %E vs. initial pH of Co^{2+}, Ni^{2+} and Cu^{2+} extracted with BIIM and PIM from a dilute sulfate medium.

---

[1] Okewole, A.I.; Magwa, N.P.; Tshentu, Z.R. *Hydrometallurgy*, 2012, **121-124**, 81-89.

P26

Square planar nano-particles with Cu(II) on inversion centers for catalytic oxidation.

Pule Petrus Molokoane[a], *Gideon Steyl*[b] *and Andreas Roodt*[a]
[a] Department of Chemistry, University of the Free State, Bloemfontein 9300, South Africa. [b] 147 Coronation Drive, Milton, Queensland 4064, Australia (PO Box 1734, Milton BC, QLD 4064). E-mail: molokoanep@ufs.ac.za

Keywords: *pseudo*-first order, catechol oxidase, 3,5-di-*tert*-butylcatechol, 3,5-di-*tert*-butylquinone.

Under *pseudo*-first order conditions copper(II) nano-particles were employed as catalysts for the aerobic oxidation of 3,5-di-*tert*-butylcatechol to 3,5-di-*tert*-butylquinone. The objective of the study was to mimic the catalytic activity and behavior of the enzyme catechol oxidase and to examine electronic and steric effects on this catalytic oxidation process. A plausible selection ensured that factors such as the effect of electron donating groups on ligands, steric bulk of the complexes, etc. could be examined.

Structural data revealed that all the 3-hydroxypyrid-4-one ligands which were synthesized were all in the keto-enol tautomeric form in the solid state. Furthermore in all the cases where a clear packing order was observed, weak hydrogen bonding is present. These interactions result in the formation of dimers, which stabilizes the structures. This data also indicated a C=O bond length increase with increasing electron donation in the synthesized *O,O'*-bidentate ligands systems.

The synthesized copper complexes were planar with slight deviations from planarity and the copper atoms were on inversion centers. These complexes exhibit strong intramolecular hydrogen interactions. The solution study results suggest that the complex with the least electron donating group on the ligand was the most effective catalyst; however, the same complex was coincidentally the most sterically demanding complex in the study. As catechol oxidase is a macro-molecule which is very sterically crowded, the data suggests that steric effects play an important role in the catalytic process and this was successfully demonstrated at a small-molecular level of detail *via* solution modelling experiments.

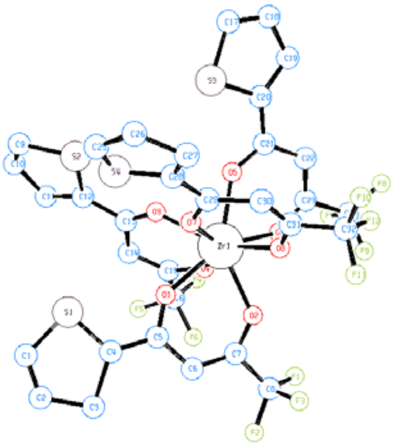
P27

The Separation of Hafnium and Zirconium: Crystal Structure of Tetrakis(trifluorothiophenylacetonato)-zirconium

L T. Mphure, H.G. Visser, Andreas Roodt

Department of Chemistry, University of Free State, P.O. Box 339, Bloemfontein 9300, South Africa.
E-mail: tmphure@gmail.com

O'O-donor bidentate β-diketones ligands of the form $R_1C(\text{-}OH)C(\text{-}R_3)(=O)\ R_2$[1], have been extensively researched with group IV oxophillic metals. Group IV metals coordinate to form six membered rings with β-diketones. These complexes are sometimes referred to as acetonates[2]. High coordination number metalacetonates have been report to exhibit lability in solution[3-5]. For this reason a β-diketone with thiophene and fluorine substituents was synthesized. These substituents influence the stereochemical non-rigidity that β-diketones exhibit in solution and allows for Nuclear Magnetic Resonance characterization and mechanistic studies of the hafnium and zirconium acetonates[6].



The aim of the study is to attempt to develop a separation method for hafnium and zirconium. Through synthesizing hafnium and zirconium complexes with similar ligands, then investing significant differences brought about by the ligands to the two metals. These differences will assist in separating and purifying the two metals from each other. In the study O'O-bidentate ligand in the form of a variation of a β-diketones, have been utilized for the synthesis of hafnium and zirconium complexes. Characterization and mechanistic studies were performed by Nuclear Magnetic Resonance (NMR) and the crystal structure studied by X-ray Diffraction (XRD), to help establish significant differences between the hafnium and zirconium complexes.

---

[1] M. Steyn (2009) Speciation And Interconversion Mechanism Of Mixed Halo And O,O- And O,N-Bidentate Ligand Complexes Of Zirconium. Unpublished Masters thesis, University of the Free State, Bloemfontein, South Africa.

[2] E.J. Bierschenk, N.R. Wilk, Jr. and T.P. Hanusa, *Inorg. Chem*, **50**, 12126 (2011)

[3] A.C. Adams and E. M. Larsen, *lnorg. Chem.*, **8**, 228 (1966)

[4] T.J. Pinnavaia and R. C. Fay, *lnorg. Chem.*, **5**, 233 (1966)

[5] F.A. Cotton, P. Legzdins and S. J. Lippard, *J. Chem. Phys.*, **46**, 3461 (1966)

[6] M. Elder, *Inorg. Chem* **8**, 2103 (1969)

P28

Solid State Investigation of Numerous Novel Copper(II) Bis-O,O'-Bidentate Complexes and Copper(I) Phenyl Complexes.

Kina Ann Muller[a], *Andreas Roodt*[a] , *Marietjie Schutte-Smith*[a] *and Gideon Steyl*[b]

[a] Department of Chemistry, University of the Free State, Nelson Mandela Avenue, Bloemfontein 9300, South Africa, E-mail: kinavdmerwe@gmail.com. [b] Golder Associates, 147 Coronation Drive, Milton, Queensland 4064, Australia

Keywords: copper, phenolic, oxidation.

The processes used in the production of industrial chemicals have placed immense stress on the environment. Various techniques are used to treat industrial waste present in our water systems. Waste material is generally composed of organic pollutants such as phenols [1].

It is imperative, not only to synthesize sustainable complexes which reduce or eliminate the use or formation of hazardous waste products, but also to develop novel methods to lower energy consumption [2]. The development of cost effective and efficient processes for the treatment of waste-water is of tremendous importance for industrial applications [1].

The demand for derivatives of phenolic compounds has gradually increased in the world market [3]. The aerobic oxidation of organic pollutants primarily composed of phenols using various metals like copper has proven to be an inexpensive process. These copper complexes can be employed as oxidizing agents for use on substituted phenolic compounds. The process results in the organic compounds being oxidised to carbon dioxide and water [1]. The oxidation of substituted phenolic compounds plays a fundamental role in biological systems [3]. Numerous copper complexes can be utilized as anti-inflammatory, antimicrobial, antiviral, enzyme inhibitors, antitumor agents or even chemical nucleases[4].

In this study a series of copper complexes were prepared containing various O,O-bidentate ligands such as pyranone ligands and 1-hydroxy-2-naphthoic acid, structural and electronic studies are evaluated and discussed.

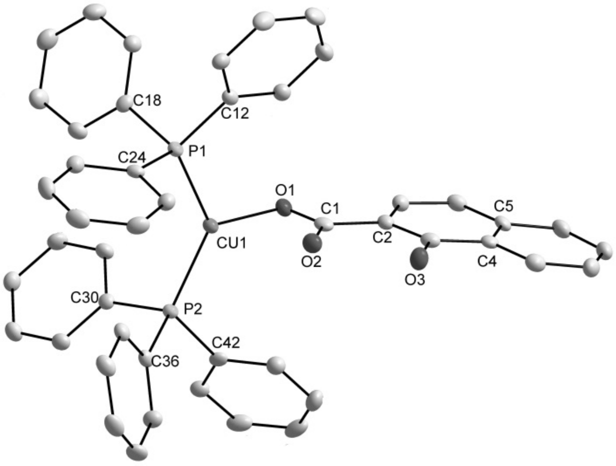


Fig. 4: Bis[(triphenylphosphine)-1-hydroxy-2-naphthoate]copper(I).

---

[1] A. Alejandre, F. Medina, P. Salagre, A. Fabregat and J.E. Sueiras. *Applied Catalysis B: Environmental*, 1998, **18**, 307-315.

[2] L. Que, Jr and W.B. Tolman. *Nature*, 2008, **455**, 333-340.

[3] H. Sun, K. Harms and J. Sundermeyer. *J. Am. Chem. Soc.*, 2004, **126**, 9550.

[4] I. Iakovidis, I. Delimaris and S.M. Piperakis. *Molecular Biology International*, 2011, 1-13.

P29

Preparation of Multinanoporous TiO_2 Thin Films by Anodic Oxidation: Optimization of Experimental Parameters

Ekoko Bakambo, Lobo Kanza-Kanza, Mvele Muamba, Mbongo Kimpanza, Muswema Lunguya, Mangwala Kimpende
Department of Chemistry, University of Kinshasa, Kinshasa 190 Kin XI , DR of the Congo,
E-mail: jeremie.muswem@unikin.ac.cd; jeremiemuswem@yahoo.fr

Keywords: nanoporous films, titanium dioxide, anodic oxidation, photocatalytic activity.

In the most recent research devoted to water purification, TiO_2-mediated photocatalysis is considered as an advanced oxidation process, which produces highly degrading hydroxyl radicals ($HO^\bullet$) in solution, known as strong oxidative species, responsible for the oxidation of organic pollutants present in waste water [1], [2].

The anodic oxidation method has been applied to the preparation of multinanoporous TiO_2 thin films. Experimental parameters such as the electrolyte nature, the oxidation voltage, and the oxidation time have been carefully controlled. Their influence on the structure, morphology, and photocatalytic activity of the prepared TiO_2 films has been evaluated by measuring the current density, X-ray and SEM patterns. The result showed that there was a relatively wide range of preparation conditions, and the internal relationship between the structure and the photocatalytic properties of the TiO_2 films was analyzed. Fig.1 and Fig. 2 present the X-ray spectrum, and Scanning Electron Microscopy image, respectively, of the TiO_2 prepared under optimized conditions.

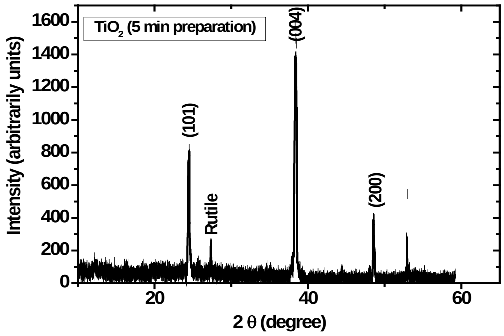


Figure 1: XRD spectrum of TiO_2

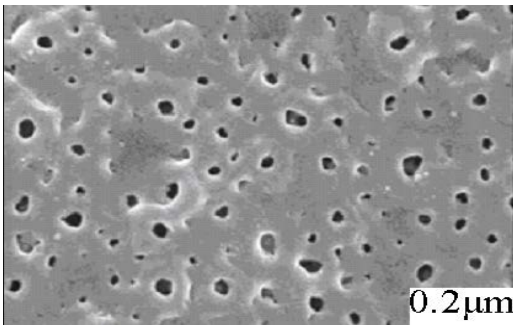


Figure 2: SEM micrograph of the optimized surface of TiO_2

In order to prepare multinanoporous TiO_2 thin films, with appreciable photocatalytic properties, the optimized experimental conditions are found to be as follow: 5 min of anodization with a voltage of 130 V, in an aqueous solution of 1.0 mol dm^{-3} H_2SO_4 used as electrolyte.

As compared with conventional techniques like plasma spray or sol-gel, this paper shows that the nanostructure of the TiO_2 films (with diameter size less than 100 nm) can be easily obtained at lower cost by electrochemical oxidation on metallic titanium substrates. Finally, the structures and morphologies of the TiO_2 films can be controlled according to the anodizing conditions. The easy control of microstructures of the anodic film should be a major advantage for many technical applications especially in wastewater treatment.

---

[1] Ekoko, G.B.; Lobo, J.K-K.; Mvele, O.M.; Mbongo, A.K.; Muswema, J.L.; Lefuni, C.Z. *S. Afr. J. Chem.*, 2013, **66**, 1–6.

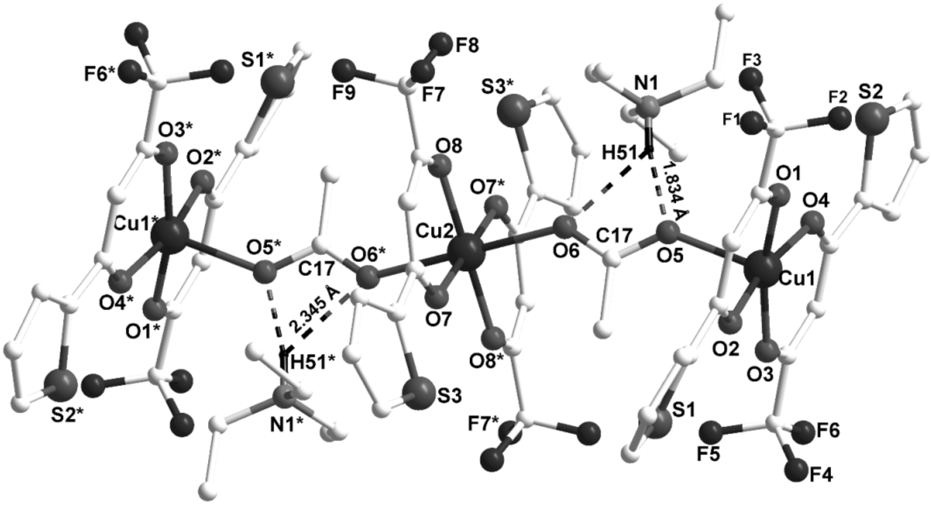
[2] Ekoko, G.B.; Lobo, J.K-K.; Mvele, O.M.; Muswema, J.L.; Yamambe, J.-F.S. *American Journal of Physical Chemistry*, 2014, **3 (4)**, 41–46.

P30

Reactivity of 2-Thenoyltrifluoroacetone towards First Row Transition Metal Ions

Nagarajan Loganathan, *Andreas Roodt.*
Department of Chemistry, University of the Free State, P. O. Box 339, Bloemfontein, 9300, South Africa.
Email: loganathann@ufs.ac.za

Keywords: Cobalt(II), Copper(II), *β*-diketonate, Acetate, Radio-pharmaceuticals.



We synthesized several transition metal complexes containing *β*-diketonates, pyrazoles and/or carboxylate as ligands. In one such reaction involving $Cu^{II}(CH_3COO)_2{\cdot}H_2O$, 2-thenoyltrifluoroacetone (TTA), 3,5-dimethylpyrazole (DMPzH) (2:1:1 ratio) in presence of excess triethylamine base (>3 equiv.), afforded $\{[Et_3NH][Cu_{1.5}(CH_3COO)(TTA)_3]\}_2$ (**1**) a linear dianionic Cu_3 [1a] and $[Cu_2(TTA)_2(DMPz)_2(DMPzH)]$ (**2**) a neutral Cu_2 oligomeric compounds in 60 and 32% yields respectively; n-hexane is the solvent of crystallization for both **1** (first crop) and **2** (second crop). Following the crystallization, re-dissolving **1** in methanol-acetone mixture (1:1) and **2** in toluene, provided a dinuclear mono-anionic $\{[Et_3NH][Cu_2(CH_3COO)(TTA)_4]\}$ **(3)** and a tetrameric diamond-cored $[Cu_2(TTA)_2(\mu\text{-}OH)(DMPz)]_2$ **(4)** copper(II) compounds respectively. The excess base not only deprotonate the ligands, it also helps to transform the metal coordinated water to the corresponding hydroxide and oxides. This is clearly evident in compound **4** which contains two bridging hydroxide units.

In an analogous reaction involving 5-(thiophen-2-yl)-3-(trifluoromethyl)pyrazole (CF_3SPzH) instead of DMPzH results in $[Cu(CF_3SPz)(TTA)]_2{\cdot}MeOH$ (**5**) an other interesting Cu_2 compound. Also, $[Co(TTA)_2(DMPzH)_2{\cdot}MeOH]$ (**6**) a mononuclear cobalt(II) compound was obtained from $Co^{II}(CH_3COO)_2{\cdot}4H_2O$ as a starting material. Our long standing interest on Re(I) and Mn(I) complexes as a model for radio-pharmaceuticals,[1b-c] provoked us to identify similar such metal (e.g. cobalt, copper etc.,) complexes for the same. Accordingly, all these complexes will be first tested for its biological application in particular the anti-cancer activities, followed by optimizing the reactants and conditions to obtain stable complexes for the use in radio-pharmaceuticals.

---

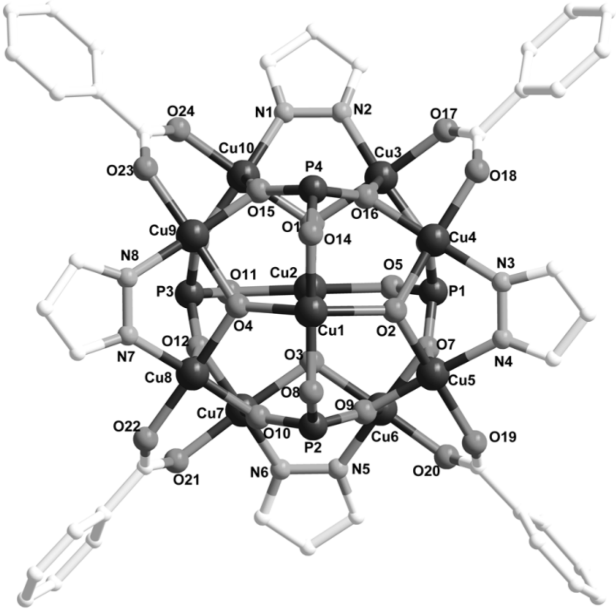
[1] (a) Loganathan, N; Roodt, A. *Chinese J. Struct. Chem.* 2014, **33**, 19-26. (b) Brink, A; Visser, H; Roodt, A. *Inorg. Chem.* 2013, **52**, 8950-8961. (c) Schutte, M; Visser, H; Roodt, A. *Inorg. Chem.* 2012, **51**, 11996-12006.

P31

Tetra-, Deca- and Dodecanuclear Copper(II) Phosphonate Cages Built from Pyrazole, *t*-Butylphosphonate and/or Carboxylate Ligands

Nagarajan Loganathan, *Andreas Roodt.*
Department of Chemistry, University of the Free State, P. O. Box 339, Bloemfontein, 9300, South Africa.
Email: loganathann@ufs.ac.za

Keywords: Coordination compounds, Copper(II), Phosphonate, D4R core, DNA cleavage.



The reaction of metal ions with the sparingly soluble phosphonate (RPO_3^{2-}) ligand predominantly forms layered structures rather than the molecular structure in the solid state. We discovered the use of highly soluble ancillary ligands such as pyrazole in the presence of a base, *in situ* generate the lipophilic metal pyrazolide assembly, which then reacts with RPO_3^{2-} ligands and forms molecular metal phosphonates [1]. This approach is known as the ancillary ligand approach or *Chandrasekhar approach*. Thus, our multi-component strategy involving copper(II) salt, 3-mono or 3,5-disubstituted pyrazoles, *t*-butylphosphonic acid and triethylamine base under the reaction conditions allowed us to isolate a series of high nuclear copper(II) phosphonate cages [1].

It includes a cubic Cu_4 cage, the core of which resembles the *D4R* core present in the zeolite materials [1a]; couple of iso-structural Cu_{10} phosphonates containing either 3-methylpyrazole and acetate or pyrazole and benzoate ligands; couple of Cu_{12} complexes consist of either 3,5-dimethylpyrazole or 3,5-bis(trifluoromethyl)pyrazole ligands [1b]. In spite of the complexity of the reaction system (3-5 components, multiple functional groups) often we were able to isolate a single product in major yield. The presence of dominant antiferromagnetic interaction at lower temperature has been inferred from their SQUID magnetic measurement. Thermo gravimetric analysis of the Cu_4 cage shows that it is thermally stable until 280°C. We also tested the nuclease activity of the Cu_4 and Cu_{12} cages to modify the plasmid pBR322 DNA. All shows 100% conversion from supercoiled form I to nick form II within 2 minutes in presence of an oxidizing agent Magnesium monoperoxyphthalate (MMPP).

---

[1] (a) Chandrasekhar, V; Nagarajan, L; Clérac, R; Ghosh, S; Verma, S. *Inorg. Chem.* 2008, **47**, 1067- 1073. (b) Chandrasekhar, V; Nagarajan, L; Clérac, R; Ghosh, S; Senapathi, T; Verma, S. *Inorg. Chem.* 2008, **47**, 5347-5354.

P32

Disentangling the binding surfaces of the listerial virulence factor InlC and human neuronal Wiscott-Aldrich Syndrome Protein on human Tuba

Mthawelanga Ndengane and Wolf-Dieter Schubert
Structural Biology of Infectious Diseases Research Group, Department of Biochemistry, University of Pretoria

Keywords: Listeria monocytogenes, InlC, Tuba SH3-6, N-WASP, cortical tension, cell-to-cell spread.

Throughout history, pathogens have infected and killed humans. Invading microorganisms mostly enter their hosts through inhalation, by exchange of body fluids or by ingestion of contaminated foods. *Listeria monocytogenes*, a food-borne bacterial pathogen, is the causative agent of listeriosis, symptoms of which include gastroenteritis, sepsis, meningitis and miscarriage. *Listeria* is ubiquitous in nature, surviving low and moderately high temperatures as well as acidic and saline conditions. These characteristics cause the bacterium to be a particular problem for the food industry. *L. monocytogenes* uses the virulence factors internalin (InlA) and InlB to invade normally non-phagocytic cells such as the cells lining the small intestine. Once engulfed by the phagosome, the bacterium secretes a pore-forming toxin listeriolysin (LLO) as well as phospholipase A (PlcA) to escape the phagosome. Once in the cytoplasm, the bacterial protein ActA recruits and reorganizes the actin cytoskeleton, imparting a high degree of motility to the bacterium. During this intracellular stage of infection *L. monocytogenes* secretes the virulence factor InlC. InlC binds the sixth or C-terminal SH3 domain of the human adopter protein Tuba. The interaction displaces N-WASP, the physiological partner of Tuba, locally disrupting the cellular cortical tension to increase the malleability of the cell membrane. This allows the bacterium to form protrusions of the cell membrane into neighboring cells. Upon separation and escape the bacterium is again free to multiply in the next cell. The aim of this project is to identify residues of Tuba SH3-6, which exclusively interact with either InlC or N-WASP. The results will be used for intracellular analyses of InlC and Tuba function *in vivo*.

P33

Structural Analysis of complexes between Internalin of Listeria monocytogenes with human and murine N-cadherins

Daniel Ndima and Wolf-Dieter Schubert
Structural Biology of Infectious Diseases Research Group, Department of Biochemistry, University of Pretoria

Keywords: *Listeria monocytogenes*, virulence factors, InlA^{m}, cadherins, crystallography.

The Gram-positive foodborne pathogen *Listeria monocytogenes* (*L.m*) infects and invades its host using a range of virulence factors amongst which are the internalins (InlA-InlK). Two Internalins (InlA and InlB) are used in the internalization of the pathogen into host cells through interactions with their respective receptors, E-cadherin and Met. Studies have shown that double variant mutations (S192N and Y369S) on InlA increase internalization of *L.m* into epithelial host cells, furthermore, these mutations allow internalization of *L.m* into transgenic mice expressing human E-cadherin. Recently, it was found that these mutations broaden receptor repertoire of *L.m* thus infection of neural cells of mice. However, the crystal structure of the complex between mutated InlA and neural cells receptors (N-cadherins) has not solved. Therefore, the current study aims to determine the complex structure between InlA and N-cadherin to elucidate the cause of the specificity broadening at the atomic level.

P34

Synthesis, Characterization and Photocatalytic Activity of Cr-N co-Doped ZnO Nanoparticles for Degradation of Thymol Blue (TB).

Alebel Nibret [a], *O.P. Yadav* [b] *and Abi Tadesse* [b]
[a] Department of chemistry, Bahir Dar University, Ethiopia, email:crossispower@gmail.com,[b] Department of chemistry, Haramaya University Ethiopia.

Keywords: As-synthesized photocatalysts, direct precipitation method, incipient wetness impregnation method, photo-degradation, rate constant, thymol blue dye.

Zinc oxide (ZnO) nanoparticles were synthesized by the direct precipitation method via the reaction between zinc nitrate [$Zn(NO_3)_2 \cdot 6H_2O$] and ammonium carbonate [$(NH_4)_2CO_3$] in aqueous solutions with proper concentration. Modified photocatalysts (Chromium-doped ZnO and nitrogen-doped ZnO) were synthesized by the incipient wetness impregnation method and by mixing as-synthesized ZnO, and urea respectively whereas chromium-nitrogen co-doped ZnO (CrNZ) nanomaterials were prepared from the already prepared ZnO and N-doped ZnO nanomaterials, respectively. The synthesized photocatalysts were investigated by X-ray diffraction (XRD), fourier transform infrared spectrometer (FTIR), atomic absorption spectrometer (AAS), and UV–Vis spectrophotometers to study the crystalline phase, molecular interaction and functional groups, elemental analysis, and band gap determination, respectively. Photocatalytic degradation of thymol blue using the photocatalysts was studied under visible as well as UV irradiations. Modified zinc oxide photocatalysts show higher photocatalytic activity compared to pure zinc oxide, both under visible as well as UV irradiations. Calcined zinc oxide (Zc) shows better photocatalytic activity than commercial zinc oxide (ZCO) under both visible as well as UV irradiations. Highest photocatalytic degradation efficiency of chromium-nitrogen co-doped zinc oxide (CrNZ) is attributed to the lower rate of recombination of the photo-generated electrons and holes as well as to its lower band gap energy. Photocatalytic degradation is found to follow pseudo first order kinetics. The rate constants for photocatalytic degradiation of TB under dark, visible and UV irradiations using ZCO, Zc, NZ, CrZ, and CrNZ photocatalysts were calculated as 2.39×10^{-4}, 2.89×10^{-4}, 1.39×10^{-4}, 1.89×10^{-4}, 3.11×10^{-4}, 2.08×10^{-3}, 4.94×10^{-3}, 11.32×10^{-3}, 8.44×10^{-3}, 22.3×10^{-3} and 1.18×10^{-4}, 3.63×10^{-3}, 5.02×10^{-3}, 6.37×10^{-3}, 8.53×10^{-3} min^{-1}, respectively.

P35

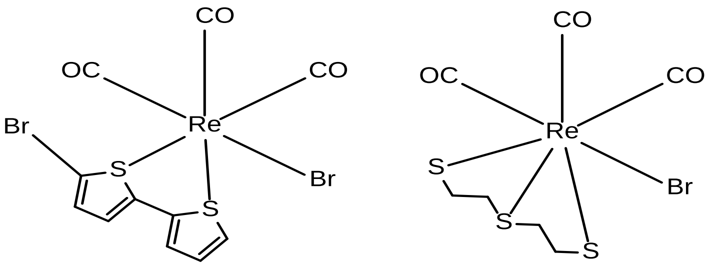
Synthesis of rhenium (I) tricarbonyl complexes using sulphur, oxygen and nitrogen containing ligands and the potential use as radiopharmaceuticals.

Nkoe I Pheello, Marietjie Schutte-Smith, Alice Brink
Department of Chemistry, University of the Free State, P.O. Box 399, Bloemfontein 9300, South Africa.
Email: pheello@hotmail.com

Keywords: Rhenium, tricarbonyl, sulphur ligands.

There is a significant interest in the radioactive nuclides of technetium and rhenium for nuclear medicine purposes. One of the approaches by researchers is the labeling of biomolecules with organometallic rhenium compounds for radiotherapy and technetium compounds for imaging.[1]

fac-$[M(CO)_3X_3]^{2-}$ (M = ^{99m}Tc, Re, X = Br/H_2O) anions are excellent starting materials for the synthesis of technetium and rhenium complexes. Most of the ligand exchange procedures described are directed towards the labeling of biomolecules and majority utilize nitrogen and oxygen donor atoms.[2] It is known that thiourea and thiourea derivatives can replace the methanol or aqua ligand in *fac*-$[Re(L,L'\text{-Bid})(CO)_3(CH_3COH/H_2O)]^n$ (with L,L'-bid = various bidentate ligand systems).[3,4] The main focus of this project is to exploit the excellent result with S-donor ligands on the Re(I) tricarbonyl core and to expand on the almost non-existing knowledge of Re(I) tricarbonyl complexes with S,S-bidentate and S,S,S-tridentate ligands. Sulphur ligands serve as an alternative approach to fully exploit the potential of the *fac*-$[M(CO)_3]^+$ moiety (M = Re, Tc) for the design of radiotracers. A schematic representation of a typical S,S-bidentate (5-bromo-2,2`-bithiophene) ligand and S,S,S-tridentate (2,2`-thiodiethanethiol) ligand coordinated to the Re(I) tricarbonyl is shown in Figure 1.



(a) (b)

Figure 5: Illustrations of (a) 5-Bromo-2,2`-bithiophene ligand and (b) 2,2`-Thiodiethanethiol ligand coordinated to the Re(I) tricarbonyl core.

---

[1] R. Alberto, R. Schibli, D. Angst. P. A. Schubiger; Transition Met. Chem., **22**, 597-601, (1997)

[2] H. Braband, U. Abram; J. Organomet. Chem **689**,2066-20772, (2004)

[3] M. Schutte, G. Kemp, H. G. Visser, A. Roodt; Inorg. Chem. **50**, 12486-12498 (2011)

[4] A. Brink, H. G. Visser, A. Roodt; Inorg. Chem. **52**, 8950-8961, (2013)

P36

Structural and biophysical characterization of CarD protein from *Mycobacterium tuberculosis*

CM Ntui and W-D Schubert
[a] Department of Biotechnology, University of Western Cape, Cape Town, South Africa 7535,
E-mail: ntuimanyo@gmail.com

Keywords: *Mycobacterium tuberculosis*, tuberculosis, CarD, RNAP.

The protein CarD from *Mycobacterium tuberculosis* (Mtb) appears to be essential for persistence of Mtb in its host. The interaction of CarD with RNA polymerase (RNAP) is critical in regulating transcription of rRNA in Mtb.

In this study, CarD from *Mycobacterium tuberculosis* was analyzed structurally and biophysically. Recombinant methods were used to produce proteins in *E. coli* strains. Proteins were detected and analyzed by SDS-PAGE. This revealed a mass of ~18 kDa for CarD, a value confirmed by both mass spectrometry and ProtParam. Theoretical biochemical parameters were derived using ProtParam while mass spectrometry and isoelectric focusing were used to determine the experimental molecular weight and the pI of CarD. CarD was observed to degrade after four days at different temperatures but could be stabilized for more than 2 weeks by the addition of glycerol. Limited proteolysis using a range of proteases confirmed protease sensitive regions as well as stable subdomains in CarD. Crystallization trials were carried out via sitting drop method.

Site directed mutagenesis was used to insert a stop codon into a full-length *carD* construct to generate a plasmid encoding the N-terminal domain of CarD only. The resulting 7 kDa N-terminal domain of CarD was found to be stable and its molecular weight was confirmed with mass spectrometer and protParam data. Experimental pIs of 5.5 and 5.6 were obtained for CarD and the CarD N-terminal domain, closely matching theoretical values from Protparam. Both CarD and N-terminus domain were found to be stable proteins that can be produced in wet lab. No protein crystals were obtained from crystallization experiments.

P37

Crystal structure of 1-Ethyl-1,4-dihydro-7-methyl-1,8-naphthyridin-4-one-3-carboxylic acid, $C_{12}H_{12}N_2O_3$,

Nzikahyel Simon[a], *Joshua Ayoola Obaleye*[b] *and Uche Basil Eke*[b]

[a] Department of Chemistry, University of Uyo, Uyo, Nigeria, E-mail: nzikahyelsimont@uniuyo.edu.ng. [b] Department of Chemistry, University of Ilorin, Ilorin, Nigeria.

Keywords: Nalidixic acid, synthesis, crystal, structure.

1-Ethyl-1,4-dihydro-7-methyl-1,8-naphthyridin-4-one-3-carboxylic acid, $C_{12}H_{12}N_2O_3$, (Nalidixic acid)crystallised in the monoclinic $P2_1$\c system. The structure was solved by charge-flipping(Superflip) and refined to R=0.079.

Nalidixic acid was obtained as a fine powder from Sigma-Aldrich, UK. The crystalline form was obtained as excess ligand in filtrate from the synthesis of its cobalt (III) complex in ethanol. The filtrate was allowed to stand for one week after which fine dirty white crystals suitable for X-ray crystallography were harvested and washed with excess ethanol. Anal. Calc. for chemical formula: $C_{12}H_{12}N_2O_3$, Mol.wt: 232.2353: C, 62.06; H, 5.21; N, 12.06. Found: C, 62.99; H, 5.56; N, 12.09.

Table1:Datacollection

Diffractometer: Bruker SMART	R_{int} = 0.039
Radiation source:	θ_{max} = 32.6°, θ_{min} = 2.4°
graphite	*h* = −13 13
ω/2θ scans	*k* = −19 19
27590 measured reflections	*l* = −14 14
3823 independent reflections	Standard reflections: 0
2851 reflections with $I > 2.0\sigma(I)$	

Table 2: Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H71···O5^{i}	0.95	2.51	3.313	142
C16—H162···O5^{i}	1.00	2.42	3.385	163
C16—H161···O1^{ii}	0.99	2.57	3.439	146
Symmetry codes: (i) −*x*+3, −*y*+1, −*z*+2; (ii) −*x*+2, −*y*+1, −*z*+2.				

Figure 1: Crystal structure of Nalidixic acid

P38

Rhodium containing 1-D Metallic Chains-A Structural Study

Carla Pretorius, *Alice Brink and Andreas Roodt*
Department of Chemistry, University of the Free State, Bloemfontein, South Africa 9300, E-mail: CPretorius@ufs.ac.za.

Keywords: rhodium, 1-D metallic chains, metallophillic interactions.

1-dimensional linear metallic chains have garnered considerable interest in the last few decades due to their unique magnetic, photophysical, conductive and catalytic properties [1]. The formation of these chains as well as their properties is attributed to the unique interactions found between the metal centres. Metallophillic interactions between metal centres of various platinum group metals result in a stacking effect between molecules giving rise to 1-dimensional chains. These chains have shown good potential as electrical conductors that could be used in application for future energy harvesting technologies [2].

Our study focused on evaluating these interactions by means of altered coordinating ligands with different electronic properties in square planar rhodium complexes. Additionally, the effect of temperature on the interactions was investigated by utilizing single crystal X-ray diffraction. Valuable insight has been gained with regards to the electronic nature of these metallophillic interactions with temperature inducing a significant change with at least one complex, [Rh(bzac)$(CO)_2$] that is illustrated below.

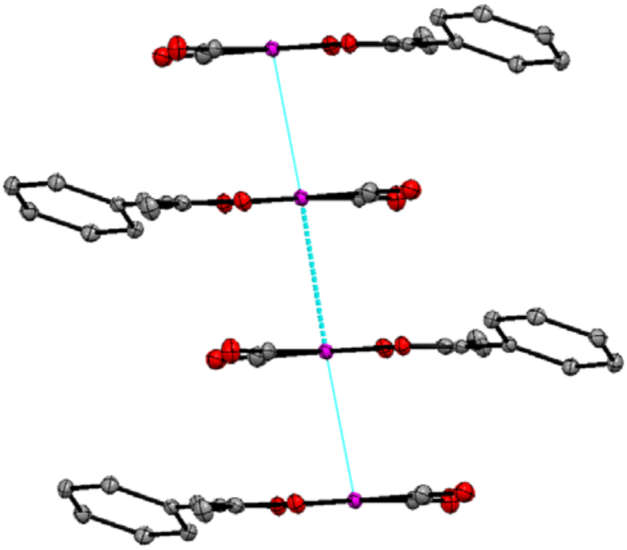


Figure 1: Metallophillic interactions as observed in the [Rh(bzac)$(CO)_2$] complex [3].

---

[1] Laurila, F; Tatikonda, R; Oresmaa, L; Hirva, P; Haukka, M. *CrystEngComm*, 2012, **14**, 8401-8408.

[2] Doerrer, L. H. *Dalton Trans.*, 2010, **39**, 3543-3553.

[3] Pretorius, C; Roodt, A. *Acta Cryst.*, 2012, **E68**, m1454-m1452.

P39

Highlighting crystallographic parameters of piezoelectric materials from Madagascar by X-ray diffraction.

Narisoa D.M. Rabe, Mariette S. Razanajatovo and Harisoa M.C. Rakotozafy
Department of Physics and Application, University of Antananarivo, Antananarivo 101, Madagascar,
E-mail: espadon44@yahoo.fr.

Keywords: piezoelectricity, crystals, crystallographic parameters, applications, Madagascar.

The objective of this study is to highlight the crystallographic parameters of piezoelectric materials from Madagascar. Piezoelectric materials are now used for several applications especially as sensors, for instance as sound vibration receivers or ultrasound receivers. Another application of piezoelectric materials is the production of clean energy. Although the use of piezoelectricity as an energy source is not yet an alternative to replace conventional energy sources, it is important to continue the studies concerning this field. Besides, Madagascar possesses numerous mineral deposits containing potentially piezoelectric crystals.

An X-ray diffractometer is expected to be used to analyze different minerals from the soil of Madagascar in order to identify those containing piezoelectric materials. The crystallographic parameters of those minerals such as **a, b, c** will be highlighted to determine the structure, and the piezoelectric properties will be studied.

The first expected result of this study is a classification of some piezoelectric materials from the island. As an example, we have the berlinite from Tsiambenana quarry, Itremo massif, Itremo Commune, Ambatofinandrahana District, Amoron'I Mania Region, Fianarantsoa Province, Madagascar [1].

Then the analyses of the parameters and properties will allow in-depth studies regarding the possible applications of those materials in Madagascar.

---

[1] Ackermand et al. *Lazulite-bearing metaquartzite of the Itremo Group (Central Madagascar); Scientific significance and economic importance* in Proceedings of the Malagasy-German Research Cooperation in Life and Earth sciences, 2006, 5-18.

P40

Rhenium (I) tricarbonyl complexes: solution and solid state effects of coordinated ligands.

<u>Marietjie Schutte-Smith</u>, Hendrik G. Visser and Andreas Roodt
Department of Chemistry, University of the Free State, Bloemfontein, South Africa 9301, E-mail: schuttemt@ufs.ac.za.

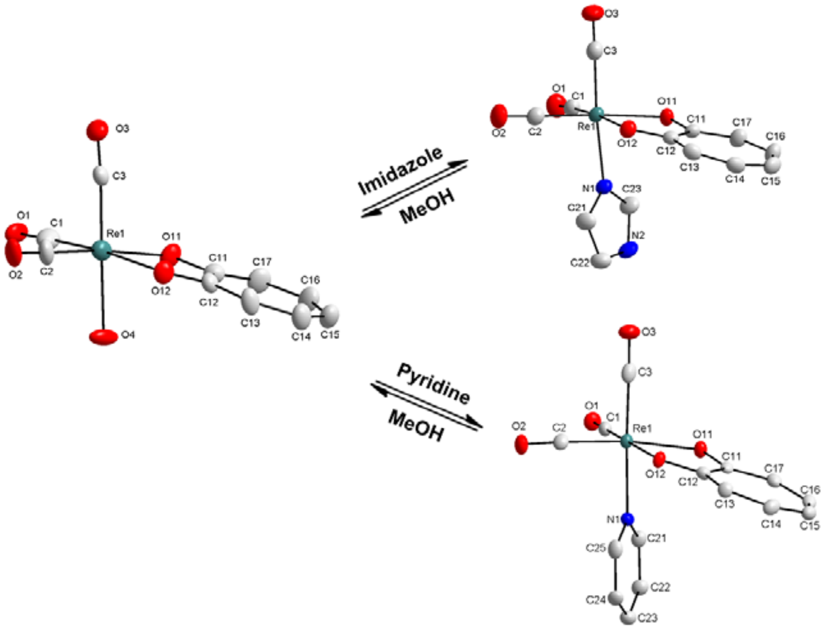
Keywords: rhenium, tricarbonyl, tropolone.

The coordination chemistry of rhenium and technetium has gained major interest for the possible use in radiopharmacy, due to its compact size, its low positive charge, coordination properties, d^6 low-spin configuration and significant stability. This interest was further fuelled when Alberto remarkably synthesized *fac*-[^{99m}Tc-$(CO)_3(H_2O)_3$] from [$^{99m}TcO_4$]$^-$ in aqueous medium and under mild conditions.

Several *fac*-[$M(CO)_3$]$^+$ (M = Re, ^{99m}Tc) type complexes have been synthesized to date with a large number of ligand systems.[1,2] The three labile aqua ligands on the starting synthon *fac*-[$Re(CO)_3(H_2O)_3$]$^+$ can easily be substituted by a variety and/or combinations of ligands producing stable compounds and potential radiopharmaceuticals with many different characteristics.

Our interest focuses on the *fac*-[$Re(CO)_3$]$^+$ moiety and related compounds by adopting the [2+1] approach.[3,4] The solid state behaviour of the complexes are explored as well as different effects such as the charge of the complexes as well as the effect of different types of donor atoms and electron donating or withdrawing systems. The influence of coordinated bidentate ligands on the rate of substitution in solution, by a variety of entering ligands, is also investigated.

Crystal structures of Re(I) tricarbonyl tropolonato complexes with various monodentate incoming ligands were obtained in the study and will form part of this presentation.



---

[1] R. Alberto, R. Schibli, R. Waibel, U. Abram, A.P. Schubiger, Coord. Chem. Rev., 1999, 190−192, 901−919.

[2] R. Alberto, R. Schibli, P. A. Schubiger, U. Abram, T. A. Kaden, Polyhedron, 1996, 15, 1079−1089.

[3] M. Schutte, H.G. Visser, A. Roodt, Inorg. Chem., 2012, 51, 11996-12006.

[4] A. Manicum, M. Schutte-Smith, G. Kemp, H. G. Visser, Polyhedron, 2015, 85, 190-195.

P41

The number and position of water in AlPO4-5

Birama Traore, Mohamed Souhassou, Florence Porcher
University of Lorraine (CRM2), Nancy (France), FST/Bamako (Mali).

AlPO4-5, with the code AFI, has as formula $[Al_{12}P_{12}O_{48}](C_{12}H_{28}N^{+})(H_2O)_x(OH^{-})$. In its non-calcined form, the number of water molecules and their position inside the porosity are not well defined, and preclude an accurate modelling of the structure itself. Hence, we investigate the calcined form of AlPO4-5 and explore the possibility to determine accurately the structure and (if possible), the charge density.

In a first step, we performed a preliminary single-crystal XRD experiment on AlPO4-5 to confirm the absence of amina. In a second step, we impregnated this empty AlPO4-5 matrix with thio-indigo and potassium permanganate.

For the impregnation in thio-indigo, we use ethanol as solvent, and water in the case of potassium permanganate. The diffraction experiments on these latter systems show that in both the cases there is 2 water molecules localized in a special position lying along a two-fold axis. These molecules exhibit high thermal parameters together with low occupancy factor. One of the water molecules bonded to Al and the second to P atom. They are located in the 4 member ring of AlPO4-5 and the long bond distances suggest their interaction with the framework is rather weak. They are located on the position 0.5 0.5 z_i (where z_i depend of the molecule of water), whereas the distance between the molecules of water is varied from 1.520Å to 2.334Å.

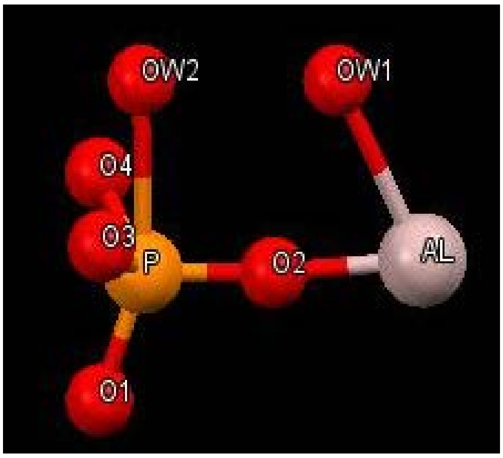


Fig. 1. Image of asymmetric AFI calcinated along b axis

P42

X-ray crystallographic study of the coordination of N,O-Bid ligands with rhenium complexes

Mampotso S. Tsosane, Alice Brink, Hendrik G. Visser and Andreas Roodt
Department of Chemistry, University of the Free State, P.O. Box 399, Bloemfontein 9300, South Africa.
Email: mampotsotsosane@rocketmail.com

Keywords: rhenium, N,O-Bidentate ligand, X-ray crystallography.

The developments in X-ray crystallography over the past 100 years is phenomenal and shows an increasing interest in potential regarding molecular biology applications [1,2,3]. X-ray crystallography provides valuable information regarding the coordination and the absolute structure of an organometallic complex for increased understanding of its chemical properties in the solid state. While other methods, such as nuclear magnetic resonance (NMR), infrared spectroscopy, UV-Vis spectroscopy, etc., provides insight into the solid and especially the solution state of complex interaction in the presence of other coordinating molecules. An in depth understanding of the chemical character of coordination complexes can be achieved with the combined use of the above mentioned techniques and is essential if the mechanistic behaviour of the complex in question is to be fully revealed [4].

Organic molecules modified with the Schiff-base reaction offers a versatile and flexible series of ligands that are capable of binding with various transition metals, including rhenium(I) and technetium(I) tricarbonyl complexes. The versatility and the manipulative capability of such ligand systems in conjunction with radio-isotopes may lead to very practical applications in developing model radiopharmaceuticals. Thus, a series of N,O-bidentate ligand systems coordinated to $[Re(CO)_3]^+$ and $[Tc(CO)_3]^+$ has been developed. The complexes, *fac*-[Re(L,L'-Bid)(X)] (L,L'-Bid = anionic N,O-bidentate ligands, X = MeOH or mono-coordinated solvents) will be used to extend the knowledge base of bifunctional chelators which may be used in radiopharmaceutical drug design. Future work includes understanding the mechanism and formation of water-soluble ligand systems which may coordinate to the Group 7 tricarbonyl series [5].

---

[1] Roodt, A; Visser, H.G; Brink, A. *Crystallogr. Rev.*,2011, **17**, 241-280.

[2] Roger Alberto, Roger Schibli, Robert Waibel, Ulrich Abram, August P. Schubiger, *Coord. Chem. Rev.*, 1999, **190-192**, 901-919

[3] Fernandes, A.C, ; Romão,C.C, *Tetrahedron Lett.*, 2005, **46**, 8881-8883.

[4] Kim, J.Y; Ji, Y.J; Ha, H; Chae, H.K. *Bull. Korean Chem. Soc.*, 2003, **24**, 504-506.

[5] Brink, A; Visser, H.G; Roodt, A. *J. Coord. Chem.*, 2011, **64**, 122-133.

P43

Investigation of Dithiadiazolyl Radical – Metalloporphyrin Complexes

Laura van Laeren, Delia Haynes and Katherine de Villiers
Department of Chemistry and Polymer Science, Stellenbosch University, Private Bag X1, 7602 Matieland,
South Africa, Email: lauravl@sun.ac.za

Keywords: dithiadiazolyl, radical, porphyrin, magnetic materials.

Thiazyl radicals have been investigated as potential building blocks for the design of molecular materials with interesting and desirable physical properties, such as conductivity and magnetism.[1] The development of new thiazyl radicals is a growing field of research. In particular, 1,2,3,5-dithiadiazolyls (DTDA) have been investigated for their remarkable properties: DTDA radicals, as well as their metal complexes, have been shown to display unusual magnetic behavior.[1] These properties are strongly dependent on the arrangement of the molecules in the solid state, as well as on the intermolecular interactions. Consequently, attempts have been made to direct the crystal structures of these materials.[2]

Metalloporphyrins are highly useful precursors in supramolecular chemistry that can be used to create assemblies with remarkable structures and properties.[3] Based on the interesting behavior of DTDA radicals in the solid state, and with the knowledge of the interesting supramolecular architectures that can be designed with porphyrin scaffolds, this research aims to investigate novel thiazyl radical-metalloporphyrin complexes in terms of their structural and functional properties. In addition to their potential to create magnetic materials, these complexes may potentially also behave as single-molecule magnets.

A coordination polymer of 4-(4'-pyridyl)-1,2,3,5-dithiadiazolyl and cobalt(II) tetraphenylporphyrin has recently been prepared by our group and was characterized as its THF solvate (1•THF). This compound shows novel co-ordination behavior and provides much promise for the use of these building blocks for the creation of interesting materials.[4]

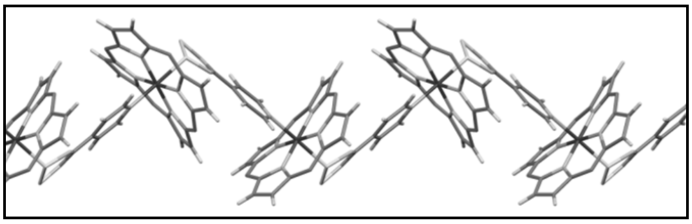


Figure 1 A coordination polymer formed from 4-(4'-pyridyl)-1,2,3,5-dithiadiazolyl and cobalt(II) tetraphenylporphyrin - one of the crystallographically independent radical-porphyrin chains formed in 1•THF shown. Phenyl substituents on the porphyrin have been removed for clarity.

The interaction between the dithiadiazolyl and the metalloporphyrin has been studied through the use of EPR. Further EPR investigations show that 4-(4'-pyridyl)-1,2,3,5-dithiadiazolyl and 4-phenyl-1,2,3,5-dithiadiazolyl interact with a variety of metallated porphyrins.

---

1. (a) Rawson, J. M., Alberola, A., Whalley, A. *J. Mater. Chem*. 2006, 16, 2560-2575. (b) Rawson, J. M., Palacio, F. *Struct. Bonding*. 2001, 100, 93-128. (c) Mailman, A., Winter, S. M., Yu, X., Robertson, C. M., Yong, W., Tse, J. S., Secco, R. A., Liu, Z., Dube, P. A., Howard, J. A. K., Oakley, R. T., *J. Am. Chem. Soc*. 2012, 134, 9886-9889.

2. Haynes, D. A. *CrystEngComm*, 2011, 13, 4793

3. Beletskaya, I., Tyurin, V. S., Tsivadze, A. Y., Guilard, R., Stern, C. *Chem. Rev*. 2009, 109, 1659-1713.

4. Van Laeren, L.J., de Villiers, K. A., Haynes, D. A., Munro, O. Q. *Manuscript in preparation.*

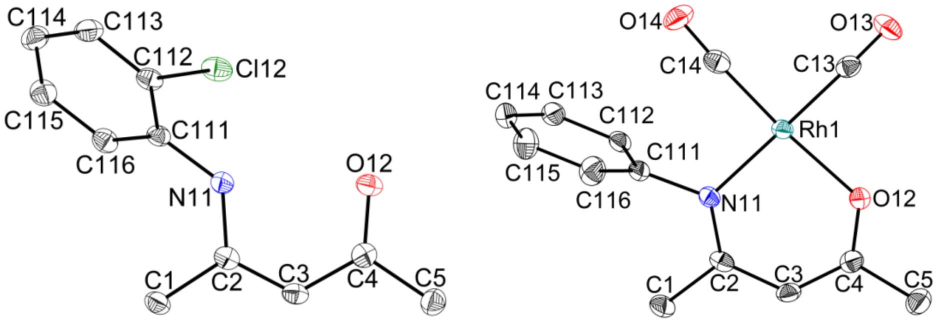
P44

Enaminoketones and Rh(I): influencing dicarbonyl and phosphine complexes through substitution

Gertruida J.S. Venter[a], *Gideon Steyl*[b], *Andreas Roodt*[a]
[a] Department of Chemistry, University of the Free State, Bloemfontein, South Africa 9301, E-mail: VenterGJS@ufs.ac.za.
[b] Golder Associates Pty. Ltd., Milton, Queensland, Australia 4064.

Keywords: rhodium, enaminoketone, catalysis, exchange.

X-PhonyH (X = aromatic substituents; PhonyH = 4-(phenyl-amino)pent-3-en-2-one) compounds belong to the group of enaminoketones. These compounds contain nitrogen and oxygen donor atoms as well as an alkene functionality (see Figure 1), and as such these electron-rich compounds are of interest in various areas, including application as liquid crystals [1], in fluorescence studies [2], the medical field [3,4] and with significant potential in homogeneous catalysis [5].



a) **b)**

Figure 1: Illustration of a) 4-(2-chloro-phenyl-amino)pent-3-en-2-one (2-Cl-PhonyH) and b) dicarbonyl-[4-(phenylamino)pent-3-en-2-onato]-rhodium(I) [Rh(Phony)$(CO)_2$].

This study is therefore concerned with the synthesis of PhonyH derivatives as ligand system and the influence of halide and aryl substitution on such ligands with regard to rhodium(I) complex formation. A range of crystal structures of the (i) free ligands, (ii) complexes of the type [Rh^I(X-Phony)$(CO)_2$] (X-Phony = 4-(phenyl-amino)pent-3-en-2-onato derivatives), and (iii) [Rh^I(X-Phony)(CO)(PPh_3)] (substitution of a CO group in (ii) by PPh_3) complexes [6,7] as catalyst precursors will be discussed. Furthermore, the exchange between free and coordinated phosphine as indicated through nuclear magnetic spin transfer techniques will be highlighted.

---

[1] W. Pyżuk, A. Krówczynsk, E. Górecka, *Mol. Cryst. Liq. Cryst.*, 1993, **237**, 75-84.

[2] M. Xia, B. Wu, G. Xiang, *J. Flu. Chem.*, 2008, **129**, 402-408.

[3] H.Y. Tan, W.K. Loke, Y.T. Tan, N.-T. Nguyen, *Lab Chip*, 2008, **8**, 885-891.

[4] W.J. Fanshawe, L.S. Crawley, S.R. Safir, G.E. Wiegand, E.C. Cooley, Substituted enaminoketones, 1974, US3997530 (Patent).

[5] V.A. Nair, M.M. Suni, K. Sreekumar *Proc. Indian Acad. Sci. (Chem. Sci.)*, 2002, **114**, 481-486.

[6] G.J.S. Venter, G. Steyl, A. Roodt, *Z. Kristallogr.*, 2013, **228**, 410-412.

[7] G.J.S. Venter, G. Steyl, A. Roodt, *Acta Cryst.*, 2009, **E65**, m1606-m1607.

P45

Crystallographic and kinetic study of ligand effects in the oxidative addition of rhodium cupferrate and related complexes

Johan Venter

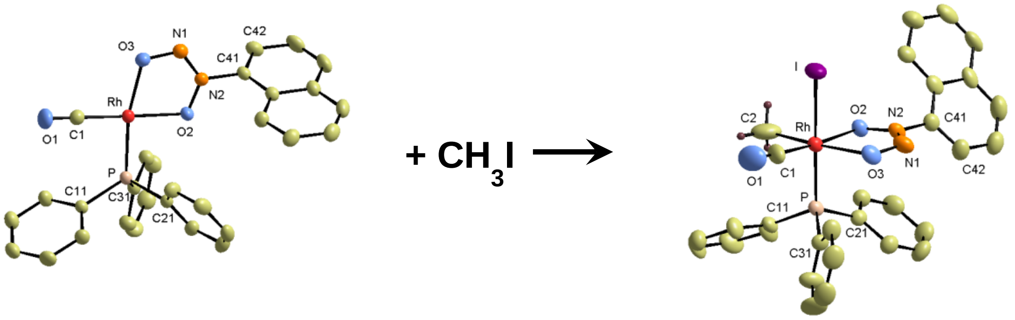
Department of Chemistry, University of the Free State, Bloemfontein, South Africa, E-mail: venterja@ufs.ac.za.

Keywords: rhodium, cupferrate, crystal structures, kinetic study.

It is 37 years since Tolman's well-known review [1] (Steric effects of phosphorus ligands in organometallic chemistry and homogeneous catalysis) was published and judged by the large number of publications still referring to it, it remained relevant. The importance of the choice of ligands in the design of complexes cannot be overestimated. In the process of obtaining the optimum complex, a fundamental approach is so often bypassed, reverting to a trial and error evaluation of complexes synthesized for a particular purpose. A ligand data base will serve to predict ligand effects and could guide experimental screening.

As a type of reaction that was thoroughly studied in our group over decades, oxidative addition was chosen to serve as model. Oxidative addition is one type of reaction that is prominent in the mechanistic representation of catalytic reactions. The key to fundamental research on catalysis is the greater understanding of the relationships between activity and catalyst structure, as well as ways to better predict, understand and control catalyst molecular architecture. The extent to which the oxidative addition step is affected by, for instance, the electronic and steric modifications to the phosphine ligand, can lead to more effective modelling of catalysts. Phoshine ligands are exceptionally well suited to manipulate the electron density and / or steric accessibility of the metal centre. Evaluation of the effect of the phosphine ligand is however complicated by the difficulty in the separation of the two effects.

The oxidative addition of iodomethane to various $[Rh(Cupf)(CO)(PX_3)]$, $[Rh(neocupf)(CO)(PX_3)]$ and $[Rh(MeCupf)(CO)(PX_3)]$ [2] complexes have been studied with an extensive kinetic and structural effort to yield a detailed reaction mechanism (cupf = cupferrate, neocupf = neocupferrate, mecupf = 2-methylcupferrate bidentate ligand, PX_3 = PPh_3, PCy_3, $P(o\text{-}Tol)_3$, $PPh_2C_6F_5$, $P(o\text{-}ClC_6H_4)_3$ and $P(p\text{-}MeOC_6H_4)_3$). Structures of starting complexes and their Rh(III) alkyl products were solved crystallographically.



The kinetic study included a solvent variation where solvents having different polarities and donicities were used. A number of factors which influence the rate and outcome of these reactions, like phosphine ligand basicity and bulkiness, the stereochemistry of reactants as well as solvent catalysis were taken into consideration. The outcome of this study yielded a possible quantitative way of defining bidentate ligands.

---

[1] Tolman C.A., *Chem. Rev.*, **1977**, *77*, 313-348.

[2] Warsink,S., Fessha, F.G., Purcell, W., Venter, J.A., *J. Organomet. Chem.*, **2013**, *726*, 4-20.

P46

Development of novel supramolecular framework materials based on organic salts

Helene Wahl[a], *Delia A. Haynes*[a] *and Tanya le Roex*[a]
[a] Department of Chemistry and Polymer Science, Stellenbosch University, P. Bag X1, Matieland, 7602, Republic of South Africa. E-mail: wahl@sun.ac.za.

Keywords: pamoic acid, framework, porous, selectivity.

Framework materials such as metal-organic frameworks (MOFs) [1], covalent organic frameworks (COFs) [2] and nanoporous molecular materials [3] have been extensively studied for their function as hosts with potential application in separation and drug delivery. The aim of this project is to use purely organic molecules to design and synthesise ionic organic framework materials based on carboxylate salts, with the intention of engineering interesting properties, such as porosity, into these materials.

This study was inspired by a serendipitous discovery of a hydrogen-bonded organic framework, 3,4-lutidinium pamoate hemihydrate, with THF-filled channels in the solid state, illustrated in Figure 1 [4]. It is a porous framework that exchanges for a wide variety of guests, with many of these exchanges occurring in a single-crystal to single-crystal fashion. The selectivity of this framework was investigated through competition experiments and the results of these experiments will be reported. The kinetics of guest exchange were studied and it was possible to identify a kinetic model that describes the process.

A second novel framework-type material, 4-phenylpyridinium pamoate, was identified during the course of this study, as well as five isostructural frameworks containing different guest molecules. In this case the framework consists of discrete units that close-pack in such a way that guest molecules are included in constricted cavities in the solid state (Figure 1). Although this framework-type material is not porous, it is thermally quite stable and also highly selective. The results of competition experiments conducted with this framework-type material will be reported.

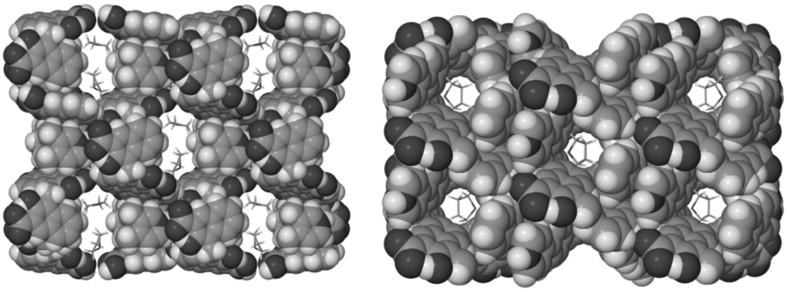


Figure 1: The porous framework with THF filled channels is shown on the right and the framework-type material with THF-filled cavities is shown on the right

---

[1] X.-D. Zheng, M. Zhang, L. Jiang and T.-B. Lu, *Dalton Trans.*, 2012, **41**, 1786-1791.

[2] H. M. El-Kaderi, J. R. Hunt, J. L. Mendoza-Cortés, A. P. Côté, R. E. Taylor, M. O'Keeffe and O. M. Yaghi, *Science*, 2007, **316**, 268-272.

[3] J. R. Holst, A. Trewin and A. I. Cooper, *Nat Chem*, 2010, **2**, 915-920.

[4] H. Wahl, D.A. Haynes, T. le Roex, *Chem. Commun.*, **48**, 2012, 1775.

P47

Structural investigations and reactivity of Rh(NHC-amido) complexes

Stefan Warsink[a], *Andreas Roodt*[b] *and Johan Venter*[b]
[a] Department of Chemistry, University of Utrecht, Utrecht, The Netherlands, E-mail: stefanwarsink@gmail.com
[b] Department of Chemistry, University of the Free State, Bloemfontein, South Africa.

Keywords: rhodium, NHC ligands, crystal structures, homogeneous catalysis.

In our research to improve the efficiency of homogeneous rhodium(I) catalysts in the carbonylation of methanol (which provides acetic acid in a multimillion tonne scale per year) through better understanding of oxidative addition and reactivity of the metal centre, we use bidentate ligands with donor sets such as O,O', N,O and S,O. [1,2].

The use of bidentate ligands, as well as the use of strongly coordinating phosphines shows improvements in the conversion of methanol to acetic acid

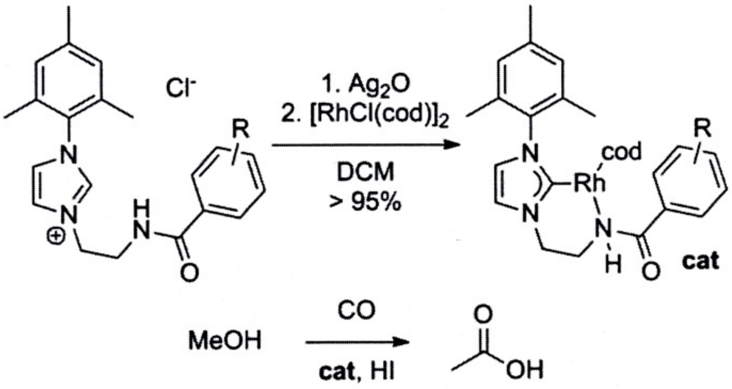
We have endeavoured to combine the characteristics of these two beneficial influences into one ligand set. Because phosphines sometimes show dissociation from the metal and are liable to oxidation, we opted for the use of N-heterocyclic carbenes (NHCs).[3] These ligands are not as well-established as phosphines, but the past two decades have shown that they are versatile ligands that give stable complexes with almost any metal in the periodic table over a wide range of reaction conditions.

As a secondary donor, an amide-functionality was chosen, because of its ease of synthesis and the possibility of coordinating as a neutral or as an anionic donor.

A series of imidazolium salt preligands was synthesized in high yields and purities by well-described methods. The NHCs were then generated by complexation to silver(I), as this provides the intermediate Ag^I(NHC) complexes in high yields without the need for inert conditions. Also, these complexes act as carbine-transfer agents when combined with a suitable metal-precursor, such as $[RhCl(cod)]_2$ (cod = 1,4-cyclooctadiene).

For several of the new compounds and complexes single crystals suitable for X-ray analysis were obtained, which gave insight into the mode of coordination of the bidentate ligand and structural properties of the complexes.

The reactivity of the ligands with different rhodium(I)-precursors, as well as the reactivity of the resulting complexes with different ligands and substrates was investigated in detail. Future research focuses on application of the Rh(NHC-N) complexes in the methanol carbonylation, of which the first step involving the rhodium-moiety is the oxidative addition of iodomethane.



---

[1] Roodt, A., Steyn, G.J.J, *Res. Research Dev. Inorg. Chem.*, **2000**, *2*, 1.

[2] Roodt, A., Visser, H.G., Brink, A., *Cryst. Rev.*, **2011**, *17*, 241.

[3] Praetorius, J.M., Crudden, C. M., *Daslton Trans.*, **2008**, 4079 - 4094.

P48

The selectivity of a Werner complex towards aromatic guest isomers

Merrill M Wicht,[a,b] *Luigi R Nassimbeni*[a,b] *and Nikoletta B Báthori*[a]
[a] Department of Chemistry, Cape Peninsula University of Technology, Cape Town 8000, E-mail: wichtm@cput.ac.za. [b] Department of Chemistry, University of Cape Town, Rondebosch, Cape Town, 7701. South Africa.

Keywords: Werner clathrate, competition experiment, selectivity.

Werner clathrates, of the general formula MX_2L_4 (where M is a transition metal, X is an anion and L is a pyridine derivative) have the ability to capture organic compounds when crystallized from their solution. The vinyl derivative is known and several crystal structures with aromatic guest compounds have been published.[1] They act as molecular sieves enabling the separation of different isomeric forms of aromatic compounds. These compounds also capture isomers selectively via solid-gas reaction.[2] One of the many possible industrial applications of these compounds enables separation of xylene isomers in the petroleum industry.[3]

A complex with NCS^- as the anion and isoquinoline as the pyridine derivative has been synthesised as the host complex and the uptake of each of the three isomers, *ortho*-, *meta*- and *para*-xylene, have been recorded. The analyses included single-crystal XRD, thermogravimetric analysis and powder XRD. Competition experiments with mixtures of the xylene isomers as the guest were carried out via crystal formation and powder-vapour experiments. Although pleasing crystals were obtained and analysed, the experiment has shown a lack of significant discrimination for one of the xylene isomers. The explanation of the difference in the action of the complex is investigated and discussed. In this presentation the kinetics of the reaction, GC headspace analyses of the clathrates formed as well as the single-crystal XRD structures and thermal gravimetric analyses will be discussed.

---

[1] Moore MH, Nassimbeni LR, Niven ML, Taylor MW. *Inorg. Chim. Acta*, 115 (1986) 211-217

[2] Lusi M. and Barbour L.J. *Angew. Chem. Int. Ed.* 51 (2012) 1-5

[3] Lipkowski J. et al., Werner Clathrates in *Comprehensive Supramolecular Chemistry.* 20: 6 (1996) 691-714

P49

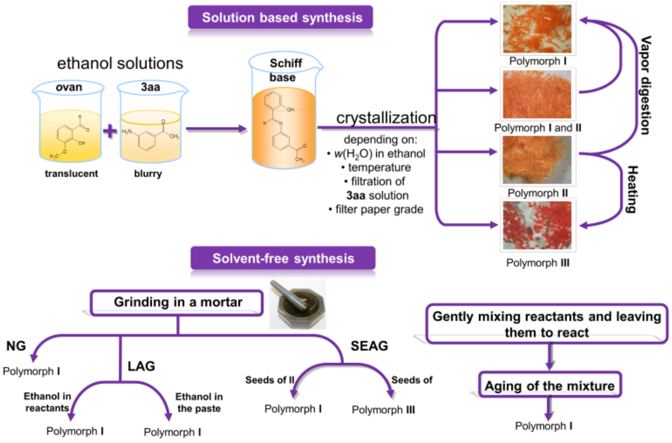
Polymorphism Control of a Schiff base *via* solvent-free and solution based synthesis

Marija Zbačnik[ab], *Ivana Nogalo*[a] *and Dominik Cinčić*[a]
[a] Laboratory of General and Inorganic Chemistry, Department of Chemistry, University of Zagreb, Zagreb, Croatia 10002, E-mail: mzbacnik@chem.pmf.hr. [b]Department of Chemistry, University of the Free State, Bloemfontein 9300, South Africa, E-mail: ZbacnikM@ufs.ca.za.

Keywords: Schiff base, Polymorphism, Mechanochemistry.

Schiff bases can be effortlessly obtained by condensation of aldehydes (or ketones) and primary amines[1] and thereafter used as ligands in coordination chemistry of transition metals.[2] On the other hand, the research of prosperous methods of synthesis such are mechanochemical ones provides new insights into faster, environmentally more friendly and economically more acceptable ways to prepare new but also already known compounds.[3] A study of Cinčić *et al* had recently revealed that the relative humidity (RH) plays an important role in the formation of the Schiff bases in the solid state and that the moisture actually acts as a catalyst in this solid state reaction.[4] Furthermore, it was also shown lately that the route of the mechanochemical reaction does not have to be the same when grinding is used and when the product is obtained merely by mixing reactants with a spatula and leaving the reaction mixture to age.[5] All the above mentioned show that numerous influences on the result of such a simple reaction are jet to be discovered.

Herein, we report a study of the dependence of the water amount in ethanol used as solvent and temperature during crystallization on the result of the synthesis of three polymorphic forms of a Schiff base derived from *o*-vanillin and 3-aminoacetophenone (***o*****van3aa**). The mechanochemical methods of preparation: neat grinding (**NG**), liquid-assisted grinding (**LAG**) and seeding-assisted grinding (**SEAG**) and vapor digestion were also thoroughly investigated (Scheme 1).



Scheme 1 Factors influencing polymorphism of (***o*****van3aa**).

---

[1] Schiff, H; *Ann. Chim.*, 1864, **131**, 118.

[2] Cinčić, D; Kaitner, B; *CrystEngComm*, 2011, **13**, 4351.

[3] James, S L; Adams, C J; Bolm, C; Braga, D; Collier, P; Friščić, T; Grepioni, F; Harris, K D M; Hyett, G; Jones, W; Krebs, A; Mack, J; Maini, L; Guy Orpen, A; Parkin, J; Shearouse, W C; Steedk, J W; Waddelli, D C; *Chem. Soc. Rev.*, 2012, **41**, 413.

[4] Cinčić, D; Brekalo, I; Kaitner, B; *Chem. Commun.*, 2012, **48**, 11683.

[5] Zbačnik, M; Kaitner, B,; *CrystEngComm*, 2014, **16**, 4162.

P50

ICSU Regional Office for Africa: Action Plan and Science Activities

Daniel Nyanganyura
International Council for Science Regional Office for Africa, Pretoria, South Africa, Email: d.nyanganyura@icsu-africa.org

Keywords: innovation, research collaboration, universality, science for policy.

The mandate of the International Council for Science (ICSU) Regional Office for Africa (ROA) is to promote the advancement of science, engineering, technology and innovation for the socio-economic development of Africa. Over the years, ICSU ROA engages in several science activities that seek to achieve this goal. Through its activities, the Regional Office pursues strengthening of international science for the benefit of society on the continent. It seeks to promoted and bring scientific activities of the ICSU family closer to individual scientists, educational and research institutions, national and regional professional bodies, policy and decision makers/implementers as well as other stakeholders in the region. At the same time, the Office endeavours to ensure that the voice of the African scientific community influences the international science agenda, and that scientists from the continent are involved in international scientific research guided by regional priorities.

To achieve this, the Regional Office strives to plan and roll out scientific activities that aim to build and/or strengthen intra- and inter-regional linkages and collaborations as well as foster south-south and north-south collaborations. ICSU ROA has taken it upon itself to work with partners and stakeholders in the region with the aim of developing links and strengthening engagements between the scientific community in Africa and the policy/decision makers. In pursuing these objectives, ICSU ROA fulfils the three fundamental principles of ICSU as enshrined in its Strategic Plans 2006 – 2011 and 2012-17, namely: (i) International Research Collaboration; (ii) Universality of Science; and (iii) Science for Policy.

P51

Structural study of Rh-acac complexes for use in oxidative addition.

Thato Taoana, *Andreas Roodt, Linette Twigge and Johan Venter*
Department of Chemistry, University of Free State, P.O.Box 339, Bloemfontein 9300, South Africa.
E-mail: thatotaoana@yahoo.com

Keywords: Rhodium, β-diketones, Phosphine ligands, Homogeneous catalysis, Carbonylation.

Oxidative addition was extensively studied on various Rhodium Acetylacetonato (acac) complexes containing tertiary phosphine ligands [1-3]. The importance of oxidative addition is emphasised in the Monsanto process, where it is the rate determining step [4-5]. Different types of acac have been utilised, and different degrees of success have been reported [6,7].

Tertiary phosphine ligands with different alkyl and aryl substituents, exhibiting different electron donating properties have also been tested, with the aim of improving yield and selectivity. This has been achieved by altering the steric bulk on the phosphine [8], which was one of the aims of this study.

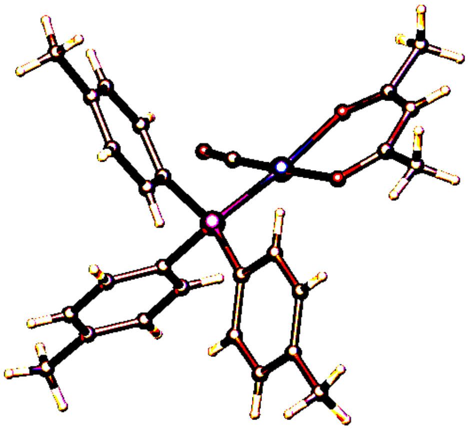


Figure 1: Crystal structure for [Rh(acac)(CO)P(*p*-tol)$_3$][9]

The synthesised [Rh(acac)(CO)P(*p*-tol)$_3$] was studied by IR, NMR and X-ray crystallography [see Fig. 1], and the results of this and related complexes will be discussed in this presentation.

---

[1] Otto, S.; Roodt, A.; Erasmus, J.J.C. and Swarts, J.C. *Polyhedron*, 1998, **17**, 2447

[2] Warsink, S.; Fessha, F.G,; Purcell, W. and Venter, J.A. *Journal of Organometallic Chemistry*, 3013, 726, 14

[3] Steyn, G.J.J.; Roodt, A.; Poletaeva, I. and Varshavsky,Y.S. *Journal of Organometallic Chemistry*, 1997, 536-537, 124

[4] Steyn, G.J.J.; Roodt, A.; and Leipoldt, J.G. *Inorg. Chem.* 1992, **31**, 3477

[5] Brink, A.; Roodt, A.; Steyl, G. and Visser, H.G. *Dalton Trans.*, 2010, **39**, 5572

[6] Trzeciak, A.M.; Borak, B.; Ciunik, Z.; Ziółkowski, J.J.; da Silva, M.F.C.G. and Pombeiro, A.J.L.*Eur. J. Inorg. Chem.* 2004. 1141. 1419.

[7] Lamprecht, D.; Lamprecht, G.J.; Botha, J.M., Umakoshi, K. and Sasaki, Y. *Acta Crystallography*, 1997, 1403

[8] Burrows, A.D.; Mahon, M.F.; Varrone, M. *Dalton Trans.* 2004. 3321

[9] Taoana, T.N.; Twigge, L, and Venter, J.A. Unpublished results.

DELEGATES

Surname	Given name	Affiliation	Program	Page	E-mail
Alexander	Orbett	University of the Free State	P1	57	orbettalexander@yahoo.com
Andriamanantena	Laza	University of Antananarivo	P18	74	lazatman@yahoo.fr
Antalis	Pari	Bruker	SK8	41	pari.antalis@bruker.com
Anye	Valentine	University of the Western Cape	P2	58	valentine.anye@gmail.com
Auf der Heyde	Thomas	DST			
Barbour	Len	University of Stellenbosch	KN1	12	ljb@sun.ac.za
Bibelayi	Didi	University of Kinshasa	P5	61	ddikima@gmail.com
Billing	Dave	University of Witwatersrand	KN2	13	dave.billing@wits.ac.za
Birama	Traore	University of Nancy/Bamako	P41	97	biramatraore23@yahoo.fr
Boeyens	Jan	University of Pretoria	S1	32	jan.boeyens@up.ac.za
Boughzala	Habib	Univeristy of Tunis El Manar	KN8	19	boughzala@yahoo.com
Bourne	Susan	University of Cape Town	KN4	15	susan.bourne@uct.ac.za
Bradley	John	University of Witwatersrand	SK7	40	john.bradley@wits.ac.za
Brink	Alice	University of the Free State	Y3	50	brinka@ufs.ac.za
Bungu	Paul	University of the Free State	P3	59	bungueps@ufs.ac.za
Comba	Peter	University of Heidelberg	KN16	27	peter.comba@aci.uni-heidelberg.de
Conradie	Jeanet	University of the Free State	P4	60	conradj@ufs.ac.za
Dillen	Jan	University of Stellenbosch	P6	62	jlmd@sun.ac.za
Dina	R	Madagascar	SI5	46	
Dippenaar	Bernard	University of Stellenbosch	P7	63	abdippenaar@sun.ac.za
Du Plessis	Esna	Sasol	KN13	24	esna.duplessis@sasol.com
Elmakki	Mohammed	University of the Free State	P8	64	elmakkim@ufs.ac.za
Engel	Emile	University of Stellenbosch	P10	66	ere@sun.ac.za
Engelbrecht	Ilana	University of the Free State	P9	65	engelbrechti@ufs.ac.za
Esterhuysen	Marisca	University of the Free State	P11	67	2008005060@ufs4life.ac.za
Esterhuysen	Catharine	University of Stellenbosch	KN10	21	ce@sun.ac.za
Fernandez	Manuel	University of Witwatersrand	Y2	49	Manuel.fernandes@wits.ac.za
Forbes	Roy	Sasol	Y9	56	roy.forbes@sasol.com
Freitag	Roxanne	University of the Free State	P12	68	roxannefreitag@gmail.com

DELEGATES

Surname	Given name	Affiliation	Program	Page	E-mail
Garcia-Grande	Santiago	University of Oviedo	SK1	34	acrata@fq.uniovi.es, sgg@uniovi.es
Gitari	Patricia	University of Nairobi	SI2	43	patricia.gitari@uonbi.ac.ke
Groenewald	Ferdi	University of Stellenbosch	P13	69	14874911@sun.ac.za
Haynes	Delia	University of Stellenbosch	Y1	48	dhaynes@sun.ac.za
Hill	Tania	University of Witwatersrand			tania.hill@wits.ac.za
Kama	Tom	University of the Free State	P14	70	kamadv@ufs.ac.za
Kanyankogote	Prosper	University of Kinshasa	SK2	35	kanyapros@yahoo.fr
Kennedy	Bianca	University of the Free State	Y4	51	kennedyb@ufs.ac.za
Kimani	Serah	University of Cape Town	Y5	52	swkimani@gmail.com
Koen	Renier	University of the Free State	P15	71	koenr@ufs.ac.za
Kpomah	Bridget	Delta State College of Physical Education	P16	72	tressurekpomah@yahoo.com
Kritchenkov	Andreii	Saint Petersburg State University	P17	73	platinist@mail.ru
Kroon	Ted	University of the Free State	KN17	28	kroonre@ufs.ac.za
Lee	Michael	Nelson Mandela Metropolitan University	KN14	25	michael.lee@nmmu@ufs.ac.za
Levendis	Demetrius	University of Witwatersrand	I1	30	demetrius.levendis@wits.ac.za
Loganathan	Nagarajan	University of the Free State	P30, P31	86, 87	loganathann@ufs.ac.za
Lungelo	Mandyoli	University of Pretoria	P20	76	lungelo.lungz@gmail.com
Maikoo	Samam	University of KwaZulu-Natal	P19	75	smaikoo7@gmail.com
Mangwala Kimpende	Peter	University of Kinshasa	Y8	55	mangwala@yahoo.fr
Manicum	Amanda-Lee	University of the Free State	P21	77	volminkae@ufs.ac.za
Mapotsane	Thuso	University of Pretoria	P22	78	zmapotsane@gmail.com
Marake	Daniel	University of the Free State	P23	79	maraketd@gmail.com
Mensah	Priscilla	University of the Free State	SI6	47	mensahpdna@ufs.ac.za
Mokolokolo	Pennie	University of the Free State	P24	80	2007102482@ufs4life.ac.za
Moleko	Puleng	Nelson Mandela Metropolitan University	P25	81	moleko.puleng@gmail.com

DELEGATES

Surname	Given name	Affiliation	Program	Page	E-mail
Molokoane	Pule	University of the Free State	P26	82	molokoanep@ufs.ac.za
Mphure	Lebohang	University of the Free State	P27	83	tmphure@gmail.com
Muller	Kina	University of the Free State	P28	84	vdmerwek@ufs.ac.za
Muller	Theuns	Langer Heinrich Uranium (Pty) LTD	SI3	44	muller.theunis@gmail.com
Munro	Orde	University of KwaZulu-Natal	KN11	22	munroo@ukzn.ac.za
Muswema	Jérémie	University of Kinshasa	P29	85	jeremie.muswem@unikin.ac.cd
Nana	Odette	Cameroon			ngnana86@yahoo.fr
Nassimbeni	Luigi	University of Cape Town	S2	33	luigi.nassimbeni@uct.ac.za
Ndengane	Mthawelanga	University of Pretoria	P32	88	mthandengs@gmail.com
Ndima	Daniel	University of Pretoria	P33	89	ndima.daniel@gmail.com
Ngome Abiaga	Jean-Paul	UNESCO	SK6	39	jj.ngome-abiaga@unesco.org
Ngoune	Jean	University of Dschang	KN6	17	jeangoune@yahoo.com
Nibret	Alebel	University of the Free State	P34	90	crossispower@gmail.com
Nkoe	Pheello	University of the Free State	P35	91	pheello@hotmail.com
Ntui	Clifford	University of Pretoria	P36	92	ntuimanyo@gmail.com
Ntwaeaborwa	Martin	University of the Free state	I2	31	ntwaeab@ufs.ac.za
Nyanganyura	Daniel		P50	106	d.nyanganyura@icsu-africa.org
Oliver	Clive	University of Cape Town	Y6	53	clive.oliver@uct.ac.za
Omondi	Bernard	University of Kwazulu-Natal	Y7	54	Owaga@ukzn.ac.za
Pretorius	Carla	University of the Free State	P38	94	cpretorius@ufs.ac.za
Rabe	Dina	University of Antananarivo	P39	95	espadon44@yahoo.fr
Roodt	Andre	University of the Free State			roodta@ufs.ac.za
Saki	Zoleka	SAASTA			
Schubert	Wolf-Dieter	University of Pretoria	KN18	29	wolf-dieter.schubert@up.ac.za
Schutte-Smith	Marietjie	University of the Free State	P40	96	schuttem@ufs.ac.za
Seitelo	Nina	University of the Free State			
Simon	Nzikahyel	University of Uyo	P37	93	nzikahyelsimon@uniuyo.edu.ng
Smith	Vincent	University of Stellenbosch	SI1	42	vjs@sun.ac.za

DELEGATES

Surname	Given name	Affiliation	Program	Page	E-mail
Steynberg	Petrie	Sasol	SK4	37	petrie.steynberg@sasol.com
Taoana	Thato	University of the Free State	P51	107	thatotaoana@yahoo.com
Thalal	Abdelmalek	University of Marocco	KN3	14	thalal@uca.ma
Tredoux	Marian	University of the Free State	KN7	18	mtredoux@ufs.ac.za
Tsosane	Mampotso	University of the Free State	P42	98	2008119386@ufs4life.ac.za
Tsotetsi	Tsietsi	University of the Free State			tsotetsita@ufs.ac.za
van Laeren	Laura	University of Stellenbosch	P43	99	lauravl@sun.ac.za
van Rooyen	Jason	University of Cape Town	KN5	16	jason.vanrooyen@uct.ac.za
van Rooyen	Peet	University of Pretoria			phvr@up.ac.za
Venter	Johan	University of the Free State	P45	101	venterja@ufs.ac.za
Venter	Truidie	University of the Free State	P44	100	ventergjs@ufs.ac.za
Venter	Andrew	Necsa	KN15	26	andrew.venter@necsa.co.za
Visser	Deon	University of the Free State	KN12	23	visserhg@ufs.ac.za
Wahl	Helene	University of Stellenbosch	P46	102	wahl@sun.ac.za
Warsink	Stefan	University of Utrecht	P47	103	stefanwarsink@gmail.com
Wicht	Merrill	Cape Peninsula University of Technology	P48	104	wichtm@cput.ac.za
Yav	Zephirin	University of Kinshasa	KN9	20	zephirin.yav@unikin.ac.cd
Zamxaka	Mthuthuzeli	SAASTA	SI4	45	zamxaka@gmail.com
Zbačnik	Marija	University of the Free State	P49	105	mzbacnik@gmail.com
Zema	Michele	University of Pavia	SK5	38	michele.zema@unipv.it

SPONSORS:

UNIVERSITY OF THE
FREE STATE
UNIVERSITEIT VAN DIE
VRYSTAAT
YUNIVESITHI YA
FREISTATA

UFS·UV
NATURAL AND
AGRICULTURAL SCIENCES
NATUUR- EN
LANDBOUWETENSKAPPE
CHEMISTRY
CHEMIE

science
& technology
Department:
Science and Technology
REPUBLIC OF SOUTH AFRICA

2014
international year of
crystallography
United Nations
Educational, Scientific and
Cultural Organization
International
Union of
Crystallography
Partners for the International Year of Crystallography 2014

IUCr

BRUKER

NRF
National Research
Foundation
SAASTA
South African Agency for Science
and Technology Advancement

www.ccdc.cam.ac.uk

NRF
National
Research
Foundation

HySA Public Awareness
Hydrogen South Africa

NANOTECHNOLOGY
PUBLIC ENGAGEMENT

DECTRIS®