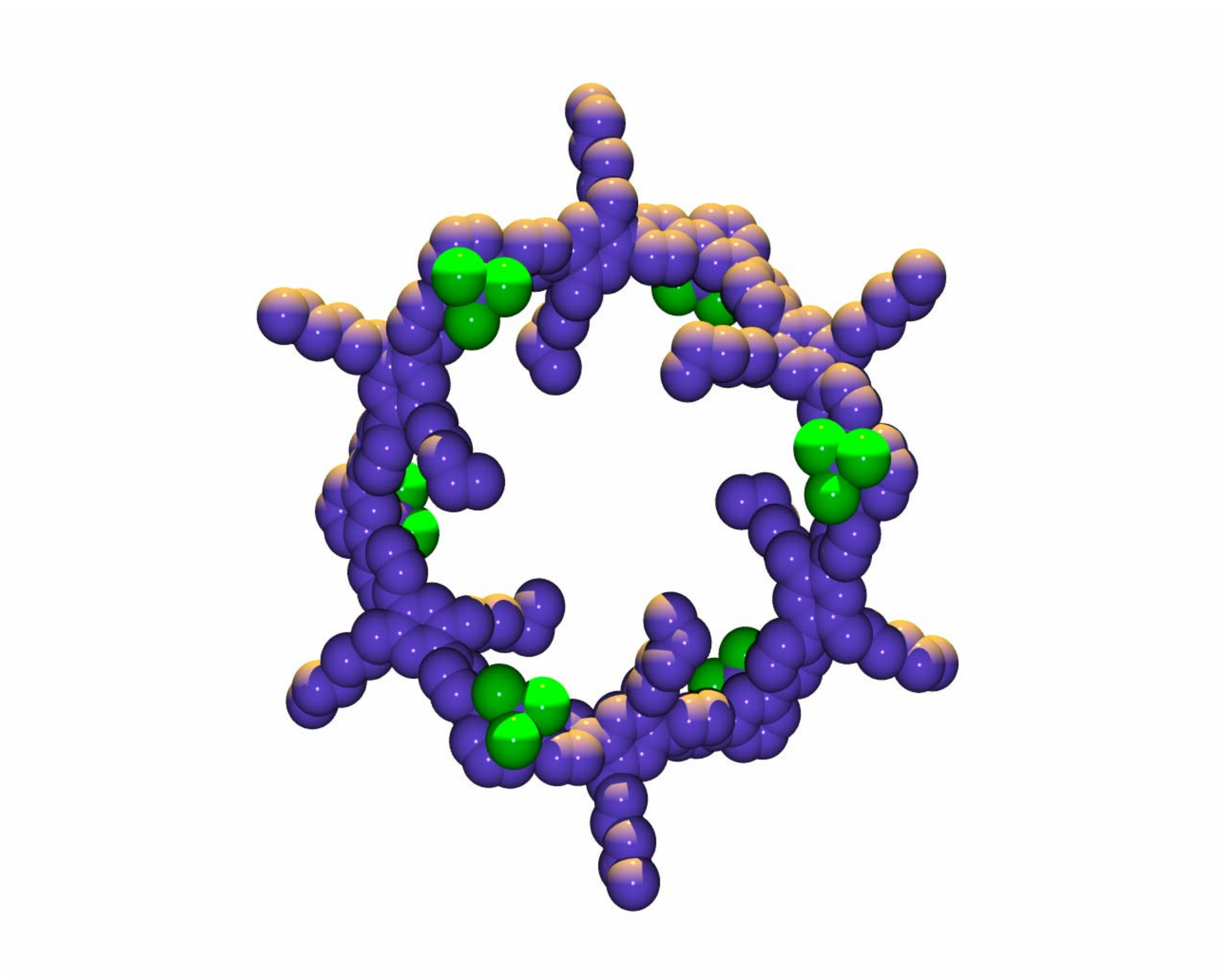
MIT Department of Chemistry
X-Ray Diffraction Facility

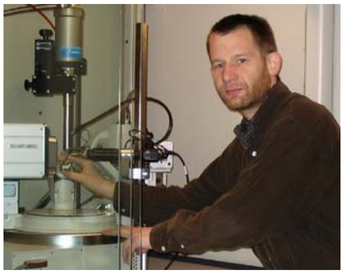
10TH ANNUAL BRUKER/MIT SYMPOSIUM

X-RAY DIFFRACTION – MORE THAN BONDS & ANGLES

Friday, February 17 and Saturday, February 18 2006



A Message from the Director of the Diffraction Facility



Dear participants of the Bruker/MIT Symposium,

As the director of the X-Ray Diffraction Facility of the MIT Department of Chemistry, it is my pleasure to welcome you to the 10th annual Bruker/MIT Symposium. This is the second meeting of this kind for me and I am happy to see so many of you returning.

X-ray diffraction is the single most powerful method in modern structure determination, and frequently the results from an X-ray analysis give a chemist's research a completely new direction. However, the amount of information that can be gained from a crystal structure grows dramatically with the knowledge the chemist has about the method. I am convinced that the posters and talks, as well as discussions along this meeting will demonstrate how much more information than just bond lengths and -angles can be derived from an X-ray structure, and I hope, this symposium will contribute towards communication and mutual understanding of chemists and crystallographers.

In this spirit I wish us all a successful and enjoyable meeting,

Sincerely

Peter Mueller
Director, X-Ray Diffraction Facility
MIT Department of Chemistry

ABSTRACTS:

APEX2: A NEW GENERATION OF SOFTWARE FOR CHEMICAL CRYSTALLOGRAPHY.

Charles Campana, Michael Ruf, Bruker AXS
Inc., 5465 East Cheryl Parkway, Madison, WI
53711-5373, e-mail: Charles.Campana@bruker-axs.com

The new Bruker APEX2 Crystallographic Software Suite utilizes a modular approach to carry out all of the tasks associated with crystal structure analysis within a single Graphical User Interface. The design is intuitive, with tasks organized in a logical 'flow-chart' order. This suite incorporates the most powerful crystallographic algorithms into a modern SQL database environment, with a variety of utilities to import and export data in standard formats. The APEX2 client software is available for both Windows XP and Linux platforms. The modular instrument interface (Bruker Instrument - BIS) supports many combinations of instrument hardware configurations. New algorithms facilitate crystal face indexing, on-line searching with the CSD ConQuest routines, powder diffraction (Phase ID) applications, and automatic structure determination.

ADVANCES IN SOURCE AND DETECTOR TECHNOLOGY FOR X-RAY CRYSTALLOGRAHY.

Roger D. Durst, Bruker AXS Inc., 5465 East
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e-mail: Roger.Durst@bruker-axs.com

Recent improvements in X-ray source and optics design are described which are capable of delivering intensities that approach those of second-generation synchrotron beamlines. Together with new, enhanced detector technologies this offers the freedom to accomplish many experiments in the home lab that would have previously required synchrotron radiation.

EXPLORING TRHOUGH-SPACE π-π INTERACTIONS IN CONJUGATED MATERIALS.

Anne McNeil, Timothy M. Swager,
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Our focus is on the design and synthesis of π-conjugated materials containing intramolecular, through-space π-π interactions. More specifically, we utilize rigid molecular scaffolds to introduce perpendicular and parallel π-π interactions. One example evaluates the electronic and optical effects of a series of arene rings proximate to a poly(*p*-phenylene butadiynylene) backbone. The second example investigates through-space charge transfer interactions between donor and acceptor substituents in phenylene ethynylenes. In both examples, visualization of the three-dimensional structures via x-ray crystallography fueled and even altered our research directions.

INSIGHTS INTO CHEMICAL REACTIVITY AND PHYSICO-CHEMICAL PROPERTIES GAINED FROM CRYSTALLOGRAPHY.

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The preparation of a series of trisprazolylborate complexes of the group 1 and 2 metals is reported along with thalium(1). The new ligand contains hemilabile ether groups which allows the coordination of the ligand to vary from 1 to 6. The structures determined from single crystal studies provide insight into the chemical reactivity of the complexes seen in solution. These reactivities relate to dynamic NMR behavior, group transfer and ring opening polymerization catalysis. In a different study, the use of powder X-ray data is shown to be most useful for applications of direct space methods for the determination of the ordering of MM quadruply bonded paddle-wheel complexes in the solid state. This ordering, together with conformational effects, controls such properties as color and magnetism.

CRYSTAL STRUCTURE VALIDATION.

Anthony L. Spek, Utrecht University, The Netherlands, e-mail: spea@chem.uu.nl

Crystal structure validation has become mainstream. Most journals now require authors to validate the crystal structures that are reported in their papers. The machinery involved was pioneered by the International Union of Crystallography. Validation is the answer to the problem that the number of reported structures today is too large to be inspected in detail by knowledgable referees. Their valuable time can now be used to sort out potential problems reported in the form of ALERTS. The latter not always point to errors but also to interesting features that deviate from the expected.

LEARNING MORE ABOUT PHOTOSYNTHESIS WITH THE AID OF SYNTHETIC MANGANESE CLUSTER COMPLEXES.

William H Armstrong, Eugene F. Merkert, Chemistry Center, Boston College, 2609 Beacon Street, Chestnut Hill, MA 02467-3860, e-mail: armstwi@bc.edu

A tetranuclear manganese complex (Mn_4), held together by oxo (O^{2-}) atom bridges, is thought to be the active site for the conversion of water to dioxygen in plant and bacterial Photosystem II (PSII). A calcium ion is closely associated with Mn_4. Many tetranuclear oxo-bridged manganese aggregates have been synthesized *in vitro* and some of them provide insight into the properties of the biological cluster. We are interested in preparing compounds that mimic the physical and chemical properties of PSII Mn_4 in its higher oxidation states. This work would not be feasible were it not for the ease with which x-ray crystal structures can be obtained using modern instrumentation. X-ray absorption studies of PSII reveal that Mn···Mn distances lengthen significantly during the PSII S_2 to S_3 transition. The S_n states are intermediates in the enzyme catalytic cycle. We have observed that one of our tetranuclear complexes, namely the 'dimer-of-dimers' $[(Mn_2O_2)_2(tphpn)_2](ClO_4)_4$, undergoes a dramatic structural change when it is oxidized by one electron. We suggest that a similar rearrangement may occur in the PSII Mn_4 when it is oxidized. When $[(Mn_2O_2)_2(tphpn)_2](ClO_4)_4$ is *reduced* by one electron, a hyperfine rich EPR spectrum appears. This spectrum strongly resembles that of an oxidation state of PSII called S_0. We propose that when the structure of this latter synthetic species is elucidated, we will have an accurate picture of PSII Mn_4 for the first time. The second major topic to be examined will be ligand exchange chemistry for the adamantane-shaped $[Mn_4O_6(bpxa)_4](ClO_4)_4$ and reaction characteristics of the exchange products. The tridentate nitrogen donor ligand bpxa can be exchanged for a host of other tridentate ligands. With the proper choice of ligands, we can access a $Mn_4(IV_3,V)$ oxidation state, whereas the original complex has the oxidation state $Mn_4(IV_4)$ and can be oxidized no further. In the higher oxidation state, the manganese oxo core is more reactive. Under electrospray ionization conditions, we have mass spectral data consistent with loss of dioxygen, which is of course the product of water oxidation in photosynthesis.

STUDIES RELATED TO THE CATALYTIC REDUCTION OF DINITROGEN TO AMMONIA IN STERICALLY CROWDED TRIAMIDOAMINE COMPLEXES.

Richard R. Schrock, Massachusetts Institute of Technology, Department of Chemistry, 77 Massachusetts Avenue, Cambridge, MA 02139-4307, e-mail: rrs@mit.edu

It is now possible to reduct dinitrogen catalytically by molybdenum complexes that contain the $[HIPTN_3N]^{3-}$ ligand ($[HIPTN_3N]^{3-}$ = $[(HIPTNCH_2CH_2)_3N]^{3-}$ where HIPT = 3,5-(2,4,6-$i\text{-}Pr_3C_6H_2)_2C_6H_3$) at room temperature and pressure with protons and electrons. A total of 7-8 equivalents of ammonia are formed out of ~12 possible (depending upon the Mo derivative employed). No hydrazine is formed. Numerous x-ray studies of proposed intermediates in the catalytic cycle suggest that N_2 is being reduced at a sterically protected, single Mo center operating in oxidation states between Mo(III) and Mo(VI). Subtle variations of the $[HIPTN_3N]^{3-}$ ligand are not as successful as a consequence of an unknown shunt in the catalytic cycle that consumes reduction equivalents to yield (it is proposed) dihydrogen.

Poster abstracts

MAGNETIC EXCHANGE IN COPPER HALIDES.

Rob Butcher, Clark University, Worcester,
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A magnetic superexchange pathway that has received extensive attention in the past several years is the direct halide-halide contact in copper(II) halide salts. The magnitude of these so called 2H exchange interactions (J2H) that occur between the ferromagnetic layers in the $(NH_3RNH_3)CuX_4$ layered perovskite structures have been previously summarized by Willett et al. It has been found that the strength of the interactions are primarily a function of the Cu-X-X-Cu distance, Cu-X-X angle, and the electronic nature of the halide ion. A crucial conclusion from these studies is that the 2H exchange interactions in the Br salts are 5-10 times larger than those in the Cl salts with comparable 2H contact distances and angles. In recent years, the crucial nature of these 2H exchange pathways has been realized in the development of novel magnetic systems. Landee and co-workers have exploited these contacts in developing a series of 2d spin Heisenberg AFM systems. These interactions have also been observed to lead to the development of a series of spin ladder systems.

Magneto-structural studies in dimeric $A_2Cu_2X_6$ compounds have been researched extensively in the past. These compounds generally form stacks or chains of the Cu_2X6_2- dimers based on the formation of two or one semi-coordinate bonds between adjacent dimers. The discussion of exchange pathways in these studies has focused on the through bond pathways, *i.e.*, intradimer and intrachain/stack interactions. Unfortunately, the discussion of the role of the close halogen-halogen (2H) contacts within these dimer structures has generally been ignored. However, recently two neutron scattering studies in $A_2Cu_2Cl_6$ salts have shown that the 2H pathways are stronger than the intrachain/stack interactions. Since this is true in chloride salts, it is expected that the 2H pathway will play an even more significant role in bromide salts.

X-RAY STRUCTURE OF THE POLYNUCLEAR Cu_4Ni_8 COMPOUND: IDENTIFICATION AND ASSIGNMENT OF METAL POSITIONS.

Alexander S. Filatov, Rodolphe Clark, Marina A. Petrukhina, University at Albany, 1400 Washington Ave, Albany , NY, 12222,
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Reaction of copper(II) trifluoroacetate hydrate, $Cu_2(TFA)_4\ 2H_2O$, and syn-2-pyridinealdoximate nickel(II), $Ni(PaO)_2$, led to a discret polynuclear heterometallic $Cu(II)_4Ni(II)_8O_4(PaO)_8(TFA)_8$ cluster. This complex consists of four linear trinuclear moieties each comprised of two Ni(II) and one Cu(II) centers. The identification and assignment of metal positions is discussed based on structural considerations.

FE-CYANIDE CHEMISTRY: DOING 18TH AND 19TH CENTURY CHEMISTRY IN THE 21ST CENTURY

Stephen Koch, SUNY Stony Brook, Chemistry Department, Stony Brook, NY 11794-3400 e-mail: stephen.koch@sunysb.edu

No abstract submitted.

SMALL MOLECULE REDUCTIONS BY COPPER(I) BORYL COMPLEXES

David Laitar, Massachusetts Institute of Technology, Department of Chemistry, 77 Massachusetts Avenue, Cambridge, MA 02139-4307, e-mail: dlaitar@mit.edu

The first well-characterized copper boryl complex inserts a variety of unsaturated small molecules such as olefins, aldehydes, and carbon dioxide into the Cu-B bond. These reactions form the basis for several catalytic systems including the addition of diboron reagents across the C=O bond of aldehydes, and the deoxygenation of carbon dioxide using bis(pinacolato)diboron as the stoichiometric reductant.

NEW LIGANDS SYSTEMS BASED ON THE TACH FRAMEWORK

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X-ray crystallography has been an integral tool in our research group's examination of different chelate systems and the chemistry behind their cytotoxic effects (or lack thereof). Headed by Roy Planalp, our focus has been on N6-ligands based on the triaminocyclohexane framework (tach) and their coordination chemistry with divalent metal ions, especially iron, copper, and zinc. For example, tach-6-Mepyr (tachpyr with a 6-methyl on the pyridine ring) was shown to have no cytotoxic effects, as a sharp contrast to similar analogues. X-ray crystallography was able to demonstrate that the steric effects from the 6-methyl groups make it a poor chelator and therefore not harmful to the cell (Childers *et al.* (2005) *Eur. J. Inorg. Chem.*, 3971-3982).
Alternately, it has opened other avenues of thought: tachpyr was originally considered toxic due its excellent complexation (and therefore sequestration) of iron within the cell. However, x-ray crystallography data indicated that zinc also fits well with tachpyr, suggesting that there may be other reasons for the cytotoxic nature of these chelators (Park, G. *et al.* (2003) *Dalton Trans*. 318-324). I am currently at work synthesizing new N3S3 ligand systems based on the tach framework and will be complexing them soon. Having a better understanding of some of the intricacies of x-ray crystallography data will help me further my understanding when working with these future crystal structures.

SYNTHESIS OF A NOVEL TRIPODAL LIGAND BASED ON THE TAME FRAMEWORK AND ITS COORDINATION CHEMISTRY WITH MN(II), FE(II), CO(II), NI(II), CU(II), AND ZN(II)

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The synthesis of the novel chelator tamepyr-(N,N',N – tris (2 – pyridylmethyl) - 1,1,1-tris(aminomethyl)ethane) and complexation of the ligand with Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) has been studied. The coordination chemistry of tamepyr has been compared with another tripodal chelator tachpyr-(N,N',N – tris (2 – pyridylmethyl) - cis,cis-1,3,5-triaminocyclohexane), which has been shown to be cytotoxic to human tumor cells, an effect attributable to chelation of the biometals Fe, Zn, and Cu. Treating the Ni(II) complex with excess sodium cyanide liberated the free ligand. The Mn(II) and Co(II) complexes have high spin electron configurations (meff = 5.9 B.M., and 4.9 B.M. respectively), based on solution magnetic susceptibility, and electronic spectral studies. The Fe(II) complex has a low spin electron configuration based on ^{1}H-NMR. X-ray crystallographic studies of $[Zn(tamepyr)]^{2+}$ indicates the ligand preference for octahedral geometry, whereas the Cu(II) complex appears to exhibit a classic Jahn-Teller distortion as indicated by solution electronic spectroscopy. As was previously seen for tachpyr, the Co(II) and Fe(II) tamepyr complexes undergo a series of oxidative dehydrogenation reactions in the presence of oxygen resulting in the formation of a variety of polyimino complexes. The Fe(II) tamepyr complex, although, is slower to oxidize than the corresponding tachpyr complex. The rigid nature of the complexed ligand and the effectiveness of the chelator for the aforementioned metals in an aqueous medium will be discussed.

CRYSTALLOGRAPHIC CHARACTERIZATION OF BUCKYBALLS: MOLECULAR GEOMETRY, ENANTIOMERS, AND SOLID STATE PACKING.

Marina A. Petrukhina, Yulia Sevryugina, Kristian
W. Andreini, Edward A. Jackson, Lawrence T.
Scott, University at Albany, SUNY, 1400
Washington Ave, Albany , NY, 12222,
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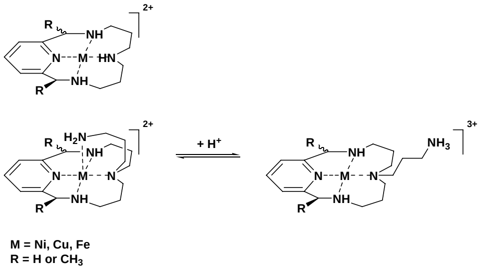
Crystallographic characterization of several bowl-shaped polyarenes, such as corannulene ($C_{20}H_{10}$), dibenzo[a,g]corannulene ($C_{28}H_{14}$), hemifullerene ($C_{30}H_{12}$), and 1,3,5,7,9-penta-tert-butyl-corannulene ($C_{40}H_{50}$) will be presented. Molecular geometry and solid state packing motifs will be compared for the above curved polyarenes. Difficulties in structure solution associated with existence of statistical mixtures of enantiomers as well as with rotational disorders of symmetrical bowls will be discussed.

COMPARISON OF STRUCTURAL AND SPECTROSCOPIC PROPERTIES IN A SERIES OF TRANSITION METAL COMPLEXES OF PYRIDINE-CONTAINING MACROCYCLES.

Sonia Taktak, Aida M. Herrera, Wanhua Ye,
Elena V. Rybak-Akimova, Department. of
Chemistry, Tufts University, Medford, MA
02155, e-mail: sonia_tak@yahoo.com)

Nickel(II), Copper(II) and Iron(II) complexes of pentadentate and tetradentate pyridine-containing macrocycles were synthesized and characterized. Nickel complexes were prepared by template condensation. Copper and Iron complexes were obtained by transmetallation from the corresponding Nickel species. Most complexes were characterized by X-ray crystallography using a Bruker SMART CCD based diffractometer. In the case of complexes bearing neutral pentadentate ligands, square pyramidal geometries were observed regardless of the nature of the metal. The four nitrogen donors of the macrocycle occupy the equatorial positions and the fifth nitrogen from the pendant arm, the axial position. Upon protonation of the amine group on the ligand arm, a change in geometry occurs to form square planar metal centers with weakly bound axial acetonitrile molecule(s). Spectroscopic properties and reactivity of these species will be discussed and compared to that of the metal complexes of the related tetradentate ligand without an arm.



SYNTHESIS AND REACTIVITY OF NEW CATIONIC MOLYBDENUM IMIDO ALKYLIDENE COMPLEXES

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The new imido alkylidene complexes Mo(NAr)(CHCMe$_2$Ph)(TMHD)(OTf)(S) (TMHD = tetramethylheptanedionato, S = THF, **1a**; quinuclidine, **1b**; 2,4-lutidine, **1c**) and Mo(NAr)(CHCMe$_2$Ph)(N^N)(OTf) (**3**, N^N = 2,6-dimethylphenyl-Nacnac) have been prepared in high yield by salt metathesis reactions from the bistriflate precursors. A crystal structure of **1a** shows it to be a pseudo octahedral six-coordinate complex with the THF ligand residing *trans* to the alkylidene. Addition of Na[B(3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$ (NaBAr^F$_4$) to **1a** yields the cationic alkylidene complex {Mo(NAr)(CHCMe$_2$Ph)(TMHD)(THF)}{BAr^F$_4$} (**2**) which has been characterized by NMR spectroscopy and X-ray diffraction. The solid-state structure of **2** displays a distorted square pyramidal geometry with the alkylidene occupying the axial position. Metathesis reactions of **2** with ethylene give an unexpected cationic metallocyclopentane complex, which appears to form through C-C reductive elimination of the metallcyclobutane intermediate. Addition of Na(THF)$_x$[B(C$_6$F$_5$)$_4$] to **3** also gives a cationic alkylidene complex of the formula {Mo(NAr)(CHCMe$_2$Ph)(N^N)(THF)}{B(C$_6$F$_5$)$_4$} (**4**), which has been characterized by NMR spectroscopy. In contrast to **2**, reaction of ethylene with **4** gives the expected cationic metallocyclopropane complex

STRUCTURES OF GIANT BISMUTH OXO-CLUSTERS: ONLY WITH BRUKER APEX CCD!

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e-mail: hz7426@albany.edu

Fluorinated bis(gem-diol), 1,1,1,5,5,5-hexafluoropentane-2,2,4,4-tetraol (H4hfac), can be easily obtained by hydration of hexafluoroacetylacetone (Hhfac). The deprotonated form of the tetraol, (hfpt)$^{4-}$, is capable to act as a controlled source of both diketonate and oxo-groups by undergoing a facile cleavage of the two C CO bonds. Using hfpt^{4-} as a reactant, we have obtained the first bismuth oxo-diketonate, Bi$_9$O$_7$(hfac)$_{13}$, which consists of the Bi$_6$O$_7$ central core with three Bi-diketonate arms attached to its periphery. In coordinating solvents this molecule irreversibly dissociates to give Bi(hfac)$_3$ and high-nuclearity bismuth oxo-diketonate clusters. The crystal structures of two such remarkable nanosized clusters having Bi$_{22}$O$_{26}$$^{14+}$ and Bi$_{38}$O$_{45}$$^{24+}$ cores will be discussed.

Thanks be to

Liz McGrath for helping with everything (nothing here would have worked without her)

Paul Baumgardner and **Phil Long** (MIT computing) for lending us 5 laptop computers

Kemper Thompson and **DELL** for lending us 12 great desktop computers

Ed Udas for his assistance in setting up everything

David G. Bray for lending us the coffee maker

Guy Barbagelata for moral (and other) support

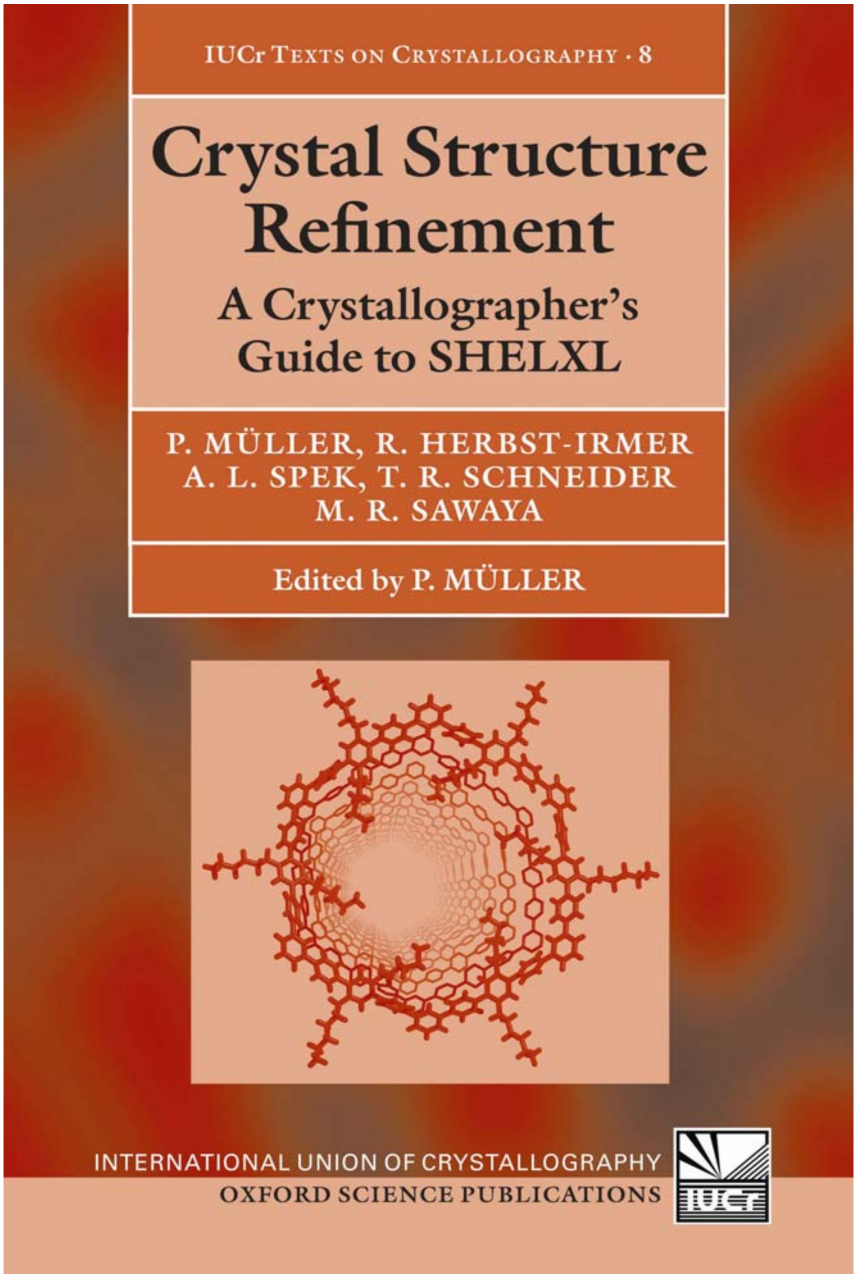
all speakers,
workshop teachers,
and poster-authors

and

BRUKER-AXS for financial support

Advertisement

Oxford University Press has announced a new textbook to appear this summer: Crystal Structure Refinement – A Crystallographer's Guide to SHELXL. The book contains over 20 examples, covering the most relevant aspects of crystal structure refinement. It comes with a CD-ROM containing all datasets.



IUCr TEXTS ON CRYSTALLOGRAPHY · 8

Crystal Structure Refinement

A Crystallographer's Guide to SHELXL

P. MÜLLER, R. HERBST-IRMER
A. L. SPEK, T. R. SCHNEIDER
M. R. SAWAYA

Edited by P. MÜLLER

INTERNATIONAL UNION OF CRYSTALLOGRAPHY
OXFORD SCIENCE PUBLICATIONS

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http://www.oup.co.uk/isbn/0-19-857076-7

SCHEDULE

Friday, February 17: 2:00 p.m. to 5:00 p.m. in **room 6-321** (Moore room)
Refinement Workshop:
Eftichia Alexopoulos, Chuck Campana, Peter Mueller, Richard Staples

Saturday, February 18: 8:30 a.m. to 5:15 p.m. in **room 66-110**

08:30 - 09:00 Light Breakfast

09:00 - 09:15 Opening Remarks by Stephen J. Lippard

09:15 - 10:00 Charles Campana (Bruker-AXS)
New Software Tools and Advanced Applications for Chemical Crystallography

10:00 - 10:30 Roger Durst (Bruker-AXS)
Detectors for X-Ray Diffraction: The State of the Art and Future Directions

10:30 - 10:45 Coffee Break

10:45 - 11:15 Anne McNeil (MIT)
Exploring Through-Space π-π Interactions in Conjugated Materials

11:15 - 12:15 Malcolm Chisholm (Ohio State)
Insights into Chemical Reactivity and Physico-chemical Properties Gained from Crystallography

12:15 - 02:15 Lunch with Poster Session in **room 6-321** (Moore room)

02:15 - 02:45 Anthony L. Spek (Utrecht University)
Crystal Structure Validation

02:45 - 03:45 William H. Armstrong (Boston College)
Learning More about Photosynthesis with the Aid of Synthetic Manganese Cluster Complexes

03:45 - 04:00 Coffee Break

04:00 - 05:00 Richard R. Schrock (MIT)
Studies Related to the Catalytic Reduction of Dinitrogen to Ammonia in Sterically Crowded Triamidoamine Complexes

05:00 - 05:15 Poster Prizes and Closing Remarks