

POSTER ABSTRACTS

Advanced Methods in X-ray

Diffraction Analysis: the XD

Programming Package

Buffalo NY, 12-17 May 2003

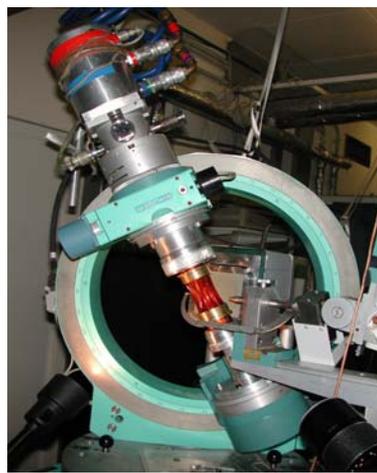
POSTER ABSTRACTS

SESSION P10X

Tuesday, May 13, Natural Sciences Bldg. room 218, 16.30-17.30

P101: High resolution experiments at 20K with a closed cycle helium cryostat, M. Messerschmidt and P. Luger, *Freie Universität Berlin, Institut für Kristallographie Takustraße 6, D-14195 Berlin, Germany.*

We have equipped a Huber 4-circle-goniometer with a 2-stage-helium-cryostat and a Bruker-Apex detector. Low running costs and good temperature stability are the main advantages of closed cycle Helium cryostats in low temperature diffraction experiments. These cryostats are normally used with carbon or beryllium vacuum chambers, that produce a lot of powder lines. To overcome the problems a new vacuum chamber was constructed from 0.1mm Kapton film. This gives small and unstructured background. Through spanning inside a large Huber Eulerian cradle the cylinder can be stabilized, so that only support on top and bottom is needed. The low leak rates make measurements of some weaks at 20 K possible. When using transparent Kapton film it is also possible to center the crystal optical inside the camber. So we run our setup routinely at 20 K. Results of some high resolution experiments at medium sized organic compounds are compared.



Workshop on the Advanced Methods in X-ray Diffraction Analysis

May 12-17, 2003

Amherst (North) Campus, UB SUNY@Buffalo, Buffalo, New York, USA

P102: In situ time-resolved X-ray diffraction of solid state reactions in the system LiCl-Al(OH)₃-H₂O, K. A. Tarasov,¹ V. P. Isupov¹ and D. O'Hare,² ¹*Institute of Solid State Chemistry and Mechanochemistry, SB of RAS, Novosibirsk, 630128, Russia;* ²*Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QR, UK.*

Monitoring chemical reactions in situ can provide valuable information on the processes occurring as well as kinetic data by allowing them to be studied under normal conditions. In recent years the development of high flux synchrotron X-ray and neutron sources has led to such studies becoming much more routine. In particular energy-dispersive synchrotron X-ray experiments, which use polychromatic radiation and an energy discriminating detector, have yielded valuable kinetic and mechanistic information on a number of solid state reactions [1].

Intercalation of lithium salts into crystalline Al(OH)₃ giving rise to layered double hydroxides of formula [LiAl₂(OH)₆]_nX·qH₂O (Xⁿ⁻ is an interlayer anion), have recently been studied in situ using time-resolved energy-dispersive X-ray diffraction technique (EDXRD). The intercalation is a reversible reaction, and as a result under certain conditions [LiAl₂(OH)₆]_nX·qH₂O can decompose giving rise to initial Li_nX and Al(OH)₃ [2]. The aim of the work was to investigate kinetics of the deintercalation of lithium salts from [LiAl₂(OH)₆]Cl·qH₂O in water using EDXRD. We have investigated some parameters affecting the rate of the deintercalation: temperature, ratio liquid/solid in the suspension and nature of the interlayer anion.

The temperature dependence of the rate of the reaction yields activation energies of 94 kJ mol⁻¹ for mono-dispersed [LiAl₂(OH)₆]Cl·qH₂O (particle size 5-10 μm) and 117 kJ mol⁻¹ for poly-dispersed [LiAl₂(OH)₆]Cl·qH₂O (particle size 1-30 μm). We have found that increase of ratio liquid/solid upon suspending [LiAl₂(OH)₆]Cl·qH₂O in water leads to increase of the rate of the deintercalation. The rate of the reaction has been shown to depend on the type of the interlayer anion, and for chloride and nitrate anions it corresponds to the series of anionic affinity in relation to the host. These results have been analyzed in comparison with the data obtained for the reverse reaction – intercalation of LiCl into Al(OH)₃.

References:

- [1] O'Hare, D., Evans, J. S. O., Fog, A., O'Brien, S. (2000). *Polyhedron* **19**, 297.
- [2] Isupov, V., Chupakhina, L., Belobaba, A., Trunova, A. (1999). *J. Mater. Synth. Proc.* **1**, 7.

Workshop on the Advanced Methods in X-ray Diffraction Analysis

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P103: Charge density study from image-plate intensity data of (1'R,2'R)-3-[(cis)-2'-Cyclohexylmethyl-cyclopentylimino]-2-azabicyclo[2.2.2]octane, A. Meents,¹ A. Kirfel,² D. Lübbert¹ and E. Weckert,¹ ¹HASYLAB-DESY, Notkestr. 85, 22607 Hamburg, Germany; ²Mineralogisch-Petrologisches Institut der Universität Bonn, Poppelsdorfer Schloss, 53115 Bonn, Germany.

In order to explore the feasibility of using an image-plate-scanner for electron charge density studies we have investigated a crystal of the title compound as a model substance. High quality crystals of this compound were available. The structure of this semicyclic amidine with sum formula $C_{19}H_{33}N_2^+Br^-$, which stimulates insulin release in pancreatic B cells, was known [1]. It crystallizes in the orthorhombic space group $P2_12_12_1$, with lattice constants of $a=11.245 \text{ \AA}$, $b=11.725 \text{ \AA}$, and $c=14.476 \text{ \AA}$.

Measurements were done at the CEMO-beamline at HASYLAB/DESY. Data were collected at a temperature of 100 K and an energy of 28 keV using a MAR345 image-plate-scanner. To obtain for the electron density study a dataset with a sufficient dynamic intensity range three passes with different exposure times were carried out. Altogether 211066 observations with a completeness of 100% were made up to a resolution of $\sin\theta/\lambda = 1.10 \text{ \AA}^{-1}$. The internal R-value of the dataset containing 21436 unique reflections was $R(F^2) = 0.034$.

A first refinement of the structure model [1] was performed with SHELXL-97 converging at $R1 = 0.0248$. The hydrogen positions used were calculated and refined in a riding model. Further calculations on the basis of neutral atoms were carried out using the VALRAY program package [2]. For the non hydrogen-atoms, multipoles were expanded to the 3. order (octupoles), using a common expansion coefficient α for each atom. For the hydrogen-atoms with fixed positions obtained from the above mentioned riding model, only mono- and dipolar deformations were allowed. This refinement converged to a final $R(F)$ -value of 0.0137.

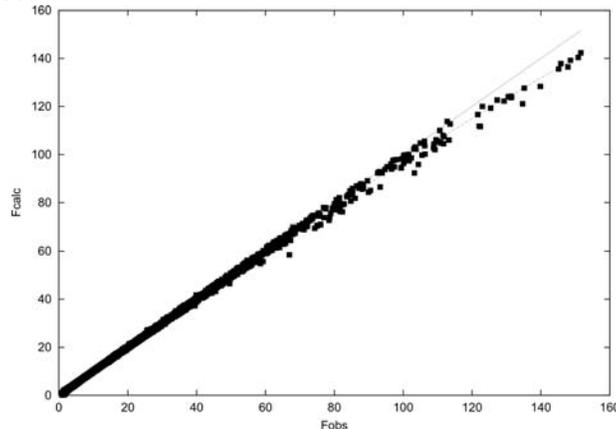


Figure 1: $|F(calc)|$ versus $|F(obs)|$ after the first multipole refinement.

A comparison of the $|F(obs)|$ with the corresponding $|F(calc)|$ shows systematically too high $|F(obs)|$ values for the strong reflections (see Fig. 1). The reason for this unexpected finding is most probably an insufficient erasing of the strong reflection intensities on the image plate. A correction function was fitted to the data and the data were subsequently corrected by applying this function. A new multipole refinement carried out on the basis of the corrected intensities $|F_{corr}|^2$ resulted in $R(F)=0.0130$ ($GoF=0.767$). Summing up, the image-plate-scanner is well suited for charge density studies provided the problem of insufficient intensity erasion can be properly dealt with.

References:

- [1] Hartmann, S., Weckert, E., Frahm, A. W. (1999). *Acta Cryst. C* **55**, 806.
- [2] Stewart, R. F., Spackman, M. A., Flensburg, C. (2000). VALRAY Users Manual.

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May 12-17, 2003

Amherst (North) Campus, UB SUNY@Buffalo, Buffalo, New York, USA

SESSION P20X

Thursday, May 15, Natural Sciences Bldg. room 218, 17.00-18.00

P201: Charge density study of the blue protein model compound, M. Fronc,¹ J. Kožíšek,¹ M. Breza,¹ H. Fuess,² P. Coppens,³ G. Wu³ and C. Paulmann,⁴ ¹*Department of Physical Chemistry, Slovak Technical University, 812 37 Bratislava, Slovakia;* ²*Material Science, Darmstadt University of Technology, D-64287 Darmstadt, Germany;* ³*Department of Chemistry, SUNY at Buffalo, Buffalo, NY 14260-3000, USA;* ⁴*Mineralogisch-Petrographisches Institut, Universität Hamburg, Grindelallee 48, D-20146 Hamburg, Germany.*

Blue copper proteins are part of the electron transfer proteins which play an important role in many processes in living organisms (e.g. photosynthesis and respiratory systems). Their characteristic properties include deep blue color, EPR spectrum with a small hyperfine coupling constant and high electron transfer rates. Due to some factors, which limit the studies on natural proteins, the so-called model compounds with the similar properties as the active center of the blue proteins are used.

In this work, electron density distribution in the [Cu(bite)](BF₄) (bite = biphenyldiimine dithioether, C₂₈H₂₂N₂S₂) will be described. It is a reduced form of the model compound for blue proteins ([Cu(bite)](BF₄)₂ represents its oxidized form).

Data were collected at the X3 beamline of the National Synchrotron Light Source at Brookhaven National Laboratory (T = 20 K, $\lambda = 0.6430 \text{ \AA}$) and at beamline F1 at HASYLAB/DESY in Hamburg (T = 100 K, $\lambda = 0.5604 \text{ \AA}$). The crystal used at Brookhaven had dimensions of 0.064×0.111×0.143 mm³. There were 109 890 (17 619 unique) reflections collected. Two crystals of a different size were used at DESY. The smaller one had dimensions of 0.08×0.1×0.30 mm³ and was measured with 2 θ from 10 to 50 degrees. The larger one (0.17×0.35×0.50 mm³) was used in order to get high-angle data ($\sin \theta/\lambda \sim 1.37 \text{ \AA}^{-1}$) and was measured in the region 2 θ from 40 to 70 degrees. 159 280 reflections were collected (25 935 unique). To increase the number of low-angle reflections, another measurement was performed at DESY with use of point detector.

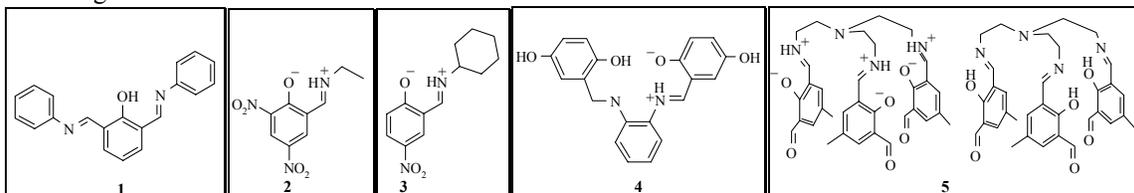
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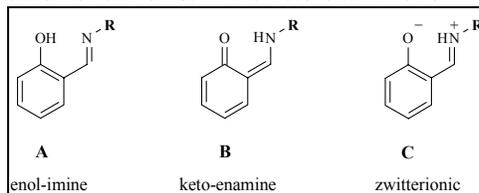
Amherst (North) Campus, UB SUNY@Buffalo, Buffalo, New York, USA

P202: Neutral and ionic hydrogen bonding in Schiff bases, P. M. Dominiak,¹ P. Mallinson² and K. Woźniak,¹ ¹Department of Chemistry, The University of Warsaw, ul. Pasteura 1, 02 093 Warszawa, Poland, E-mail: pdomin@chem.uw.edu.pl; ²Chemistry Department, University of Glasgow, Glasgow G12 8QQ, UK.

Low-temperature, high resolution X-ray studies of charge distributions have been carried out in the following five Schiff bases:



These types of compounds are of particular interest due to an asymmetric intramolecular hydrogen bond formed between oxygen and nitrogen atoms. Depending on the position of the H-atom in this O...H...N bond, the o-hydroxy Schiff bases exhibit two tautomeric forms (see below): the OH-form (**A**) or the NH-form (**B**). Additionally, the NH tautomer can exist in the keto-enamine form **B** or the zwitterionic form **C**.



Properties of the H-bonded rings in the five Schiff bases studied show a variation depending on the position of the H-atom. In the case of compound **1**, it is covalently bonded to the oxygen atom. In the compounds **2** and **3**, the H-atom is covalently bonded to the nitrogen atom. The structure of molecule **4** illustrates a competition between two types of these H-bonding occurring in the same single molecule. Finally, the compound **5** is the first example of a multiple Schiff base (2 independent moieties) being a complex of two moieties containing neutral and ionic hydrogen bonds separated in individual moieties in the crystal lattice.

We will present details of electron density distributions for these two extreme types of hydrogen bonding involved in more and more complex interactions in the crystal lattices - with the hydrogen atom at oxygen or at nitrogen - with particular reference to the hydrogen bonding region and the aromatic moiety.

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P203: Charge density distribution of dichlorobis(D,L-proline)zinc(II), M. Lutz and R. Bakker, *Bijvoet Center for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands.*

Neutral, zwitterionic amino acids form adducts with metal salts like LiCl, CaCl₂ and ZnCl₂. To obtain a deeper insight into the interaction of amino acids with Zn²⁺ ions, we studied the charge density distribution in the neutral salt of racemic D,L-proline with ZnCl₂ [1]. The results are compared with the charge density of the free amino acid, which is available from the literature [2]. By this comparison, significant differences in the topology of the carboxylate group were found.

Intensity data were measured at a temperature of 110(2) K using Mo-K_α radiation (rotating anode, graphite monochromator) on a Nonius KappaCCD diffractometer up to a resolution of $\sin(\theta/\lambda) = 1.08 \text{ \AA}^{-1}$. The EvalCCD program was used for the integration of the intensities, based on an accurate description of the crystal form and the diffraction geometry [3]. The data were scaled and merged with the SortAV program [4]. Multipolar refinement was performed with the XD package [5].

References:

- [1] Lutz, M., Bakker, R. (2003). *Acta Cryst. C* **59**, m18-m20.
- [2] Koritsanszky, T., Flaig, R., Zobel, D., Krane, H.-G., Morgenroth, W., Luger, P. (1998). *Science* **279**, 356-358.
- [3] Duisenberg, A.J.M., Kroon-Batenburg, L.M.J., Schreurs, A.M.M. (2003). *J. Appl. Cryst.* **36**, 220-229.
- [4] Blessing R.H. (1987). *Crystallogr. Rev.* **1**, 3-58.
- [5] Koritsanszky, T., Howard, S., Mallinson, P. R., Su, Z., Richter, T., Hansen, N. K. (1997). *XD - Computer Package for Multipole Refinement*, Freie Universität Berlin, Germany.

P204: The cause of the calculated "in-crystal" dipole moment of the dinitramide negative ion in its ammonium salt, J. P. Ritchie [1,2], *Center for Computational Research, SUNY/Buffalo, Buffalo, NY 14260-1800, USA.*

CRYSTAL98 [3] with 6-21G**/B3LYP methodology and AIM [4] analysis gives an "in-crystal" dipole moment of 1.08 D for the dinitramide negative ion computed in the inertial frame. The comparable single molecule calculation gives 0.49 D. The enhancement is caused by a pattern of hydrogen-bonding that polarizes the atomic charges determined by AIM, while leaving the atomic dipoles relatively unchanged. In the single molecule, the directions of these contributions to the total molecular dipole moment vector are nearly 180° apart and, hence, act largely to offset one another. In the crystal, the change in the magnitude of these components is relatively small, but the angle between them has changed and is predominantly responsible for the "in-crystal" enhancement.

References:

- [1] Abstracted from: Ritchie, J. P., Zhurova, E. A., Pinkerton, A. A., in preparation.
- [2] This work was performed in the laboratory of A. A. Pinkerton, University of Toledo, with financial support through contract number N00014-95-1-013, Office of Naval Research. The crystal structure determination was done by Dr. A. Martin.
- [3] Saunders, V. R., Dovesi, R., Roetti, C., Causà, M., Harrison, N. M., Orlando, R., Sicovich-Wilson, C. M. (1998). *CRYSTAL98 User's Manual*, University of Torino, Italy.
- [4] Bader, R. F. W. (1990). *Atoms in Molecules: A Quantum Theory*, Oxford, Clarendon Press.

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Amherst (North) Campus, UB SUNY@Buffalo, Buffalo, New York, USA

P205: Charge density of nanoporous semiconductors, M. Christensen,¹ A. E. C. Palmqvist² and B. B. Iversen,¹ ¹Department of Chemistry, University of Aarhus, DK-8000 Aarhus, Denmark; ²Department of Applied Surface Chemistry and Competence Centre, for Catalysis, Chalmers, University of Technology, SE-412 96 Göteborg, Sweden.

Low temperature data were measured on two Cetineite like structures at X3, NSLS.

The Cetineites are nanoporous crystalline solids [1], with potential application as chemical sensors, catalysts, adsorbents, ion-exchangers, electro-optics and thermoelectrics. The cetineites have the general composition: $A_6[\text{Sb}_{12}\text{O}_{18}][\text{SbX}_3]_2(6-mx-y)\text{H}_2\text{Ox}[B^{m+}(\text{OH})_m]_y$ with $A=\text{Na}^+, \text{K}^+, \text{Rb}^+$; $X=\text{S}^{2-}, \text{Se}^{2-}$; $B=\text{Na}^+, \text{Sb}^{3+}$ [2]. Data were measured on a structure having the unit cell content: $\text{K}_6[\text{Sb}_{12}\text{O}_{18}][\text{SbSe}_3]_2 \cdot 6\text{H}_2\text{O}$ (abbreviated [K;Se]). In addition measurements were done on the recently reported nanoporous material called SBC-1 $\text{K}_{18}[\text{Sb}_{12}\text{O}_{18}]_3\text{Te}_{36} \cdot 18\text{H}_2\text{O}$ (abbreviated [K;Te]) [3]. The structure [K;Se] has previously been described as a $2 \times 2 \times 1$ super structure of the original cetineites with axis $a = b = 29.26 \text{ \AA}$ and $c = 5.62 \text{ \AA}$ and crystallizes in the $P6_3$. Our results do not show this super structure and we find that the structure crystallizes in the space group $P6_3/m$. The structure [K;Te] differs remarkably from the cetineites by having the $[\text{SbX}_3]$ pyramids replaced by a telluride tubular structure, see Figure 1. The structure crystallizes in the space group $R\bar{3}$ with hexagonal axes $a = b = 27.34 \text{ \AA}$ and $c = 5.61 \text{ \AA}$. SBC-1 has the narrowest bandgap of any known nanoporous material with a value of 250 meV compared to around 2.0 eV for the cetineites [3].

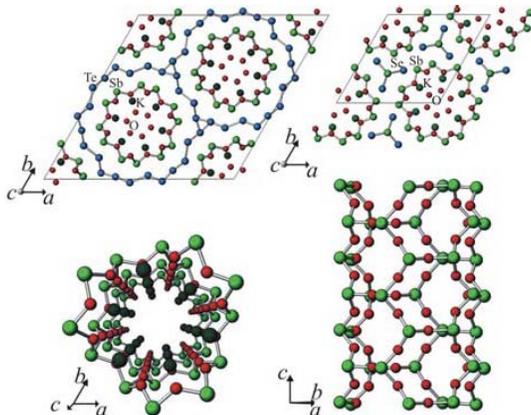


Figure 1: The structure of [K;Te] and [K;Se] and the Sb_2O_3 tubes seen along different axes.

The beamline X3 at NSLS was used to measure low temperature high resolution data for charge density studies. The table below gives some relevant data.

	Reflections	Unique	R(int)	2 θ
[K;Se]				
High order	22253	10298	2.99%	-65°
Low order	11494	2748	6.16%	-25°
[K;Te]	240181	40682	3.52%	
High order	156795	39402	2.21%	-65°
Low order	83061	13994	3.97%	-25°

References:

- [1] Sabelli, C., Nakai, I., Katsura, S. (1988). *Am. Miner.* **73**, 398-404.
- [2] Wang, X., Liebau, F. (1998). *Eur. J. Solid State Inorg. Chem.* **35**, 27-37.
- [3] Palmqvist, A. E. C., Iversen, B. B., Zanghellini, E., Behm, M., Stucky, G. D. (2003). *Angew. Chem. Int. Ed.*, in press.

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Amherst (North) Campus, UB SUNY@Buffalo, Buffalo, New York, USA

P206: X-ray charge density of a new covalent network anti-ferromagnet: synthesis, multi-temperature structural characterization, magnetic properties, heat capacity and X-ray charge density, R. D. Poulsen,¹ A. Bentien,² M. Chevalier¹ and B. B. Iversen,¹ ¹Department of Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark; ²Max Planck Institute for the Chemical Physics of Solids, Dresden, Germany.

There has been an explosion of interest in metal-organic framework (MOF) systems [1]. Recent highlights include nanoporous systems based on Zn centers coordinated by various di-carboxylate acids to form cubic host structures [2]. By variation of the length of the acid linker incremental increases in pore sizes over a large range was achieved, and one member of this series of compounds exhibits the highest capacity for methane storage observed so far in a porous system.

Crystals of $\text{Mn}_3\text{O}_{14}\text{N}_2\text{C}_{34}\text{H}_{32}$, $(\text{Mn}_3(\text{BDC})_6(\text{DEF})_2)$, BDC = benzenedicarboxylate, DEF = diethylformamide) were obtained from synthesis procedures similar to the ones published for related non-magnetic MOFs [2]. In Figure 1 the structure is shown based on 20 K synchrotron X-ray diffraction data obtained at beam line X3A1 at NSLS. The macroscopic crystal shape directly reflects the skewed unit cell of the nanoporous framework, Figure 2. The inner part of the voids are occupied by the DEF solvent molecules, which are firmly bound at one coordination site to Mn(2) creating a crystalline system with decreased structural disorder. Even at room temperature the DEF molecule is only slightly disordered, and as the temperature is lowered to 20 K the disorder disappears. Two polymorphs with different interatomic manganese distances have been found and characterized and the transition from long to short manganese distance has been observed. The transition does not appear to be temperature dependent.

Data sets of both polymorphs were collected at 20 K at NSLS, whereas conventional multitemperature data have been collected on a Bruker SMART CCD diffractometer at Department of Chemistry, University of Aarhus. We are currently modelling the electron density of the system for several temperatures with the multipole program XD. Once a reliable electron density models has been established we will extract experimental d-orbital population for the two Mn centers based on the refined multipole populations. We will also carry out Bader topological analysis of the electron density, and e.g. use the topological properties to characterize the metal-ligand bonds.

References:

- [1] O'Keeffe, M., Eddaoudi, M., Li, H., Reineke, T., Yaghi, O. M. (2000). *J. Solid. State Chem.* **152**, 3.
- [2] Eddaoudi, M., Kim, J., Rosi, N., Vodak, D., Wachter, J., O'Keeffe, M., Yaghi, O.M. (2002). *Science* **295**, 469.

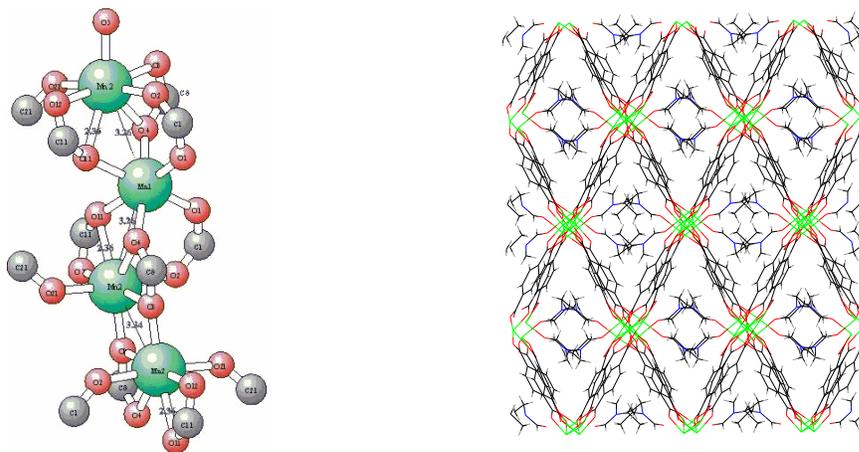


Figure 1: The molecular structure of $\text{Mn}_3(\text{BDC})_6(\text{DEF})_2$. Figure 2: The nanoporous framework along b-axis.

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SESSION 30X

Friday, May 16, Natural Sciences Bldg. room 218, 17.00-18.00

P301: Measuring the bonding and charge states of ions in crystals by quantitative electron diffraction (QCBED), B. Jiang and J. C. H. Spence, *Department of Physics and Astronomy, Arizona State University, Tempe, AZ 85287-1504, USA.*

Accurate structure factors (phase and amplitude) in crystals (Cu, TiO₂, AlN and GaN) are measured by quantitative higher energy convergent beam electron diffraction (QCBED). Charge density refinement using combined data sets of electron and X-ray diffraction showed bonding and charge states of ions in crystals. Models for charge density refinement are also discussed, including Fourier synthesis, multipole and bonding charge models.

P302: From electron density to optical properties of tartaric acid crystals, M. Pitak and K. Stadnicka, *Faculty of Chemistry, Jagiellonian University, ul. Ingardena 3, 30-060 Kraków, Poland.*

For the crystals of (+)-(2R,3R)-2,3-dihydroxybutanedioic acid, known under the common name L-tartaric acid, a big discrepancy was found between the experimentally determined principal components of the gyration tensor and the optical rotation calculated from the structural data assuming atom polarizabilities derived from dipole-dipole interactions only [1]. The computations did not include the polarizability from the three-dimensional network of very strong intermolecular hydrogen bonds. Since the contribution of the molecule itself was estimated as relatively small, the predominating intermolecular contribution was expected to be responsible for the high gyration tensor components.

Studies of charge density and topological properties for the crystal of L-tartaric acid have been undertaken to explore the character and role of both inter- and intramolecular hydrogen bonds in the structure, and attempt to utilize the polarizability of the electron density at the hydrogen bonds towards gyration tensor components determination.

A data set analysis was carried out with the program package XD [2] using the aspherical atom multipole formalism [3]. Next, topological analysis gave the possibility to determine the electron distribution in a quantitative manner [4]. The topological analysis of the charge density according to the AIM theory [5] made it possible to derive the charge density, its second derivative, and the ellipticity at the bond critical points of the molecule. It was interesting to compare different electron density distribution of the same functional groups of the molecule (-OH or -COOH) resulting in a decrease of the molecular symmetry (C₂→C₁).

Another point to explain was how the strong hydrogen bonds manifest themselves in the topological analysis. The problem to solve is how the polarizability of electron densities at different hydrogen bonds could be incorporated in the calculations of the gyration tensor components.

References:

- [1] Mucha, D., Stadnicka, K., Kaminsky, W., Glazer, A. M. (1997). *J. Phys.: Condens. Matter* **9**, 10829-10842.
- [2] Koritsanszky, T., Howard, S., Mallinson, P. R., Su, Z., Richter, T., Hansen, N. K. (1996). *XD - A Computer Program Package for Multipole Refinement and Analysis of Charge Densities from X-ray Diffraction Data*, Free University of Berlin, Germany.
- [3] Hansen, N. K., Coppens, P. (1978). *Acta Cryst. A* **34**, 909-921.
- [4] Coppens, P. (1998). *Acta Cryst. A* **54**, 779-788.
- [5] Bader, R. F. W. (1995). *Atoms in Molecules: A Quantum Theory*, Oxford, Clarendon Press.

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Amherst (North) Campus, UB SUNY@Buffalo, Buffalo, New York, USA

P303: Structure and bonding in alpha-copper phthalocyanine studied by electron diffraction, J. S. Wu and J. C. H. Spence, *Department of Physics and Astronomy, Arizona State University, Tempe, AZ 85287-1504, USA.*

We use energy-filtered quantitative electron diffraction at low temperature to examine the atomic structure and bonding of metastable alpha-Cu phthalocyanine crystals. Three theoretical methods (kinematic, kinematic with excitation errors, and Bloch-wave) were employed for the intensity calculations. The Bloch-wave method was found to account for dynamical effects by greatly reducing the residual factor between experimental and simulated results. A new method for calculating electron scattering factors for partially charged ions is proposed, and the sensitivity of electron diffraction to charge transfer is discussed. The atomic charge states were analyzed for alpha-Cu phthalocyanine using a charge cloud model in which gaussian bond charge is positioned along the bonds. Spot patterns were collected in the Kohler mode at various beam energies to reduce error. Using the best-fit model, a deformation charge density map is produced and compared to the neutral-atom model. From this, the atomic charge transfer in the alpha-Cu phthalocyanine structure can be seen in the (010) plane.

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P304: Capability of X-ray diffraction to the determination of the non linear optical properties in a crystalline environment: the case of 3-methyl 4-nitropyridine N-oxide (POM), F. Hamzaoui, *Laboratoire STEVA Département de Chimie Université de Mostaganem, Algérie.*

In the optical domain, it was proposed in a series of early papers by Robinson [1], Flytzanis and Ducuing [2] that a set of simplifying models or approximations [3] applied far from resonance, would permit to connect susceptibilities to the various spatial moments of the charge distribution in the ground state. The model of Robinson offers the opportunity to connect the susceptibility tensors of rang n to the multipolar charge distribution (in the fundamental state) of order 2^n . Thus, the linear polarizability is associated to the quadrupole moment, whereas the first order hyperpolarizability is linked to the octupolar moment of the charge distribution.

The present study is mainly based on the ground state charge distribution inferred from X-ray diffraction data and the application of the Unsöld approximation [3] through the Robinson model [1]. This model has been applied to the POM a prototypical nonlinear organic crystal by Hamzaoui, Baert and Zyss [4], whereby relations between polarizabilities and multipolar moments of the electronic charge distribution have been evidenced. From the Robinson's model and using some matrix algebra we led to the following relation ship for the linear polarizability α and the first non linear hyperpolarizability β :

$$\alpha_{xy} = \frac{2m}{\hbar^2} Q_{xy} (Q_{xx} + Q_{yy} + Q_{zz}) \quad \text{and} \quad \beta_{xxx} = \frac{3m^2}{\hbar^4} Q_{xy} Q_{xxx}$$

The components of the polarizability are directly expressed in terms of the molecular quadrupole moments whereas the hyperpolarizability is expressed in terms of the electrostatic octupolar and quadrupolar moments.

The experimental electronic density analysis has been carried out by use of an aspherical model of Hansen and Coppens [5]. The electrostatic moments Q_{xy} and Q_{xxx} were then estimated by direct integration methods using both discrete and fuzzy boundary space partitioning [6]. Concerning the components estimated from the equations given above, the Unsöld approximation gives relatively good results for α but fails in the β estimate.

It seems difficult to infer from the Unsöld approximation a faithful description of the molecular optical properties, whereas an estimation of the first order hyperpolarizability components of β seems out of reach. Comparison of the results obtained on the free molecule using a Point Charge Model (semi-empirical calculations) with those derived from the experimental charge distribution seems to reveal interesting information as to the influence of the crystal field effects on the molecular properties.

The connection between the moments of charge distribution and the NLO properties through the Robinson model based on Unsöld approximation will be fully and critically discussed along the presentation.

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Workshop on the Advanced Methods in X-ray Diffraction Analysis

May 12-17, 2003

Amherst (North) Campus, UB SUNY@Buffalo, Buffalo, New York, USA

P305: Combination of structure factors from X-ray and Convergent Beam Electron Diffraction, J. Friis,¹ B. Jiang,² K. Marthinsen³ and R. Holmestad,¹ ¹*Department of Physics and* ³*Department of Materials Technology, Norwegian University of Science and Technology (NTNU), 7491 Trondheim, Norway;* ²*Department of Physics and Astronomy, Arizona State University (ASU), Tempe, AZ 85287-1504, USA.*

Extinction is often a problem for accurate X-ray measurements of the intense low order structure factors in small unit-cell inorganic crystals. On the other hand, very accurate low order structure factors can for these materials be achieved by *convergent beam electron diffraction* (CBED). This technique is however limited to small scattering angles (up to $\sin \theta/\lambda = 0.6 \text{ \AA}^{-1}$). Therefore a combination of these two techniques seems to be very promising for multipole refinements and charge density studies. Such a combination has indeed been shown successful [1,2].

Since electrons interact strongly with the crystal potential, they are very sensitive to small changes in the charge distribution. The CBED method treats the low order structure factors as refinable parameters in a Bloch-wave simulation of the fast incident electrons. In this way both extinction and scaling errors are eliminated and accuracy up to 0.1% can be achieved. The largest source of errors comes from uncertainties in temperature parameters that are difficult to determine by CBED due to small scattering angles. The effect of temperature factors on the Bloch-wave simulation itself is small, but it is important when converting the Fourier components of the crystal potential (electron structure factors) to X-ray structure factors. It gets even more important when CBED data is going to be combined with X-ray data. A small extension to the XD-program is therefore suggested, which allows electron structure factors to be entered together with X-ray structure factors and separate temperature parameters to be refined.

Examples from charge density studies based on combined data sets are demonstrated for copper [2] and magnesium [3].

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