

diimine ligands constructing infinite chain structure. The assignments of intense emission bands of these oligo-copper compounds are complicate because weak interacted multi-copper centered (CC) charge transfer is often concurrent with common Cu(I) to ligand charge transfer. We have tried to observe direct geometrical distortion of the complex by photo excited state crystallographic technique in order to figure out this emission nature.

Single crystal X-ray diffraction experiments were performed by using the low-temperature vacuum X-ray camera at SPring-8 BL02B1 beamline. Full intensity data of both under light irradiated and non-irradiated conditions were collected by multiple-exposure method by using IP detector. Photo-difference Fourier syntheses show that a small portion of two I atoms in $\{\text{Cu}_2\text{I}_2\}$ unit move toward close to each other, while two Cu atoms tend to move apart from each other toward N atom of the bipyridine ligand.

[1] Henary M., Wootton J.L., Khan S.I., Zink J.I., *Inorg. Chem.*, 1997, **36**, 801.
[2] Ozawa Y., Terashima M., Mitsumi M., Toriumi K., Yasuda N., Uekusa H., Ohashi Y., *Chem. Lett.*, 2003, **32**, 62.

Keywords: photochemistry coordination compound, accurate measurement, crystallography instrumentation synchrotron radiation

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Multitemperature X-ray Diffraction Analysis in the Study of Phase Transitions, Molecular Dynamics and Crystal Disorder

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Routine ability to analyze crystal structures of different compounds at many temperatures (including "low" temperatures - up to 100K, and "very low" ones - up to 20-30K or even less) is important in many cases for different applications in the study of phase transitions, the nature of crystal disorder, and the study of dynamics of molecular (atomic) motions in the solid state. In addition, low-temperature data collection allows one to increase dramatically real accuracy of diffraction data and to increase the field of its analytical applications (the study of low-melting and/or unstable compounds). In particular, several methods of low-temperature crystallization techniques were elaborated during last time to analyze crystal structures of compounds which are liquids or even gases at normal conditions. Some new examples of the low/multitemperature X-ray diffraction analysis of molecular crystals will be demonstrated. These examples include the study of strong H-bond dynamics in organic compounds, polymorphism, phase transitions in liquid-crystalline precursors, structural studies of high-energetic and non-linear optical materials.

Keywords: multitemperature X-ray diffraction analysis, phase transitions, crystal disorder

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Melting-point Variation in Isomeric Dibromobenzenes

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Single crystals of 1,2- and 1,3-dibromobenzenes have been *in situ* pressure crystallized in diamond anvils and studied by X-ray diffraction. Both structures are orthorhombic: 1,2-dibromobenzene (0.3 GPa), space group *Pbca*, $Z = 8$, $a = 7.831(1) \text{ \AA}$, $b = 15.256(1) \text{ \AA}$, $c = 11.701(2) \text{ \AA}$; 1,3-dibromobenzene (0.2 GPa), space group *P2₁2₁2₁*, $Z = 8$, $a = 4.105(1) \text{ \AA}$, $b = 12.899(5) \text{ \AA}$, $c = 25.987(28) \text{ \AA}$. The relationship between the molecular symmetry and the melting point of the dibromobenzene isomers has been discussed. According to the empirical Carnelley's rule high molecular symmetry is related with high melting point [1], [2]. This effect however can be justified in various ways. The melting points are: 278-280 K for 1,2-, 266 K for 1,3-, and 356-360 K for 1,4-dibromobenzene. The Br...Br intermolecular interactions are distinct in both these structures, and they can be considered to be the main factor responsible for the

molecular rearrangements in these crystals.

[1] Carnelley T., *Philos Mag. 5th series*, 1985, **13**, 112-130. [2] Brown R. J. C., Brown R. F. C., *J. Chem. Educ.*, 2000, **77**, 724-731.

Keywords: high-pressure structure determination, halogens, structure-property relationships in solids

MS25 STRUCTURE DETERMINATION FROM POWDER DIFFRACTION DATA (ORGANICS)

Chairpersons: Andrew Fitch, John Faber

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Solving Organic Structures from Powder Diffraction: News from the FOX

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FOX, "Free Objects for Xtallography" [1][2] is a program for *ab initio* crystal structure solution using direct-space methods. While it was first developed and used to solve inorganic structures (oxides, intermetallic, hydrides), the algorithms used were not dedicated to any type of compound and organic structures could also be solved.

Over the last two years many modifications have been brought to the algorithm (mostly through a restraint-based description rather than a z-matrix one), to allow a better, more flexible description of molecular compounds.

We will present how the evolution of the algorithm has improved the ability to solve organic structures, along with new Fox features (multiple solutions, maximum likelihood,...).

[1] Favre-Nicolin V., Černý, R., *J. Appl. Cryst.*, 2002, **35**, 734. [2] Favre-Nicolin V., Černý R., *Z. Kristallogr.*, 2004, **219**, 847.

Keywords: powder structures, *ab initio* structure determination, algorithms

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Molecular Crystal Structures from Low-Resolution Powder Diffraction Data: Reliability and Validation of the Results Obtained

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In recent years, an obvious progress has occurred in the determination of molecular crystal structures *ab initio* from powder diffraction data. There are no doubts now, the molecular crystal structures with the known connectivity set in the molecule(s) can be routinely solved even from the data measured at the laboratory powder diffractometer. However, there are the questions still waiting for an exhaustive answering. One of them is a question on how to estimate the reliability of the solution obtained. Another one concerns the accuracy of structural parameters extracted. These questions are exceptionally important for the results obtained at laboratory commonly used devices. There are problems, which can not be clarified with the use of laboratory data only. So the problem of positioning of the selected hydrogens is beyond the facilities of many laboratory X-ray powder diffractometers, which are virtually "insensitive" to the position of H atoms. In this particular case, the neutron diffraction often helps to find a correct position, especially when some, or even all, of the hydrogens are replaced by the deuteriums.

For the new crystal structure solved from laboratory powder data we have a good chance to validate its correctness by the comparison of the results with those, obtained either from high-resolution synchrotron data or, in some cases, from neutron powder diffraction data. The aforementioned comparison allows us to estimate the real accuracy of the results derived from the laboratory powder pattern.