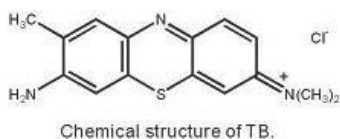


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Toluidine blue O (TB), one of popular cationic dyes, has been used in biological and medical fields as a important cytological probe because of its metachromatic effects. Its metachromasy has been considered to be caused by the formation of a certain dye aggregate. It is very important to understand the relationship between the metachromatic spectral change and the aggregates, in order to obtain structural information of biomolecules from metachromatic staining. But regarding TB, structural data of both TB itself and TB - biomolecule complexes have not been reported. We then approached the structure analysis of TB. TB was crystallized as blue needles by means of solvent diffusion method using ion-exchanged water and acetone as good and poor solvents, respectively. However, the thickness of the needles was unsuitable for X-ray structure analysis. On the other hand, thick crystals were obtained after exchanging the chloride ion to hexafluorophosphate ion. Its crystal analysis is now under investigation.



Keywords: crystal structure of organic compounds, dye compounds, molecular biology

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### Structure of new organic semiconductors with cobalt bis(dicarbollide) bromine anion

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New molecular semiconductors on the base of 8,8'-dibromo cobalt bis(dicarbollide) anion, (BEDT-TTF)<sub>2</sub>[8,8'-Br<sub>2</sub>-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] (1), (BEDT-TTF)[8,8'-Br<sub>2</sub>-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] (2) and (BMDT-TTF)<sub>4</sub>[8,8'-Br<sub>2</sub>-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] (3) were synthesized and investigated. Recently we have started investigation of the structure-property relationship in a series of fulvalene salts of cobalt bis(dicarbollide) anion and its derivatives [1,2]. These counter anions are particularly interesting owing to their enormous variability. The cobalt bis(dicarbollide) anion [3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>]<sup>-</sup> offers several distinct ways of chemical modification: (1) substitution at carbon atoms; (2) substitution at boron atoms in upper belt of the dicarbollide ligand; and (3) substitution at boron atoms in lower belt of the dicarbollide ligand. As a result, molecules with a wide variety of properties in almost unlimited variations can be prepared. In this contribution, we present synthesis and structure of the first electroconducting salts of the dibromo derivative of cobalt bis(dicarbollide) anion [8,8'-Br<sub>2</sub>-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>]<sup>-</sup>. Crystal structure of (BEDT-TTF)<sub>2</sub>[8,8'-Br<sub>2</sub>-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] (1) is formed by the BEDT-TTF radical cations in general positions of the unit cell, and the [8,8'-Br<sub>2</sub>-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>]<sup>-</sup> anions in special centrosymmetric positions (Fig.1). Fig. 1. Atomic designations in (BEDT-TTF)<sub>2</sub>[8,8'-Br<sub>2</sub>-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] (1)

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V.A., Sivaev I.B., Lobanova I.A., Bregadze V.I., Buravov L.I., Dyachenko O.A., *J. Organomet. Chem.* 692 (2007) 5033.

Keywords: organic conductors, X-ray analysis, materials properties

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### Optical activity of *N*-benzoylglycine crystals

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Every chiral organic crystal has inherent optical activity. The sign and the magnitude of the optical activity of an organic crystal should reflect the molecular structure and the packing arrangement because the freedom of molecules is severely restricted in the crystal lattice. We report here the optical rotatory power of chiral crystals self-assembled from achiral *N*-benzoylglycine determined by HAUP (high accuracy universal polarimeter) method. The magnitude of rotatory powers was 10 to 100 times larger than that for ordinary organic crystals. It revealed that the helically arranged aromatic p electrons as well as the helical ionic and hydrogen bond networks in the crystal contributed to the enhancement of the magnitude of these rotations.

Keywords: optical activity, *N*-benzoylglycine, chiral crystal

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### New photoluminescent microporous metal phosphate as a hybrid intrinsic yellow phosphor

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Photoluminescence is a new property of microporous materials. Recently some extra-large channel zinc and gallium phosphates are found to emit blue light[1-5] or even synchronize dual wavelengths to give out white light under the excitation of UV light [6]. Th intriguing optical property has allowed us to discover microporous metal phosphates a new class of inorganic phosphors with distinct emission centers different from conventional understanding. In current lighting technology, yellow light phosphor integrated with blue LED to produce white light is of the most importance. Demands on inorganic yellow-light phosphors are increasing. Yet they are limited in number and kind. Existing inorganic yellow phosphors are all extrinsic illuminants, i.e. a condensed host lattice with doped lighting elements. No inorganic host without doped metal activators could emit yellow light. The extraordinary intrinsic yellow emission of NTHU-4 is speculated to closely correlate with defects resulting from the disorderliness near large pores. In this presentation, we report the synthesis, structure and some property of a new yellow phosphor, NTHU-6 [7], which has a unique MOF-like organic-inorganic hybrid open framework with high PL quantum efficiency (PLQE). It is the first hybrid microporous yellow light phosphor ever discovered.

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Keywords: photoluminescence, gallium oxalato-phosphate, organic-inorganic hybrid material

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### New 1D, 2D and 3D azido Mn, Cd and Zn complexes with magnetic and non-linear optical properties

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Supramolecular chemistry is concerned with weak interactions that occur between molecules, i.e. all non-covalent bonds, as well as weak coordination bonds. Such interactions are important in biological, magnetic and optical systems. Here we describe coordination compounds used as building blocks in crystal engineering. We present a number of supramolecular 1-D, 2-D and 3-D complexes of Mn<sup>II</sup>, Cd<sup>II</sup> and Zn<sup>II</sup> with the azido bridge as a networking agent. The versatility of the azide ligand affords chains with Mn<sup>II</sup> in which ferrimagnetic behavior is clearly observed for 1-D and 2-D Mn<sup>II</sup> systems with quinoline derivatives [Mn(H<sub>2</sub>O)(μ-N<sub>3</sub>)(N<sub>3</sub>(quinaz)<sub>2</sub>)<sub>n</sub> and [Mn(μ-N<sub>3</sub>)<sub>2</sub>(quinaz)<sub>2</sub>]<sub>n</sub> (quinaz = quinazoline) and [Mn(μ-N<sub>3</sub>)<sub>2</sub>(pyzamid)<sub>2</sub>]<sub>n</sub> and [Mn<sub>2</sub>(3-ampy)<sub>4</sub>(μ-N<sub>3</sub>)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub> (pyzamid = pyrazineamide and 3-ampy = 3-aminopyridine). The field of non-linear optics (NLO) is of considerable interest for many commercial applications. In particular, second-order harmonics generation, i.e. frequency doubling, which can be used in the conversion of red laser into blue laser light, is a desirable property. This requires a lack of inverse centre, an easy task in crystal engineering of coordination polymers with chiral components. We report the synthesis, spectral and structural characterization of some Cd<sup>II</sup> and Zn<sup>II</sup> complexes. The Kerr effect was studied as a property of the NLO materials for complexes [Cd<sub>3</sub>(nic)<sub>4</sub>(N<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub>, [Zn(nic)(N<sub>3</sub>)<sub>n</sub> (nic = nicotinate anion), [Cd(2,5-dmpyz)(N<sub>3</sub>)<sub>2</sub>]<sub>n</sub>, (dmpyz = dimethylpyrazine) and [Zn(bipy)(N<sub>3</sub>)<sub>2</sub>]<sub>n</sub> (bipy = 2,2'-bipyridine).

Keywords: supramolecular structures, metal-organic compounds, structure-function relationships in solids

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### Motion of inclusion gas molecules in clathrate hydrate observed by neutron powder diffraction

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Methane hydrate has attracted great interest as an energy resource after the discovery in the deep seabed as huge reservoirs of methane gas. Moreover, carbon dioxide hydrate is paid much attention as a storage medium of carbon dioxide gas to prevent the global warming. These clathrate hydrates are inclusion compounds in which the hydrophobic guest molecules exist in a host ice-framework called 'cage'. Their structural stabilities are deeply related with the physical properties of inclusion gases. In this study, we carried out neutron powder diffraction measurements of carbon dioxide and Xe deuterohydrates using the HRPD at JRR-3, JAEA. The diffraction data were analyzed by the combination of the Rietveld and the maximum entropy method (MEM) to clarify the motion of inclusion gases. The motions of carbon dioxide and Xe molecules in the small cages show the different manner from those in the large cages. These motions have small temperature dependences, in contrast to the methane hydrate case where the motion of methane molecules in the large cage shows large temperature dependence. Details on the motions of gas molecules in the hydrates are discussed.

Keywords: clathrate hydrate, neutron powder diffraction, MEM

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### Possible non-centrosymmetric structure of vaterite type yttrium orthoborate

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Yttrium and Lanthanide Orthoborates are promising candidates to be used in new-generation flat-panel display phosphors technologies. Despite extensive research on the Eu<sup>3+</sup> luminescence, in these compounds, fundamental questions remain unanswered regarding the relation between the vaterite type structure and the resulting Eu<sup>3+</sup> spectral features. High-resolution luminescence spectra do not permit to unambiguously distinguish between the alternatives of having either two or three cation sites in the structures, which are compatible with the crystal structures solved by single-crystal X-ray and neutron powder diffraction, respectively. Three samples: YBO<sub>3</sub>, Y<sub>0.85</sub>Eu<sub>0.15</sub>BO<sub>3</sub> and Y<sub>0.85</sub>Yb<sub>0.15</sub>BO<sub>3</sub> were prepared by solid-state reaction. We have undertaken an investigation, combining optical spectroscopy, second harmonic generation, X-ray powder diffraction and first-principles calculations, to correlate the optical features with the crystalline structure. Some remarkable results have been achieved: 1) all the samples show similar SHG intensities than the KDP and these increases with the doping concentration; 2) from Rietveld refinement and first-principles calculations we can distinguish between the hexagonal, orthorhombic and monoclinic symmetry. Moreover, doped samples are better refined in the acentric C<sub>2</sub> space group, thus, we can correlate the number of sites of Yttrium and point symmetry with the results obtained from Yb<sup>3+</sup> and Eu<sup>3+</sup> optical spectra. Complementary first-principles total-energy calculations also are shedding light in the structural analysis of the systems [1].

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