

desirable to attach organic functionalities covalently to the surface of polyoxoanions. As part of a broad program centered on the functionalization of polyoxometalates, we have been interested in the derivatisation of Lindqvist type polyoxoanions with organosilyl moieties. The condensed polyoxometalate  $(nBu_4N)_4[(TaW_5O_{18})_2O]$  which is synthesized by reacting  $[TaW_5O_{19}]^{3-}$  with  $BuSnCl_3$ , crystallises in the orthorhombic system, space group *Pbnm* with lattice parameters  $a = 15.7981(14)$ ,  $b = 17.939(3)$ ,  $c = 35.216(6)$  Å,  $V = 9980$  Å<sup>3</sup> and  $Z = 4$ . The crystallographic study of  $(nBu_4N)_4[(TaW_5O_{18})_2O]$  shows that the dimer is composed from two polyoxoanions fragments linked by linear Ta-O-Ta bridge. Such a linkage readily reacts with organosilyl (Lewis electrophilic reagents), such as  $RR'{}_2SiOH$  ( $R = R' = Et, iPr, OtBu, Ph$ ;  $R = tBu, R' = Me$ ) to yield monomeric plenary Lindqvist derivatives  $(nBu_4N)_2[W_5O_{18}Ta(O)SiR'_2]$ . These derivatives are characterized in the solid state by IR and in solution by multinuclear NMR (<sup>13</sup>C, <sup>29</sup>Si, <sup>183</sup>W). The crystallographic study of  $(nBu_4N)_2[(W_5O_{18}Ta(O)SiPh_3)]$  indicates that  $\{SiPh_3\}^+$  is grafted on the surface of the polyanion through the terminal O-Ta oxygen atom.

Keywords: polyoxometalates, X-ray structure, NMR spectroscopy

### P09.03.27

*Acta Cryst.* (2008). A64, C482

#### Octamolybdates - promising materials for industry and medicine

Wiesław Lasocha<sup>1,2</sup>, Maciej Grzywa<sup>2</sup>, Wojciech Nitek<sup>1</sup>, Bartłomiej Lasocha<sup>3</sup>, Bartłomiej Gawel<sup>1</sup>, Alicja Rafalska-Lasocha<sup>1</sup>  
<sup>1</sup>Jagiellonian University, Faculty of Chemistry, Ingardena 3, Krakow, woj. Malopolskie, 30-060, Poland, <sup>2</sup>Institute of Catalysis PAS, Niezapominajek 8,30-239 Krakow, Poland, <sup>3</sup>Collegium Medicum, Jagiellonian University, Krakow, Poland, E-mail : lasocha@chemia.uj.edu.pl

Molybdates are interesting and perspective candidates for various applications in electronics and medicine (cancer therapy) [1], catalysis and environment protection. Polymolybdates are a numerous group of compounds and despite of enormous work done so far, synthesis of selected types of polymolybdates is still a challenging and demanding task, requiring experience, intuition and vast experimental work. Recently a group of 5 new beta-octamolybdates was obtained in our lab. We solved the crystal structures and investigated selected properties of: 1/ Ammonium tris(triethylammonium) octamolybdate, (*a, b, c, alpha, beta, gamma*, SG)25.230(5), 10.859(2), 19.033(3), 121.92(1), *C* 2/ Tetrakis(trimethylammonium) octamolybdate dihydrate; 1 0.433(3), 10.486(2), 10.708(4), 102.40(2), 101.78(3), 118.35(3), *P*-1 3/ Tetrakis(naphthalen-1-aminium) octamolybdate tetra(1-naphthylamine); 15.561(5), 18.969(8), 7.54(3), 100.80(3), 103.04(3), 73.42(3), *P*-1 4/ Bis(1-amino-1-phenyleneammonium) bis(2-methylbenzimidazolium) octamolybdate; 8.541(5), 10.293(5), 13.018(5), 80.03(5), 83.74(5) 75.12(5), *P*-1 5/ Tetrakis(2,6-dimethylanilinium) octamolybdate: 11.878(3), 10.533(3), 11.586(2), 101.12(2), 120.26(1), 75.46(2), *P*-1 Compounds 1 - 2 were obtained in hydrothermal conditions while 3-5 from hot mixtures of H<sub>2</sub>MoO<sub>4</sub>, amine and H<sub>2</sub>O. Most of these compounds crystallise in SG *P*-1, in compound 3 protonated and neutral amines are present, in 4 unexpected 2-methylbenzimidazolium cation was obtained. Based on the results of crystal structure determination of polymolybdates, some rules concerning the crystal engineering of isopolymolybdates, will be presented. Supported by ICDD and Polish MEiN grant 1T09A 07730

References:

1. S. Mitsui, et al, *Biomed. and Pharmacotherapy* 60, 2006, 353

Keywords: molybdenum VI oxycompounds, materials science and engineering, single-crystal X-ray analysis

### P09.03.28

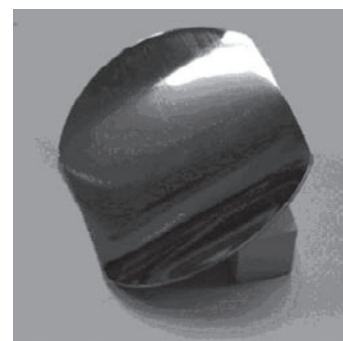
*Acta Cryst.* (2008). A64, C482

#### Strongly and accurately shaped Ge crystal for non-scanning X-ray fluorescence spectrometer

Koichi Hayashi, Kazuo Nakajima, Fujiwara Kozo

Tohoku University, Institute for Materials Research, 2-1-1 Katahira, Aoba-ku, Sendai, Miyagi, 980-8577, Japan, E-mail: khayashi@imr.tohoku.ac.jp

Plastic deformation technique of Si and Ge single crystals, which enables us to obtain the various forms, makes impact upon the field of X-ray spectroscopy, because Si and Ge are commonly used as analyzing crystals for x rays. Recently, we developed a deformation technique for obtaining strongly and accurately shaped Si or Ge wafers of high crystal quality, although covalently bonded Si or Ge crystals have long been believed to be not deformable to various shapes. The use of the deformed wafer made it possible to produce fine-focused x rays. In the present study, we prepared a cylindrical Ge wafer with a radius of curvature of 50 mm (Fig.), and acquired fluorescent x rays simultaneously from 4 elements by combining the cylindrical Ge wafer with a position-sensitive detector. The energy resolution of the x-ray fluorescence spectrum was as good as that obtained using a flat single crystal, and its gain was over 100. The demonstration of the simultaneous acquisition of high-resolution x-ray fluorescence spectra indicated various possibilities of x-ray spectrometry, such as one-shot x-ray spectroscopy and highly efficient wave-dispersive x-ray spectrometers.



Keywords: Ge wafer, X-ray spectrometer, plastic deformation

### P09.03.29

*Acta Cryst.* (2008). A64, C482-483

#### Determination of thermal treatment effect of plating sludge by phase identification: XRD technique

Ozgul Dere<sup>1</sup>, Mehmet Burcin Piskin<sup>2</sup>, Aysel Kanturk<sup>1</sup>, Muge Sari<sup>1</sup>

<sup>1</sup>Yildiz Technical University, Chemical Engineering, Davutpasa Campus, Chemical Engineering, Esenler, Istanbul, 34210, Turkey, <sup>2</sup>Yildiz Technical University, Davutpasa Campus, BioEngineering, Esenler, Istanbul, 34210, Turkey, E-mail: odere@yildiz.edu.tr

Thermal treatment was used to recover the precious metals or stabilize solid industrial wastes such as metal plating sludge which includes Zinc (Zn), Chromium (Cr), Copper (Cu), Nickel (Ni), iron etc. compounds. After thermal treatment of the samples, metal compounds were converted to metal oxides and then they were leached with suitable reagents to recover the precious metals. Moreover treatment temperature is very important in order to determine the optimum conditions. Therefore, metal plating sludge's composition changes due to operating process parameters. In addition to examined metal plating sludge's crystal structure which were shown differences when compare with the others. These

processes were used to prevent environment pollution and support valuable material recovery. The main purpose of this study was to determine the crystal phases of the metal plating sludge at different temperatures to obtain the optimum thermal treatment conditions. Sample was heated at 105, 125, 200, 400, 625, 850 and 1000°C; and X-ray diffraction (XRD) examination of the powder samples was carried out using a Philips Panalytical X'pert Pro Diffractometer. The instrument was operated at 45 kV with a filament current of 40 mA and Cu K $\alpha$  radiation. Scanning operation covered a wide range of  $2\theta$  from 5 to 70° with a scanning speed 0.0025°/s at 0.02° steps. Crystal phase identification results of thermal treated sludge samples at different temperatures concluded that sulfate complexes with metals (Zn, Cr, Cu) transformed to oxide phases such as calcium iron phosphate (Ca<sub>9</sub>Fe(PO<sub>4</sub>)<sub>7</sub>), zincochromite (ZnCr<sub>2</sub>O<sub>4</sub>) and tenorite (CuO) with Powder Diffraction File (PDF) cards: 00-045-0338, 01-073-1962 and 00-003-0884, respectively.

Keywords: waste treatment, crystal phases, metal oxides

### P09.03.30

*Acta Cryst.* (2008). A64, C483

#### Two binuclear molecular magnet: K<sub>2</sub>Fe<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)Cl<sub>6</sub>(H<sub>2</sub>O)<sub>2</sub> and K<sub>6</sub>Fe<sub>6</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>Cl<sub>14</sub>(H<sub>2</sub>O)<sub>10</sub>

Yan Zhang<sup>1</sup>, Bin Zhang<sup>2</sup>

<sup>1</sup>Peking University, Department of Physics, Institute of Condensed Matter and Material Physics, Beijing, Beijing, 100871, China, <sup>2</sup>Organic Solid Laboratory, CMS & BNLMs, Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100080, P. R. China, E-mail : zhang\_yan@pku.edu.cn

Two oxalate-bridged binuclear iron(III) compounds K<sub>2</sub>Fe<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)Cl<sub>6</sub>(H<sub>2</sub>O)<sub>2</sub> (I) and K<sub>6</sub>Fe<sub>6</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>Cl<sub>14</sub>(H<sub>2</sub>O)<sub>10</sub> (II) were synthesised. Their crystal structures were determined by single crystal X-ray diffraction. Both of them are composed of oxalate-bridged binuclear iron (III) anions with K<sup>+</sup> as cation and Cl<sup>-</sup> coordinated to iron on equator plane with oxalate group. The coordination ligands perpendicular to equator plane is different on I and II: In I, one H<sub>2</sub>O and one Cl<sup>-</sup> coordinated to Fe<sup>3+</sup> at same time. But there are two kinds of binuclear anions with different coordination environments in (II): in one anion, H<sub>2</sub>O occupy four axial positions, in another anion, one of them is replaced by Cl<sup>-</sup>. There are extensive hydrogen bonds in the crystal I and II. In I, it is only layered [4<sup>4</sup>,6<sup>2</sup>] lattice in the ac plane; in II, the hydrogen bond form a NaCl-type framework in the crystal. The cation exist in the hole between layer of II and vacant in the NaCl lattice. Their magnetic properties were measured. Both of them show anti-ferromagnetic interaction as dimer modes with J = -5.18cm<sup>-1</sup> in I and J = -1.50cm<sup>-1</sup> in II. The difference on magnetic property was determined by coordination environments and hydrogen bonds. Both of them are potential ionic conductor.

This work was supported by NSFC.20673120, MOST.2006CB601001, 2006CB932102, P. R. China

Keywords: iron compounds, oxalate-bridged, magnetic property

### P09.03.31

*Acta Cryst.* (2008). A64, C483

#### Structure diversity and reversible anion exchange properties of metal complexes with tripodal ligand

Wei-Yin Sun<sup>1</sup>, Guan-Cheng Xu<sup>1</sup>, Taka-aki Okamura<sup>2</sup>, Norikazu Ueyama<sup>2</sup>

<sup>1</sup>Nanjing University, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, Jiangsu Province, 210093, China, <sup>2</sup>Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan, E-mail : sunwy@nju.edu.cn

We focus our attention on crystal engineering and properties of metal-organic frameworks with flexible multidentate organic ligands, such as 1,3,5-tris(imidazol-1-ylmethyl)benzene (tib), 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (titmb). Systematic study of reactions of tib and titmb with varied metal salts was carried out, and coordination architectures with zero-, one-, two- and three-dimensional structures were obtained and their properties were investigated. For example, six cadmium(II) coordination polymers, [Cd(tib)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (**1**), [Cd(tib)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>·2C<sub>2</sub>H<sub>5</sub>OH (**2**), [Cd(tib)(OAc)<sub>2</sub>]<sub>4</sub>·5H<sub>2</sub>O (**3**) (OAc = acetate anion), [Cd(tib)( $\mu$ -Cl)Cl]·CH<sub>3</sub>OH (**4**), [Cd(tib)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]Cl<sub>2</sub>·4H<sub>2</sub>O (**5**) and [Cd(tib)<sub>2</sub>][Cd<sub>2</sub>I<sub>6</sub>] (**6**), were obtained by reactions of tib with the corresponding metal salts, respectively. Their structures were determined by X-ray crystallography. **1** and **6** have infinite 2D cationic double layered structures with different shapes. **2** possesses a 3D framework structure with two different kinds of channels. The structure of **3** is a two-fold interpenetrated 3D framework. **4** and **5**, synthesized by the same reactants in the same solvent, have different 2D network structures due to the different synthetic methods. The distinct structures of the complexes (e.g. **1**, **2** and **6**) indicate that the counteranions have significant influence on the structures of coordination polymers. **4** and **5** provide nice example that synthetic methods can affect the structures of the frameworks in this system. In addition, the results also attest that the flexible ligand tib can adopt different conformations and coordination modes to form complexes with varied structures. Furthermore, the reversible anion exchange properties of **1** and **2** were studied.

Keywords: crystal engineering, metal-organic complexes, supramolecular assembly

### P09.03.32

*Acta Cryst.* (2008). A64, C483-484

#### Lanthanoid, transition metal and heterobimetallic complexes with polynitrile and derivative ligands

Anthony S. R. Chesman, Stuart R. Batten, Glen B. Deacon, David R. Turner

Monash University, School of Chemistry, Wellington Road, Clayton, Victoria, 3800, Australia, E-mail: anthony.chesman@sci.monash.edu.au

Anionic polynitrile ligands such as dicyanonitrosomethanide (dcnm) have been shown to readily undergo transition metal promoted nucleophilic addition, providing a convenient pathway to simultaneous *in situ* ligand and complex synthesis. These derivative ligands have targeted coordination modes allowing the formation of 3d/4f heterobimetallic species. Solvothermal synthesis allows for the formation of networks, not accessible through bench top methods, which display ferromagnetic coupling.<sup>1</sup> Lanthanoid complexes of dcnm display a unique  $\eta^2$  nitroso bonding,<sup>2</sup> the symmetry of which can be affected by co-ligands, such as crown ethers and 1,10-phenanthroline, by introducing steric crowding into systems. This bonding mode is also observed in the water addition product, carbamoylcyanonitrosomethanide (ccnm), where extensive intermolecular hydrogen bonding influences the degree of asymmetry in the nitroso bonding. As the ccnm ligand retains its anionic character the requirement of a counter cation allows for tuneable solubility properties and has been shown to dramatically effect of the topology of resulting networks, despite the absence of any obvious