

**P.07.01.23***Acta Cryst.* (2005). A61, C300**Order-Disorder Phase Transition in Hexakis(Imidazole)Metal(II) Complex**

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Imidazole has received considerable attention as a good ligand for a variety of metals. In addition to their ability to serve as models of active sites in metalloenzymes, transition metal complexes of imidazole (Him) could lead to potential applications such as electrochromic displays, photovoltaic cells and biomaterials [1-2].

Ni(Him)<sub>6</sub>SO<sub>4</sub>·2H<sub>2</sub>O undergoes a reversible order-disorder phase transition at 223 K, monitored by differential scanning calorimetry and single-crystal X-ray diffraction. In both phases the [Ni(Him)]<sup>2+</sup> cation displays  $\bar{3}$  symmetry as in other similar complex. SO<sub>4</sub><sup>2-</sup> anions and one water are disordered, displaying 3.2 site symmetry in the P  $\bar{3}1c$  space group. It was of interest that the nature of this transition is due to the water reorientational motion, without space group change. We have estimated  $\Delta H$  from the configurational entropy. The results are similar to those obtained in thermal analysis in which  $\Delta H=3.529$  KJ/mol. The water role is confirmed by analysis of powder samples in which the phase transition is precluded by water loss.

[1] Ohtsu H., Shimazaki Y., Odani A., Yamauchi O., Mori W., Itoh S., Fukuzumi S., *J. Am. Chem. Soc.*, 2000, **122**(24), 5733. [2] Ragot F., Belin S., Ivanov V., Perry D.L., Ortega M., Ignatova T.V., Kolovov I.G., Masalitin E.A., Kamarchuk G.V., Yermenko A.V., Molinie P., Wery J., Faulques E., *Materials Science*, 2002, **20**(3), 13.

**Keywords:** order-disorder, phase transition, nickel complex

**P.07.01.24***Acta Cryst.* (2005). A61, C300**Bis-(5,5'-diethylbarbiturato)copper(II) and cadmium(II) Complexes with Ethylenediamine**

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5,5'-diethylbarbituric acid (barbH), also known as barbital is a barbiturate derivative used as a sedative and hypnotic drug, especially in the form of sodium barbital. Two new bis(5,5'-diethylbarbiturato) (barb) complexes of copper(II) and cadmium(II) with ethylenediamine (en) structurally characterized. *cis*-[Cu(barb)<sub>2</sub>(en)] **1** crystallizes in the monoclinic space group of C2/c and its asymmetric unit contains a half of the molecule, which has two-fold crystallographic symmetry. **1** consists of neutral monomeric units, in which, the copper(II) ion exhibits a highly distorted octahedral geometry by two barb anions and a neutral chelating en ligand. The individual molecules of **1** are held together by N-H...O hydrogen bonds, forming a three-dimensional network.

{[Cd(barb)<sub>2</sub>(μ-en)]·2H<sub>2</sub>O}<sub>n</sub> **2** is a one-dimensional coordination polymer and also crystallizes in the monoclinic crystal system (P2<sub>1</sub>/c). In **2**, {[Cd(barb)<sub>2</sub>(en)]} building blocks are connected in a zigzag arrangement by bridging NH<sub>2</sub> groups of en into a chain running parallel to the *c* axis, and the individual chains are further stacked by O-H...O and N-H...O hydrogen bonds to form a three-dimensional supramolecular framework. The barb ligands in both complexes act as bidentate ligands *via* the negatively charged imino N atom and one of the carbonyl O atoms adjacent to the imino N atom.

**Keywords:** 5,5'-diethylbarbiturate, ethylenediamine, copper(II)

**P.07.01.25***Acta Cryst.* (2005). A61, C300**Crystal Structure of N-picoloylhydrazide and its Binuclear Palladium Complex**

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The Ligand *N*-picoloylhydrazide(Hphz) and its binuclear palladium complex [Pd<sub>2</sub>(phz)<sub>2</sub>Cl<sub>2</sub>] were synthesized and determined by single-crystal X-ray diffraction. They belong to the monoclinic system. Crystal data: Hphz (C<sub>6</sub>H<sub>7</sub>N<sub>3</sub>O), space group C 2/c, *a* = 1.9245(2) nm, *b* = 0.38927(2) nm, *c* = 1.8073(2) nm,  $\beta$  = 107.255(2)°, *V* = 1.2931(2) nm<sup>3</sup>, *Z* = 8, *D<sub>c</sub>* = 1.409 Mg/m<sup>3</sup>, *F*(000) = 576,  $\mu$  = 0.102 mm<sup>-1</sup>, *R* = 0.0541 for 1257 observed reflections, *wR* = 0.1762, GOF = 1.124; [Pd<sub>2</sub>(phz)<sub>2</sub>Cl<sub>2</sub>] (C<sub>12</sub>H<sub>12</sub>Cl<sub>2</sub>N<sub>6</sub>O<sub>2</sub>Pd<sub>2</sub>), space group P 2<sub>1</sub>/c, *a* = 1.48274(9) nm, *b* = 1.44797(9) nm, *c* = 0.73951(5) nm,  $\beta$  = 92.719(3)°, *V* = 1.5860(2) nm<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 2.329 Mg/m<sup>3</sup>, *F*(000) = 1072,  $\mu$  = 2.62 mm<sup>-1</sup>, *R* = 0.0262 for 2937 observed reflections, *wR* = 0.0555, GOF = 0.959. The palladium(II) ion in the complex [Pd<sub>2</sub>(phz)<sub>2</sub>Cl<sub>2</sub>] is coordinated by two pyridine nitrogen atoms and two diazine nitrogen atoms, forming a distorted square arrangement of four nitrogen donors. The Pd...Pd distance is 0.38111 nm in the complex. There is a one-dimensional chain structure through intermolecular N-H...Cl hydrogen bonds in the crystal. There are  $\pi$ - $\pi$  interactions between neighboring ligands. *ab-initio* calculations show that there are intra- and intermolecular Pd...Pd interactions.  $\nu$ (C=O) and  $\nu$ (C=N) are shifted to lower frequencies and  $\nu$ (C-N) are shifted to higher frequencies in the IR spectra. The emission lines ( $\lambda_{\text{exc}}$  = 310nm) are shifted to higher frequencies in the fluorescence spectra.

**Keywords:** crystal structure, *N*-picoloylhydrazide, binuclear palladium complex

**P.07.01.26***Acta Cryst.* (2005). A61, C300**Copper-imidazole-chloride/bromide Complexes**

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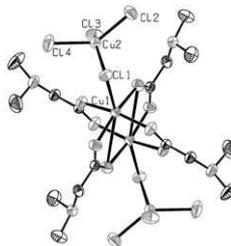
Due to the presence of histidine in most of the copper proteins, imidazole and its derivatives have been widely used in synthesis of simple copper coordination compounds as mimics of proteins' active sites. In the course of our research on copper/imidazole compounds, we have prepared new complexes: a polymeric compound of stair geometry with the [CuIm<sub>2</sub>Cl<sub>2</sub>]<sub>n</sub> composition, [CuIm<sub>2</sub>X]X (X=Cl, Br) and two examples containing well known CuOBr<sub>6</sub>Im<sub>4</sub> fragment. Their crystal structures will be presented and discussed in terms of the known structurally characterized examples.

**Keywords:** copper, imidazole, coordination polymer

**P.07.01.27***Acta Cryst.* (2005). A61, C300-C301**Bis(bis(μ<sub>2</sub>-dimethylglycine-O,O')-tetrachlorocuprate-dicopper(II) Hydrate**

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The title compound crystallizes in the space group P2<sub>1</sub>/c with two symmetry independent tetranuclear Cu(II) complexes. Each complex is centrosymmetric with the Cu(II) ions aligned in a short zigzag chain with sequence Cl-Cu-Cl-Cu-Cu-Cl-Cu-Cl. The central Cu ions are 2.7303(8) Å apart and are linked by four dimethylglycine molecules. Each of the central Cu ions is also coordinated by a [CuCl<sub>4</sub>]<sup>2-</sup> ion. The complex has an inversion centre, see ORTEP diagram where the ellipsoids were drawn at the 50% probability level. The polyhedron around Cu1 is quadrangular-pyramidal. The deviation of Cu1 from the L.S. plane of the pyramid base is 0.250(1) Å towards the apical chlorine, so that the distance Cu1-Cl1 is 2.4525(8) Å. Cu2 is coordinated by 4 chlorine atoms in a flattened tetrahedral geometry with distances and angles ranging from 2.2417(9) to 2.2925(8) Å and 96.12(3) to 97.48(4)°. The molecules of dimethylglycine adopt a



dipolar zwitterionic form. The Cu(II) complexes seem to crystallize as isolated entities since only intramolecular H-bonds are found. However two disordered water positions can be found in a Fourier difference map, and two extra oxygen atoms were included in the refinement so that their occupancy adds to unity.

**Keywords:** X-ray crystallography of coordination compounds, copper coordination compounds, single crystals

#### P.07.01.28

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#### Spectroscopic and Structural Investigation of $ZnI_2(\text{nicotinamide})_2$ , $[Zn(\text{H}_2\text{O})_2(\text{picolinamide})_2]I_2$ and $ZnI_2(\text{isonicotinamide})_2$

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The zinc(II) complexes of nicotinamide, picolinamide and isonicotinamide with iodide were synthesized and characterized by FT-IR and XRD techniques. In both the nicotinamide (na) and isonicotinamide (iso)  $Zn(II)$  complexes the  $Zn(II)$  ion is coordinated by two iodide ligands and two N atoms either of na or of iso ligands in a distorted tetrahedral coordination environment. The zinc(II) complex with picolinamide (pa) has a different environment having a stable five-membered chelate coordination through the ring N and O atoms of pa ligand and has a slightly distorted octahedral geometry.

The  $ZnI_2(\text{na})_2$ ,  $[Zn(\text{pa})_2(\text{H}_2\text{O})_2]I_2$  and  $Zn(\text{iso})_2I_2$  complexes are all crystallized in monoclinic system with space groups  $C2/c$ ,  $P2_1/n$ ,  $C2/c$ , respectively. All these complexes are stabilized through intermolecular hydrogen bondings together with  $\pi \dots \pi$  interactions.

**Keywords:** IR and XRD, zinc complexes, amides

#### P.07.01.29

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#### Green-yellow Thermochromism of (N-methyl-2,6-lutidinium) $_2$ $\text{CuCl}_4$

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The previously reported, green, room temperature phase of (N-methyl-2,6-lutidinium) $_2$   $\text{CuCl}_4$  consists of layers of square-planar  $\text{CuCl}_4^{2-}$  anions interspersed with coplanar organic cations.

The temperature behavior of the compound was studied, and a thermochromic phase transition from green to yellow found at 67 °C. The crystal structure of the high temperature yellow phase of  $(\text{C}_8\text{H}_{12}\text{N})_2\text{CuCl}_4$  was determined at 77(1) °C with unit cell parameters triclinic,  $P\bar{1}$ ,  $a = 7.9350(5)$  Å,  $b = 9.1550(7)$  Å,  $c = 16.144(2)$  Å,  $\alpha = 75.467(4)^\circ$ ,  $\beta = 86.975(4)^\circ$ ,  $\gamma = 64.505(5)^\circ$ ,  $V = 1022.64(15)$  Å<sup>3</sup>,  $Z = 2$ .

The structure of the high temperature phase consists of flattened  $\text{CuCl}_4^{2-}$  tetrahedra with the two unique organic cations now canted relative to one another rather than coplanar. The canting of the organic cations lengthens the short aromatic C-H...Cl contacts in the low temperature phase which appear to stabilize the square planar over the flattened tetrahedral anion geometry.

Previous examples of green-yellow thermochromism in the  $\text{A}_2\text{CuCl}_4$  family have occurred only in the presence of strong N-H...Cl hydrogen bonding, which stabilizes the square planar anion geometry in the low-temperature phase. The title compound is the first known to exhibit this behavior in the absence of strong N-H...Cl hydrogen bonding.

**Keywords:** copper complexes, phase transitions, hydrogen bonding

#### P.07.01.30

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#### Structure of Hydrido(carboxylato)Ir(III) Complexes and Catalytic Symmetric Hydrogenation of Imines

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Recently, we have succeeded in the isolation and characterization of  $[\text{IrCl}(\text{binap})_2]_2$  **1** {binap = 2,2'-bis(di-phenylphosphino)-1,1'-binaphthyl}. [1] Complex **1** reacted easily with methanol and water to give the oxidative addition products. [2] Here we report on the highly diastereoselective oxidative addition of carboxylic acids to  $[\text{IrCl}(\text{binap})_2]_2$ , which gave mononuclear hydrido( $\eta^2$ -carboxylato)Ir(III) complexes.

Reaction of (*S*)-**1** with several carboxylic acids proceeded smoothly at r.t. to give  $[\text{IrCl}(\text{H})(\text{O}_2\text{CR})\{(S)\text{-binap}\}]$  (*S*)-**2** (R =  $\text{CH}_3$ , *p*-tolyl, etc.) as air-stable almost colorless solids in good yields. The absolute configuration of  $[\text{IrCl}(\text{H})(\text{O}_2\text{CC}_6\text{H}_4\text{CH}_3\text{-4})\{(S)\text{-binap}\}]$  was elucidated to be (*S*)-*OC*-6-23-*A*. Catalytic activity for these complexes for asymmetric hydrogenation of prochiral imines will also be discussed.

[1] Yamagata T., Iseki A., Tani K., *Chem. Lett.*, 1997, 1215-1216. [2] Yamagata T., Iseki A., Tani K., *Angew. Chem. Int. Ed.*, 1998, **37**, 3381-3383.

**Keywords:** absolute configuration, asymmetric catalysis, carboxylate complexes

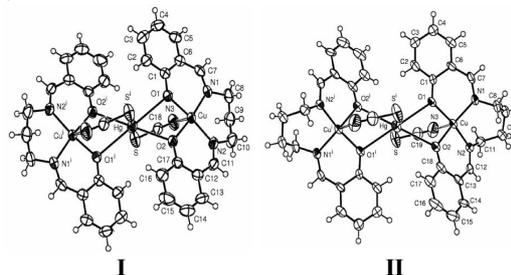
#### P.07.01.31

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#### Synthesis, Characterization and Crystal Structure of new Transition Metal Compounds of Thiocyanate

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Two similar hetero-trinuclear centrosymmetric Cu-Hg-Cu Schiff base complexes were prepared and characterized by elemental analysis, NMR, IR and UV-Vis spectroscopy. The crystal structures of the title compounds reveal that  $\text{Hg}[\text{Cu}(\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2)\text{SCN}]_2$  (I) crystallizes in the triclinic  $P\bar{1}$  space group and  $\text{Hg}[\text{Cu}(\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_2)\text{SCN}]_2$  (II) crystallizes in the monoclinic  $P2_1/c$  space group. The central Hg atom of the compounds, which is located on an inversion centre, has a distorted octahedral coordination geometry. In both compounds, there are long range interactions between Cu and N atoms of the bridging SCN group at the axial position. The coordination geometry of the inversion-related terminal Cu atoms of the compounds is square-pyramidal. The Cu-Hg pairs are triple bridged by the O atoms of the Schiff base ligands and by the SCN groups. The Cu...Hg distance is 3.7623(9) Å (I) and 3.7778(17) Å (II).



**Keywords:** crystal structure, thiocyanate complexes, copper(II) and mercury(II) complexes

#### P.07.01.32

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#### Crystal Structure of Trimethyltin hydroxide, $(\text{CH}_3)_3\text{SnOH}$

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It has been reported that  $(\text{CH}_3)_3\text{SnOH}$  has many incommensurate structures in crystalline state. So far, the precise structure analysis has not been reported. Only one X-ray crystal structure analysis without three dimensional coordinates available has been reported. [1]