

**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.

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**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

