

**PR07.00.54 CRYSTAL STRUCTURE OF THE POLYMERIC THIO-CYANATE COMPLEXES OF COPPER(I).** Vladimir N. Kokozay, Olga A. Babich and Vadim A. Pavlenko, Department of Chemistry, Kiev Shevchenko University, 252033 Kiev, Ukraine

The compounds  $\text{CuSCN}\sim\text{CH}_3\text{CN}$  (1) and  $[(\text{CH}_3)_3\text{NH}]^+[\text{Cu}_2(\text{SCN})_3]^-$  (2) have been synthesized using a direct method of interaction and characterized by X-ray crystallography. The planar  $\text{Cu}_2\text{S}_2$  units with copper-copper distance 3.095 Å (1) and 2.972 Å (2) form the base of both structures. The coordination polyhedron of copper(I) atoms is slightly distorted tetrahedron.  $[(\text{CH}_3)_3\text{NH}]^+$  cations (2) are located in pairs in crystal cavities. The complex (1) consists of the infinite puckered layers. The interlayer distance 6.657 Å corresponds to parameter  $a$  of the elementary cell. The three-dimensional polymeric anion  $[\text{Cu}_2(\text{SCN})_3]^-$  in compound (2) comprises two crystallographically independent copper(I) atoms -  $[\text{Cu}(\text{S}_2\text{N}_2)]$  and  $[\text{Cu}(\text{S}_3\text{N})]$  and two bridging thiocyanate groups with different coordinations -  $-\text{NCS}-$  and  $-\text{NCS}=$ .

Crystals are monoclinic, for compound (1)  $P2_1/c$ ,  $a = 6.657(1)$ ,  $b = 7.388(1)$ ,  $c = 11.357(2)$  Å,  $\beta = 104.72(1)^\circ$ ,  $Z = 4$ ; for compound (2)  $P2_1/n$ ,  $a = 5.784(1)$ ,  $b = 30.282(6)$ ,  $c = 7.551(2)$  Å,  $\beta = 112.46(3)^\circ$ ,  $Z = 4$ .

### Single Metal Ion

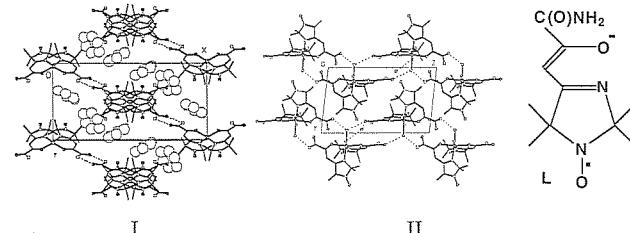
**PS07.01.01 STRUCTURE OF CIS-DIAQUA-BIS(2,2'-BIPYRIMIDINE) COBALT(II) DIPERCHLORATE MONOHYDRATE.** J. S. Brunzelle, Y. Wang, A. Fitch, S. F. Pavkovic, Department of Chemistry, Loyola University Chicago, Chicago, IL 60626, USA.

Diffusion studies in clays of complexes with bipyridine-like ligands are being carried out in our laboratory. Preparation of complexes with the ligand 2, 2'-bipyrimidine (bpm) was undertaken because this ligand could bond to both the clay surface and metal ion and that would significantly alter diffusion behavior. In fact most examples of bpm complexes show bridge-bonding between two or more metal ions to form polynuclear complexes. Mononuclear complexes of bpm are uncommon.

The complex was prepared under  $\text{N}_2$  by combining methanol solutions of ligand and  $\text{CoCl}_2$  in a 2:1 ratio, and then adding perchloric acid to yield the title compound as a yellow precipitate. Crystals suitable for diffraction were obtained from evaporation of aqueous solutions.

The compound crystallizes in space group  $C2/c$ , and is composed of mononuclear six-coordinate complex cations, independent perchlorate anions, and solvent water. The complex cation contains cobalt, two bidentate bpm ligands, and two water molecules in *cis* configuration. The cobalt resides in a special position with crystallographically imposed twofold symmetry so only one bpm ligand and one water molecule need to be specified. Both coordinated and solvent waters participate in hydrogen bonding, and the perchlorate anions are disordered. The complex is comparable to the mononuclear *cis*- $[\text{Co}(\text{bpm})_2 \text{Cl}_2]$  complex reported by De Munno, G., Nicolo, F. & Julve, M. (*Acta Cryst.* **49**, 1049-1052, 1993).

**PS07.01.02 HYDROGEN BONDS IN CRYSTAL STRUCTURES OF TWO COBALT(II) COMPLEXES WITH NITROXIDE.** A.B. Burdakov, N.V. Pervukhina, International Tomography Center Sib. Branch of RAS, Novosibirsk, Russia; Institute of Inorganic Chemistry Sib. Branch RAS, Novosibirsk, Russia.

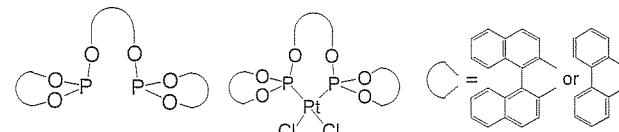


I II

Two new adducts  $\text{CoL}_2\cdot 3\text{C}_6\text{H}_6$  (I) and  $\text{CoL}_2\cdot 4\text{H}_2\text{O}$  (II) have been synthesized (I, monoclinic,  $C2/c$ ,  $a=22.573(5)$ ,  $b=10.356(2)$ ,  $c=19.040(4)$  Å,  $\beta=113.36(3)^\circ$ ,  $V=4086(2)$  Å $^3$ ,  $Z=8$ ,  $D_c=1.21$  g·cm $^{-3}$ ,  $857 I_{hkl} > 2\beta_I$ ,  $R=0.0659$ ; II triclinic,  $P1(-)$ ,  $a=9.922(1)$ ,  $b=9.977(1)$ ,  $c=15.252(1)$  Å,  $\alpha=91.17(1)$ ,  $\beta=102.14(1)$ ,  $\gamma=113.44(1)^\circ$ ,  $V=1345.2(2)$  Å $^3$ ,  $Z=2$ ,  $D_c=1.43$  g·cm $^{-3}$ ,  $2747 I_{hkl} > 2\sigma_I$ ,  $R=0.0428$ ; CAD-4, Mo K for I and II). In I the metal atom has a tetrahedral coordination with Co-O distance 1.951(6), Co-N 1.971(7) Å, OCoN 95.7(6)°. The  $\text{CoL}_2$  molecules are connected into chains by H-bonds O...H-N, the benzene molecules laying between the chains. In II Co(II) has octahedral surrounding including O and N atoms of L and two cis-H<sub>2</sub>O molecules (Co-O 2.013(3), 2.031(3), Co-N 2.111(3), 2.132(3), Co-Ow 2.199(4), 2.255(3) Å). The coordinated water molecules form H-bonds with non-coordinated H<sub>2</sub>O, amide- and nitroxide groups of L. The H-bonds seem to be the main factor in the formation of these two structures.

**PS07.01.03 CONFORMATIONS OF DIPHOSPHITES: CRYSTALLOGRAPHY AND MOLECULAR MODELLING STUDIES.** Dianne D. Ellis and A. Guy Orpen, School of Chemistry, University of Bristol, Bristol, BS8 1TS, UK

X-ray diffraction studies have been performed on a series of diphosphites<sup>1</sup> and their chelate complexes (see below). Such bidentate phosphite ligands have attracted attention because of their potential applications in asymmetric hydroformylation catalysis.<sup>2</sup>



The structures and conformations of these and related species were analysed using the CAChe<sup>2</sup> and Cerius2<sup>3</sup> modelling packages and compared with those of related compounds with known structures. Molecular mechanics (MM), using the MM2 and UFF force fields implemented within CAChe and Cerius2 packages respectively, were employed to compute minimum energy conformations for each compound. Force field parameter modifications that allowed good agreement between the solid state and minimised structures will be reported. The Cambridge Structural Database<sup>5</sup> was used to provide estimates for bond and angle parameters used. MM studies will also be presented which shed light on the pathways for conformational interconversion in these systems.

### References

1. M.J. Baker *et al.*, *J. Chem. Soc. Chem. Commun.*, 1991, 803.
2. CAChe Scientific Software, CAChe Scientific Inc., USA.
3. Cerius2, Molecular Simulations Inc., Cambridge, UK.
4. E. Billinge *et al.*, *US Pat.* 4,769,498, 1992, (to Union Carbide).
5. F.H. Allen *et al.*, *Acc. Chem. Res.*, 1983, **16**, 146; F.H. Allen *et al.*, *J. Chem. Inf. Comput. Sci.*, 1987, **31**, 187.