

m41.p31

## Polymorphism and Space Filling in Cyanopyridine Cobaloximes

J.M. Rubin-Preminger, U. Englert

Department of Inorganic Chemistry, RWTH Aachen, Landoltweg 1, D-52056, Aachen, Germany. janice.rubin@ac.rwth-aachen.de

**Keywords:** hydrogen bonding, cobaloxime, cyano-substituted pyridine, molecular volume

In our continuing work on substituted pyridine cobaloximes, we synthesized and crystallized a 3-cyanopyridine-bis(dimethylglyoxime)-nitro-cobalt (III) (**1**) and a 4-cyanopyridine-bis(dimethylglyoxime)-nitro-cobalt (III) (**2**). On characterizing the materials by single crystal XRD, we noted that the unit cell volume was unusually large, relative to the molecular volume of the 4-derivative, as compared to that of the 3-derivative. In addition, the percentage of occupied space in the unit cell was considerably lower in the 4-derivative (just 62.6% as compared to 71.1%). Examination of the molecular packing of the 4-derivative showed that the molecules pack in a relatively inefficient manner and that it was likely that a second - more efficiently packed - polymorphic form should exist.

To this end, a saturated methanolic solution of the 4-derivative was seeded with crystals of the 3-derivative (it being compatible both chemically and in molecular volume). From this solution a second, more efficiently packed (70.6%), polymorph (**2b**) of the 4-derivative was grown.

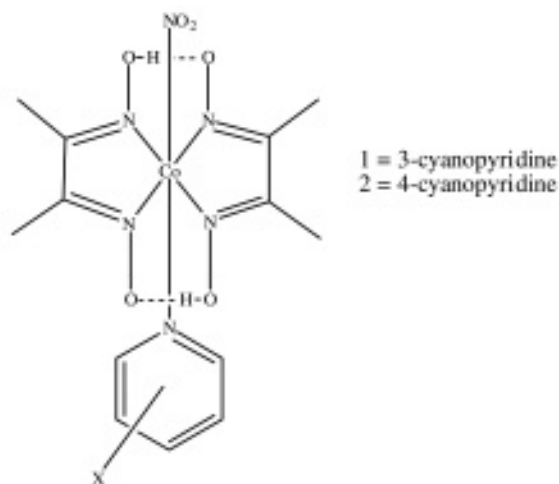


Figure 1: General structure of the *trans*-[Co(dmgh)<sub>2</sub>(NO<sub>2</sub>)(*x*-cyanopyridine)]

m41.p32

## Crystal Structures and Interactions in Packing of Copper(I) Halide Complexes Containing 3-Mercapto-4-methyl-4H-1,2,4-triazole

Saithong Saowanit<sup>a</sup>, Pakawatchai Chaveng<sup>a</sup>, and Charmant Jonathan<sup>b</sup>

<sup>a</sup> Department of Chemistry, Science Faculty, Prince of Songkla University, Hat Yai, Songkhla, 90112, Thailand <sup>b</sup> School of Chemistry, The University of Bristol, Bristol, BS8 1TS, UK. E-mail: s\_saowanit@yahoo.com

**Keywords:** copper(I) complexes, packing, 3-mercapto-4-methyl-4H-1,2,4-triazole

The series of copper(I) halide complexes with 3-mercapto-4-methyl-4H-1,2,4-triazole have been synthesized and characterized by single crystal X-ray diffraction: [Cu(C<sub>3</sub>H<sub>5</sub>N<sub>3</sub>S)<sub>2</sub>Cl](1), {[Cu(C<sub>3</sub>H<sub>5</sub>N<sub>3</sub>S)<sub>2</sub>Br]<sub>2</sub>[Cu(C<sub>3</sub>H<sub>5</sub>N<sub>3</sub>S)<sub>2</sub>Br]}(2), [Cu(C<sub>3</sub>H<sub>5</sub>N<sub>3</sub>S)Br]<sub>n</sub> (3), [Cu(C<sub>3</sub>H<sub>5</sub>N<sub>3</sub>S)I]<sub>n</sub> (4) (*n* = infinite number). The structures were solved by direct methods and refined by full matrix least-squares using SHELXTL version 6.14 program. The [Cu(C<sub>3</sub>H<sub>5</sub>N<sub>3</sub>S)<sub>2</sub>Cl](1) is a monomeric complex and the geometry around Cu atom is trigonal. Cu atom is coordinated by two S atoms from different C<sub>3</sub>H<sub>5</sub>N<sub>3</sub>S molecules and one chlorine atom. The packing of this complex is stabilized by hydrogen bonding interactions. There are two independent monomeric molecules in the asymmetric unit. Thus, there are two arrangement patterns in packing and this pack is stabilized by N-H---N (2.5994(3) Å), C-H---N (3.389(3), 3.489(4) Å) weak inter-molecular interactions. The {[Cu(C<sub>3</sub>H<sub>5</sub>N<sub>3</sub>S)<sub>2</sub>Br]<sub>2</sub>[Cu(C<sub>3</sub>H<sub>5</sub>N<sub>3</sub>S)<sub>2</sub>Br]}(2) is the mixed monomeric and dimeric structure in the unit cell. The geometry around Cu atom of the monomer is trigonal and Cu atom is bonded with two S atoms of two different C<sub>3</sub>H<sub>5</sub>N<sub>3</sub>S molecules and one Br atom. Whereas, the geometry around Cu atom of the dimer is tetrahedral and each Cu atom is coordinated by three S atoms from three C<sub>3</sub>H<sub>5</sub>N<sub>3</sub>S molecules and one Br atom. In addition, two of three C<sub>3</sub>H<sub>5</sub>N<sub>3</sub>S molecules act as bridging ligands linking between two Cu atoms via S atom. The packing of this compound is stabilized by C-H---N (3.387(5), 3.323(4) Å) and C-H---Br (3.772(3), 3.774(4) Å), respectively. The [Cu(C<sub>3</sub>H<sub>5</sub>N<sub>3</sub>S)Br]<sub>n</sub>(3) and [Cu(C<sub>3</sub>H<sub>5</sub>N<sub>3</sub>S)I]<sub>n</sub>(4) are isomorphous and both complexes are polymeric structures. The geometry of Cu atom is tetrahedral bonded with two C<sub>3</sub>H<sub>5</sub>N<sub>3</sub>S molecules through S atom and two halide atoms (Br or I). Each halide atom acts as a bridging ligand link two Cu center atoms to generate one dimensional chains. The packings of these complexes are stabilized by N-H---N interactions (2.924(4) Å for (3) and 2.974(4) Å for (4), respectively).

[1] Aslanidis, P., Cox, J.P., Divanidis, S. and Karagiannidis, P., *Inorg. Chim. Acta.* 2004, 357, 1063-1076.

[2] Kajdan, T.W., Squattrito, D.J. and Dubey, S.N., *Inorg. Chim. Acta.* 2000, 300-302, 1082-1089.

[3] Karagiannidis, P., Aslanidis, P., Papastefanou, S., Mentzafosm D., Hountas, A. and Terzis, A., *Polyhedron* 1990, 9, 981-989.