

s13.m38.p13 **Synthesis and Crystal Structure of Some Dioxomolybdenum(VI) Complexes with Thiosemicarbazonato Ligands.** Biserka Prugovečki, Dubravka Matkovic-Calogovic, Visnja Vrdoljak, Marina Cindric and Boris Kamenar, *Laboratory of General and Inorganic Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb, Croatia.* E-mail: biserka@chem.pmf.hr

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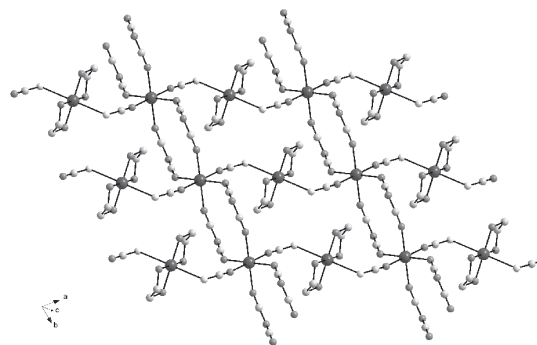
Thiosemicarbazones are ligands with interesting ONS donor and chelating properties. Some of their metal complexes have been found to be cancerostatic [1]. Mononuclear dioxomolybdenum(VI)  $[\text{MoO}_2\text{L}^1\text{L}^2]$  complexes with thiosemicarbazonato ligands have been prepared by the reaction of  $[\text{MoO}_2(\text{acac})_2]$  with  $\text{L}^1 = o\text{-vanilin 4-phenylthiosemicarbazone}$  (I and II) and salicylaldehyde 4-phenylthiosemicarbazone (III and IV) with addition of appropriate amine ( $\text{L}^2 = \text{bipyridine}$  (I and III), pyridine (II) and  $\gamma\text{-picoline}$  (IV)) [2,3,4]. Complex I crystallises in the monoclinic space group  $P2_1/c$  with cell parameters:  $a=10.692(2)$ ,  $b=14.764(2)$ ,  $c=14.009(2)\text{\AA}$ ,  $\beta=108.844(2)^\circ$ ,  $R1=0.0497$  for 4629  $F_o > 4\sigma(F_o)$ . Complex II crystallises in the monoclinic space group  $P2_1/n$  with cell parameters:  $a=10.7877(9)$ ,  $b=15.3255(11)$ ,  $c=12.926(1)\text{\AA}$ ,  $\beta=107.933(8)^\circ$ ,  $R=0.055$  for 8013  $F_o > 4\sigma(F_o)$ . Complex III crystallises in the triclinic space group  $P-1$  with cell parameters:  $a=10.780(2)$ ,  $b=10.936(1)$ ,  $c=11.808(1)\text{\AA}$ ,  $\alpha=84.952(8)$ ,  $\beta=82.580(9)$ ,  $\gamma=64.987(13)^\circ$ ,  $R=0.059$  for 7363  $F_o > 4\sigma(F_o)$ . Complex IV crystallises in the orthorhombic space group  $Pbca$  with cell parameters:  $a=10.7877(9)$ ,  $b=15.3255(11)$ ,  $c=12.926(1)\text{\AA}$ ,  $R=0.0603$  for 5512  $F_o > 4\sigma(F_o)$ . In all structures molybdenum is coordinated by a tridentate ONS chelating ligand, two oxo groups and N-donor ligands in a disturbed octahedral coordinations. The Mo=O bond length in these cis-dioxomolybdenum complexes is in range 1.6896(22) to 1.7101(25)  $\text{\AA}$ .

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s13.m38.p14 **2D Crystal Structure of Novel Heterometallic Cu/Cd Mixed-Anion Polymer  $[\text{Cu}(\text{en})_2\text{Cd}(\text{dca})_2(\text{SCN})_2]_n$  Prepared from Metallic Copper.** Oksana V. Pryma<sup>a</sup>, Svitlana R. Petrusenko<sup>a</sup>, Volodymyr N. Kokozay<sup>a</sup>, Brian W. Skelton<sup>b</sup>, <sup>a</sup>Department of Inorganic Chemistry, National Taras Shevchenko University, Volodymyrska str. 64, Kyiv 01033, Ukraine, <sup>b</sup>Chemistry Department, University of Western Australia, 35 Stirling Highway, Crawley, Western Australia 6009, Australia. E-mail: sana@univ.kiev.ua

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The design and synthesis of novel heterometallic solid-state architectures using transition metal cations and multifunctional ligands that enforce metal bridging is a prolific domain in the field of coordination and materials chemistry. The interaction of copper powder, cadmium dicyanamide and ammonium thiocyanate in methanol solution of ethylenediamine (en) in air results in the formation of a unique mixed anion heterometallic  $\text{Cu}^{\text{II}}\text{Cd}^{\text{II}}$  coordination polymer. The characterization of the compound has been based on IR spectroscopy, electronic spectroscopy and X-ray crystallographic analysis. The crystal structure of titled complex consists of uniform chains of  $\text{Cd}(\text{dca})_2$  in which adjacent metal centres are double linked by two dicyanamide bridges and  $\text{Cu}(\text{en})_2^{2+}$  units. Both copper(II) and cadmium(II) atoms join involving '-Cu-SCN-Cd-' linkage. Each Cd(II) ion is coordinated by two thiocyanate and four dicyanamide groups *via* nitrogen atoms and has a  $\text{N}_6$  donor set. The Cd-N distances vary between 2.255(4)  $\text{\AA}$ , in the case of coordination NCS-, and 2.333(5)  $\text{\AA}$ , in the case of dca. Two dicyanamide ions link two cadmium atoms to form a 12-membered  $[\text{Cd}_2(\mu_{1,5}\text{-dca})_2]$  ring and neighboring rings share the Cd(II) atoms to form a chain of  $\text{Cd}(\text{dca})_2$ . The copper(II) atom lies on an inversion centre and has an elongated octahedral environment with an  $\text{N}_4\text{S}_2$  donor set: the equatorial positions are occupied by four nitrogen atoms from two ethylenediamine bidentate chelate ligands with Cu-N distances 2.067(3) to 2.096(4)  $\text{\AA}$  with the axial positions occupied by the sulfur atoms from the bridging thiocyanate ligands [Cu-S, 2.8991(15)  $\text{\AA}$ ]. The resulting two-dimensional sheets contain a 28-membered  $[\text{Cu}_2\text{Cd}_4(\mu_{1,5}\text{-dca})_2(\mu_{1,3}\text{-NCS})_4]$  macrocycle in which two 12-membered  $[\text{Cd}_2(\mu_{1,5}\text{-dca})_2]$  rings form a section. The interlayer Cd...Cu separations through a thiocyanate group are 6.077(8)  $\text{\AA}$ .



Crystal data:  $\text{C}_{10}\text{H}_{16}\text{CdCuN}_{12}\text{S}_2$ , triclinic,  $P\bar{1}$ ,  $a = 7.321(2)$ ,  $b = 7.441(2)$ ,  $c = 9.300(2)\text{\AA}$ ,  $\alpha = 83.488(3)$ ,  $\beta = 86.790(3)$ ,  $\gamma = 72.349(3)^\circ$ ,  $V = 479.5(2)\text{\AA}^3$ ,  $Z = 1$ ,  $R = 0.037$  and  $wR = 0.048$  for 1970 independent reflections with  $F > 4\sigma(F)$ . This work was supported in part by INTAS Grant 03-51-4532.