

**s9.m3.p33** **Copper(I) and Copper(II) Halogeno Polymers with 2,1,3-benzothiazole: Variation of 1D and 2D Polymeric Structures as a Function of Reaction Conditions.** C.P. Raptopoulou, V. Psycharis and A. Gantis. *Institute of Materials Science, N.C.S.R. "Demokritos", 15310 Ag.Paraskevi, Athens, GREECE.* G.S. Papaefstathiou and S.P. Perlepes. *Department of Chemistry, University of Patras, 26500 Patras, GREECE.*  
 Keywords: polymeric structures, molecular interactions.

The study of coordination polymers continues to be of great interest in the context of their possibility to offer new functional materials with interesting magnetic, electrical or optical properties. Much work has been done in the employment of linear bidentate molecules as bridging ligands, because the dimensionality of the resultant polymeric structures can be varied with the geometry of metal ion. Much less work has been carried out on the use of the non-linear bidentate bridging ligands; an interesting such ligand with a fixed bridging angle is 2,1,3-benzothiazole (btd). The present work describes the employment of the non-chelating, bent potentially bridging ligand btd in the construction of copper(I) and copper(II) halogeno polymers. The complexes  $[\text{CuCl}_2(\text{btd})]_n$ ,  $[\text{CuCl}(\text{btd})]_n$ ,  $[\text{CuBr}(\text{btd})]_n$ ,  $[\text{CuBr}(\text{btd})_{0.5}]_n$ ,  $[\text{Cu}(\text{btd})]_n$  and  $[\text{Cu}_2\text{I}_2(\text{btd})]_n$  have been prepared and characterized by single-crystal and powder X-ray crystallography. The coordination polymers adopt 1D or 2D structures depending on the oxidation state of copper, the stoichiometry of the complexes, the nature of the anionic coligand and the coordination (monodentate, bidentate) of btd. The magnetic properties of  $[\text{CuCl}_2(\text{btd})]_n$  have also been studied.

**s9.m3.p34** **X-Ray Study of Binuclear  $\text{K}^+/\text{Ba}^{2+}$ -Transition Metal Complexes with Heterotopic Macrocyclic Ligands Based on Isothiosemicarbazide.** V.Ch. Kravtsov, Yu.A. Simonov, J. Lipkowski, V.B. Arion, N.V. Gerbeleu, J.I. Gradinaru, *Institute of Applied Physics and Institute of Chemistry of the Academy of Sciences of Moldova, MD-2028 Kishinev, R. Moldova,* *Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland*  
 Keywords: metallomacrocycles, supramolecular assemblies.

The  $\text{K}^+$  and  $\text{Ba}^{2+}$  templated macrocyclic reactions of polyether-linked bis(2-hydroxybenzaldehydes) with S-methylisothiosemicarbazide hydroiodide yield heterotopic macrocyclic ligands suitable for the simultaneous binding of alkaline or alkaline-earth and transition metal ( $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{VO}^{2+}$ ). The X-ray analysis shows that exact composition and structure of the final product strongly depends on the counterions and the length of the ether linkage  $[-\text{CH}_2\text{OCH}_2-]_n$ . In all cases, transition metal is bound to the 'soft'  $\text{N}_2\text{O}_2$  cavity, and the alkali metal cation is held by the polyether O atoms, with additional ligands bonded to  $\text{Ba}^{2+}$  or  $\text{K}^+$ . The previous studies on these ligands were undertaken using  $\text{Ni}^{2+}/\text{Ba}^{2+}$  system<sup>1</sup>. In order to clarify the influence of transition and template metals nature on complex formation we have extended the investigations. The X-ray structures of  $\text{Cu}^{2+}/\text{Ba}^{2+}$ ,  $\text{VO}^{2+}/\text{Ba}^{2+}$  ( $n=2,3$ ) and  $\text{Ni}^{2+}/\text{K}^+$ ,  $\text{Cu}^{2+}/\text{K}^+$ ,  $\text{VO}^{2+}/\text{K}^+$  ( $n=2,3$ ) metallo-macrocycles reveal a variety of complex design and the counter ions function. The association of these complexes in the crystal demonstrates the diversity of supramolecular architecture.

The centrosymmetric dimers bridged by oxygen atom of  $\text{V}=\text{O}$  groups coordinating to the  $\text{Ba}^{2+}$  cation of the neighbouring complex are present in the crystals of  $\text{VO}^{2+}/\text{Ba}^{2+}$  and  $\text{VO}^{2+}/\text{K}^+$  ( $n=2$ ) complexes and both metals participate in the dimer formation. The main difference in the structure of these metallomacrocycles is determined by the nature of counter ions coordinated to the barium at the external open side of the dimeric complexes. In the crystal structure of  $\text{VO}^{2+}/\text{Ba}^{2+}$  ( $n=3$ ) the similar dimers are united by chloride anions bonding with Ba atoms in the infinite polymeric chain. The copper-barium system ( $n=2$ ) gives another examples where two triflate anions join complexes in the dimer by bonding only with Ba atoms of adjacent heterobinuclear macrocycles. The monomeric metallomacrocyclic, where triflate anion co-ordinates both metals of the same complex and additionally bridges them has been found in the  $\text{VO}^{2+}/\text{Ba}^{2+}$  system with the longer polyether chain ( $n=3$ ). The stacking interaction between aromatic residues is the common feature for crystal structures of these compounds. The short intermolecular *ortho*-Hydrogen...Metal distances are also documented.

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[1] M.Reetz, V.Arion, R.Goddard, Yu.Simonov, V.Kravtsov, J.Lipkowski."Synthesis and structure of metallomacrocycles based on isothiosemicarbazides", *Inorg. Chim. Acta*, (1995), vol.238: 23-33.