



Cyano-Bridged Heterometallic Oligonuclear Complexes and Coordination Polymers Constructed Using Tridentate Schiff-Base Ligands: Synthesis, Crystal Structures, and Magnetic and Luminescence Properties. A New Trimeric Water Cluster

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Auteur Maxim, Catalin [1], Tuna, F. [2], Madalan, Augustin-M. [3], Avarvari, Narcis [4], Andruh, Marius [5]

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Five new Cu-II-Ag-I, Cu-II-Cu-I, and Zn-II-Au-I complexes have been obtained starting from copper(II) and, respectively, zinc(II) complexes with (NNO) Schiff-base ligands: $\{(\text{H}_2\text{O})(\text{saldmen})\text{Cu}\}-\{(\text{NC})\text{Ag}(\text{CN})\}$ 1, $(1)(\infty)[\{\text{Cu}-2(\text{salaepipH})(2)(\mu\text{-CN})\}\{\mu\text{-}[\text{Ag}(\text{CN})(2)]\}](\text{ClO}_4)(2)\text{center dot } 4\text{H}(2)\text{O}$ 2, $(1)(\infty)[\{(\text{salaepy})\text{-Cu}\}\{\mu\text{-}[\text{Ag}(\text{CN})(2)]\}]$ 3, $(1)(\infty)[\{(\text{salaepy})\text{-Cu}\}\{\mu\text{-}[\text{Cu}(\text{CN})(2)]\}]$ 4, $[(\text{salaepy})\text{Zn-NCAuCN}](2)\text{center dot } \text{H}_2\text{O}$ 5. The Schiffbase ligands (Hsaldmen, Hsalaepip, Hsalaepy) have been obtained by reacting the salicylaldehyde with N,N-dimethylethylenediamine, N-(2-aminoethyl)piperazine, and, respectively, 2-(2-aminoethyl)-pyridine. The structures of compounds 1 and 5 consist of discrete bi- and, respectively, tetranuclear species. The analysis of the packing diagram for crystal 1 reveals the formation of supramolecular double chains sustained by hydrogen-bond interactions involving the aqua ligand. Compounds 2, 3, and 4 are one-dimensional coordination polymers. The structure of 2 consists of chains constructed from $\{\text{Cu}(\text{salaepip})\}$ nodes bridged alternatively by $[\text{Ag}(\text{CN})(2)](-)$ and CN^- ions, resulted from the partial decomposition of the silver complex. The 3-D architecture of the crystal is constructed from 1-D coordination polymers, $\{[\text{Cu}-2(\text{salaepipH})(2)(\mu\text{-CN})\}\{\mu\text{-}[\text{Ag}(\text{CN})(2)]\}](n)(2n+)\}$, which are connected by three water molecules that form a triangular water cluster, resulting in a scaffold-like structure with large channels. Compounds 3 and 4 are similar. Their structures can be described as resulting from zigzag anionic chains, $[\text{M}(\text{CN})(2)](n)(n-)$ ($\text{M} = \text{Ag-I}$ or Cu-I), with three-coordinated silver(I) or copper(I) ions, to which monocationic complexes, $\{(\text{salaepy})\text{Cu}\}$, are attached. The cryomagnetic properties of compounds 1 and 2 have been investigated. Weak antiferromagnetic interactions ($J = -2.8 \text{ cm}^{-1}$), $H = -JS(1)S(2)$ mediated by hydrogen bonds are observed for compound 1. The cyanido bridge connecting the basal coordination sites of two copper(II) ions in 2 mediates a moderate antiferromagnetic coupling ($J = 55.2 \text{ cm}^{-1}$). Compound 5 exhibits blue luminescence ($\lambda = 464 \text{ nm}$, $\lambda(\text{ex}) = 400 \text{ nm}$).

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