

New One- and Two-Dimensional Heterometallic Cu/Cd Halogeno or Thiocyanato Bridged Coordination Polymers Synthesized Directly from Elemental Copper and Cadmium Oxide in the Presence of Ethylenediamine

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Z. Naturforsch. **58b**, 1117 – 1123 (2003); received June 2, 2003

Three heterometallic Cu/Cd complexes $[\text{Cu}(\text{en})_2\text{CdBr}_4]\cdot\text{dmso}$ (**1**), $[\text{Cu}(\text{en})_2\text{CdI}_4]\cdot\text{dmf}$ (**2**) and $[\{\text{Cu}(\text{en})_2\}_3\text{Cd}(\text{NCS})_6](\text{NCS})_2$ (**3**) have been synthesized by means of an open-air reaction of unactivated copper powder, cadmium oxide, NH_4X ($\text{X} = \text{Br}, \text{I}, \text{NCS}$) and ethylenediamine in non-aqueous solvents, like dmso, dmf and CH_3OH . The selection of a counter-anion in the initial ammonium salt provides a facile approach to the controlled assembly of one- or two-dimensional extended networks. Crystallographic investigations reveal that **1** and **2** possess 1D structures *via* semi-coordination ($\text{Cu}^{2+} \dots \text{X}$) and hydrogen bonds ($\text{NH}_2 \dots \text{O}_{\text{Solv}}$) forming chains with a zigzag arrangement of copper and cadmium atoms. In complex **3** the cadmium atom of each $\text{Cd}(\text{NCS})_6^{4-}$ anionic block forms bridges with $\text{Cu}(\text{II})$ ions *via* the sulfur atoms of thiocyanate groups to give 2D polymeric sheets, featuring two different ring sizes, one a 32-membered ring $[\text{Cu}_4\text{Cd}_4(\mu\text{-SCN-S}, N)_8]$ and the other a 16-membered ring $[\text{Cu}_2\text{Cd}_2(\mu\text{-SCN-S}, N)_4]$. It is noteworthy, that **3** shows a quite rare $\text{Cd}(\text{NCS})_6^{4-}$ fragment with N-bonded thiocyanate groups.

Key words: Heterometallic Coordination Polymers, Elemental Copper, Cadmium Oxide, Ethylenediamine