

Polynuclear aggregation of cobalt and manganese dichlorides. Synthesis, properties and structures of monomeric $[\text{CoCl}_2(\text{tmen})]$, ionic $[\text{Co}_3(\mu_3\text{-Cl})_2(\mu\text{-Cl})_3(\text{tmen})_3][\text{BPh}_4]$, polymeric $\text{MnCl}_2 \cdot \text{tmen}$ and tetranuclear $[\text{Mn}_4(\mu\text{-Cl})_6\text{Cl}_2(\text{tmen})_4]$ ($\text{tmen} = \text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$).

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The complexes $[\text{CoCl}_2(\text{tmen})]$ **1**, $[\text{Co}_3(\mu_3\text{-Cl})_2(\mu\text{-Cl})_3(\text{tmen})_3][\text{BPh}_4] \cdot [\text{CoCl}_2(\text{tmen})]$ **2**, $\text{MnCl}_2 \cdot \text{tmen}$ **3** and $[\text{Mn}_4(\mu\text{-Cl})_6\text{Cl}_2(\text{tmen})_4]$ **4** ($\text{tmen} = \text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$) have been synthesized and structurally characterized by X-ray diffraction. The crystals of **1** consist of the tetrahedral $[\text{CoCl}_2(\text{tmen})]$ molecules. The structure of the co-crystallite **2** is composed of two independent species, ionic $[\text{Co}_3(\mu_3\text{-Cl})_2(\mu\text{-Cl})_3(\text{tmen})_3][\text{BPh}_4]$ and molecular $[\text{CoCl}_2(\text{tmen})]$. In the first compound the trinuclear $[\text{Co}_3(\mu_3\text{-Cl})_2(\mu\text{-Cl})_3(\text{tmen})_3]^+$ cations consist of *triangulo*- $\{\text{Co}_3\text{Cl}_3\}$ units defined by three cobalt atoms with three bridging chloride atoms in the same plane. The remaining two μ_3 -chloride atoms are symmetrically placed above and below the molecular plane. The polymeric chain of compound **3** is formed by six-co-ordinate manganese(II) centres linked by double chloride bridges. Two nitrogen atoms from the co-ordinate tmen complete the octahedral co-ordination of the manganese. The crystals of compound **4** consist of tetranuclear molecules in which two internal six-co-ordinate and two peripheral five-co-ordinate Mn atoms are linked by double chloride bridges. The natures of the ligand and solvent as key factors promoting the particular aggregation of the cobalt and manganese dichlorides is discussed.

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