

ORIGINAL PAPER

Preparation, structural characterisation, and magnetic properties of $[\text{Cu}(\text{men})_2][\text{Cu}_2\text{Cd}_2\text{Cl}_2(\text{CN})_6]$ (men = *N*-methylethane-1,2-diamine)

Juraj Kuchár*, Juraj Černák

Department of Inorganic Chemistry, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 041 54 Košice, Slovakia

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The novel complex $[\text{Cu}(\text{men})_2][\text{Cu}_2\text{Cd}_2\text{Cl}_2(\text{CN})_6]$ (*I*) was isolated from the aqueous–ethanol system containing CuCl_2 , men (men = *N*-methylethane-1,2-diamine) and $\text{K}_2[\text{Cd}(\text{CN})_4]$ in the presence of dilute hydrochloric acid and chemically and spectroscopically characterised. The crystal structure of *I* consists of $[\text{Cu}_2(\text{CN})_6]$ and $[\text{Cd}_2\text{Cl}_2(\text{CN})_6]$ building units bridged by cyanide ligands and forms a three-dimensional skeleton with cavities. $[\text{Cu}(\text{men})_2]^{2+}$ cations in which two men ligands are chelated (mean Cu–N is 2.033(6) Å) are located in the cavities. The coordination polyhedron around the Cu(II) atoms is formed as a tetragonal bipyramidal by two weaker axial Cu–Cl bonds (2.8642(12) Å) with chlorido ligands from the skeleton. The Cu(I) and Cd(II) atoms in the skeleton exhibit tetra- (CuC_4 chromophore) and penta-coordination (CdN_3Cl_2), respectively. The temperature-dependent susceptibility measurements indicate a Curie–Weiss-like behaviour and the presence of weak anti-ferromagnetic interaction.

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Introduction

In cyanide complexes, with paramagnetic central atoms M linked by a diamagnetic cyanide complex $[\text{M}'(\text{CN})_x]^{n-}$ anion ($x = 2-6$, $n = 1-4$), the exchange interactions are usually negligible due to the long five-atom M–NC–M'–CN–M bridge between them (Akitsu & Einaga, 2008; Akitsu & Endo, 2009). In the case of the $\text{Cu}(\text{en})_2\text{Ni}(\text{CN})_4$ (en = ethane-1,2-diamine) complex exhibiting an one-dimensional (1D) structure, it was demonstrated that the path followed by hydrogen bonds (HBs) might serve as an alternative exchange path between the Cu(II) atoms (Orendáč et al., 1995). Exchange interactions via HBs in Cu(II) complexes may attain considerable values of exchange constant (J/k_B) up to –38.3 K (Baran et al., 2002; Tudor et al., 2006). It should be noted that HBs play a mainly structural role in these interactions as they ensure suitable orientation of the

magnetic orbitals on the neighbouring paramagnetic centres (Desplanches et al., 2002).

In order to study the relationship between the structure and the hydrogen bonding system on the one hand, and the magnetic and thermodynamic properties on the other, several compounds with the general composition of $\text{Cu}(\text{L}_N)_2\text{M}(\text{CN})_4$ (L_N is a bidentate *N*-donor ligand) were isolated and structurally characterised (Kuchár et al., 2003, 2004; Čižmár et al., 2006; Hanko et al., 2007). As a continuation of our studies of this class of compounds, we chose to study the effect of substitution of the square cyanide complex anions $[\text{M}'(\text{CN})_4]^{2-}$ with $\text{M}' = \text{Ni}(\text{II})$ and $\text{Pd}(\text{II})$ by a tetrahedral cyanide complex anion $[\text{M}'(\text{CN})_4]^{2-}$ with $\text{M}' = \text{Cd}(\text{II})$. This tetrahedral anion was previously identified in cyanidocomplexes, e.g. in $\text{Cd}(\text{en})\text{Cd}(\text{CN})_4$ (Nishikiori et al., 1979) or in $\text{Cd}(\text{py})_2\text{Cd}(\text{CN})_4$ (py = pyridine) (Yuge & Iwamoto, 1993). As a result, we isolated the compound $\text{Cu}(\text{men})_2\text{Cu}_2\text{Cd}_2\text{Cl}_2(\text{CN})_6$

*Corresponding author, e-mail: juraj.kuchar@upjs.sk