



High-dimensional mixed-valence copper cyanide complexes: Syntheses, structural characterizations and magnetism

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ARTICLE INFO

Article history:

Received 15 January 2009

Accepted 4 February 2009

Available online 27 February 2009

Keywords:

Copper cyanides
Bridging ligands
Coordination modes
Magnetic properties
Mixed-valence

ABSTRACT

Reactions of CuCl_2 with different CN complexes in presence of a neutral ancillary ligand lead to two novel mixed-valence Cu complexes $[\text{Cu}^{\text{II}}(\text{bpy})\text{Cu}^{\text{I}}(\text{CN})_3]_n$, **1** (bpy = 2,2'-bipyridine) and $\{[\text{Cu}^{\text{II}}(\text{tn})_2][\text{Cu}^{\text{I}}_4(\text{CN})_6]\}_n$ **2** (tn = 1,3-diaminopropane). For compound **1**, the asymmetric unit involves two Cu ions Cu1 and Cu2 (Cu^{I} and Cu^{II} centres, respectively) which strongly differ in their environments. The Cu1 ion presents a CuC_4 pseudo-tetrahedral geometry, while the Cu2 ion presents a CuN_5 slightly distorted square-pyramidal geometry. The extended structure of **1** is generated by three cyano ligands which differ in their coordination modes. One CN group has a μ_3 coordination mode and bridges two Cu^{I} and one Cu^{II} ion, while the two other CN groups act as μ_2 bridges leading to a sophisticated 3-D structure. As for **1**, the asymmetric unit of **2** involves three crystallographically different Cu ions (Cu1A and Cu1B, presumably Cu^{I} centres, and Cu2 presumably Cu^{II} centres). The Cu2 ion presents centrosymmetric CuN_4 coordination environments involving four nitrogen atoms from two bidentate tn ligands; while the Cu1A and Cu1B ions are three coordinated to cyano groups. The structure can be described as formed by 18-membered " $[\text{Cu}^{\text{I}}(\text{CN})_6]$ " planar metalocycles that are connected to their six neighbors to generate 2-D sheets; these sheets stack forming infinite hexagonal channels in which the $[\text{Cu}(\text{tn})_2]^{2+}$ units are located. Magnetic measurements show an unexpected weak ferromagnetic coupling ($\theta = 0.239(1)\text{K}$) of the Cu^{II} ions through the long and "a priori diamagnetic" –NC– Cu^{I} –CN– bridges in compound **1** and an essentially paramagnetic behavior in compound **2**.

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1. Introduction

During the past two decades, molecular materials based on cyanide-bridged polynuclear coordination compounds have attracted great attention not only because of their fascinating and intriguing network topologies but also because of the important role they are playing in areas such as high- T_c magnetic materials [1], photo-induced magnetism [2], spin-crossover (SCO) materials [3], host-guest chemistry [4], vapochromic materials [5], magnetochirality [6], hydrogen storage [7], biosensors [8], etc. Among these systems, those exhibiting very slow relaxation of their magnetization, such as the SMM (single-molecule magnets) [9] and SCM (single-chain magnets) [10], are of particular interest because of their potential applications in information processing and storage. The most common and controlled strategy to prepare this kind of system is the self-assembly of specifically designed precursors, typically a cyanometalate complex that acts as a ligand and a transition metal complex with free or available coordination sites for the nitrogen

atoms of the cyanide groups [11]. Alternatively, homometallic and, to less extension, heterometallic cyanide-bridged coordination compounds have been prepared through solvothermal techniques by using either cyanometallates or metal cyanides as precursors [12]. The copper cyanide system is particularly attractive because of the versatility of the $\{\text{Cu}_x(\text{CN})_y\}_n$ sub-structures to afford coordination polymeric networks in the presence of appropriate ligands (L), which may act as templating, space-filling and passivating agents [13]. The architectures and topologies of these cyanide-bridged systems are strongly influenced by the nature of the ligand L (denticity, volume, rigidity, etc.). Among them, mixed-valence $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ compounds are relatively scarce mainly because of the difficulty in controlling the final products [14]. In fact, most of the cyanide-bridged mixed-valence $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ coordination polymers have been obtained by serendipity. In addition to their attractive architectures, these compounds are of interest in order to study the coupling interaction between the copper (II) ions through long diamagnetic bridges $\{\text{Cu}^{\text{II}}-(\text{NC}-\text{Cu}^{\text{I}})_n-\text{NC}-\text{Cu}^{\text{II}} (n = 1, 2)\}$. The coupling interaction between the second nearest-neighbor metal ions has been traditionally considered to be negligible compared to that occurring between nearest-neighbor ones. However,

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some studies on cyanide-bridged metal complexes and particularly on mixed-valence $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ compounds showed non-negligible exchange interactions between second nearest-neighbor paramagnetic metal ions [15]. We report here the syntheses, structures and magnetic properties of two novel mixed-valence $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ complexes $[\text{Cu}^{\text{II}}(\text{bpy})\text{Cu}^{\text{I}}(\text{CN})_3]_n$ (**1**) (bpy = 2,2'-bipyridine) and $\{[\text{Cu}^{\text{II}}(\text{tn})][\text{Cu}^{\text{I}}(\text{CN})_6]\}_n$ (**2**) (tn = 1,3-diaminopropane). The ultimate aim of this work is to assess the effect of the rigidity and volume of the ancillary ligands on the architectures of the $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ mixed-valence polymeric systems, as well as to determine and explain the magnitude of the magnetic coupling through the $\text{Cu}^{\text{II}}-\text{NC}-\text{Cu}^{\text{I}}-\text{CN}-\text{Cu}^{\text{II}}$ exchange pathway in **1**.

2. Results and discussion

2.1. Syntheses and general characterization

Both compounds (**1** and **2**) were prepared under aerobic conditions, by diffusion through silica gel [16] in a U-tube of aqueous solutions of $\text{K}_4[\text{Mo}(\text{CN})_8]$ [17] (**1**) or $\text{K}_3[\text{Cr}(\text{CN})_5(\text{NO})] \cdot \text{H}_2\text{O}$ [18] (**2**). The opposite positions of the U-tubes were filled by a mixture of a methanolic solution of 2,2'-bipyridyl and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with an aqueous solution of sodium adipate for **1**, and by an aqueous solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 1,3-diaminopropane for **2**. Crystal structures determinations of both compounds showed that some of the starting materials ($[\text{Mo}(\text{CN})_8]^{4-}$ and $[\text{Cr}(\text{CN})_5(\text{NO})]^{3-}$ anions) were not present in the final products and that each asymmetric unit contains a Cu^{I} ion and cyanide anions which were not included as starting materials. This fact indicates that these cyanide metal complexes are acting as source of cyanide anions, as already observed in parent compounds involving copper (II) metal complexes and hexacyanometallate anions [19]. Besides their crucial role as constituent ions in both compounds, these cyanide anions also act as reducing agents for the reduction of a fraction of the aqueous Cu^{II} ions into Cu^{I} , presumably with formation of cyanogen or cyanate as previously reported for other cases [20]. All attempts to obtain compound **1** by direct combination, using aqueous solution of NaCN instead of the cyanometallate complexes, failed. In contrast, when NaCN and $[\text{Cu}(\text{tn})_2]^{2+}$ ions were used as starting materials (tn = 1,3-propanediamine), compound **2** was obtained as a mixture with a second phase, of formula $[\text{Cu}(\text{tn})_2][\text{Cu}_2(\text{CN})_4]$, analogue to the previously reported complexes $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})][\text{Cu}_2(\text{CN})_4]$ [14e] and $[\text{Cu}(\text{pn})_2(\text{H}_2\text{O})][\text{Cu}_2(\text{CN})_4]$ [13d] (pn = 1,2-propanediamine), which exhibit a single diamond-like mixed-valence network. The infrared spectra of **1** and **2** exhibit the bands expected for compounds built with $[\text{Cu}(\text{bpy})]^{2+}$ (for **1**), $[\text{Cu}(\text{tn})_2]^{2+}$ (for **2**) and CN units (in both compounds). The presence of the CN ligands is clearly indicated by strong absorption bands assignable to ν_{CN} stretching vibrations in the 2080–2187 cm^{-1} range. Previous studies have shown that the positions and number of these absorption bands in compounds involving cyanide bridges can be used as a diagnostic tool for identifying the oxidation state and the coordination of the metal ion, as well as for detecting the presence of cyanide bridges [19,21]. Free CN ion is typically characterized by an absorption band at ca. 2080 cm^{-1} [22]; its coordination to one or more metal ions results in an increase for these wave numbers and increase of the metal coordination number can result in a decrease in the $\nu(\text{CN})$ band by about 20–40 cm^{-1} [21]. For compound **1**, the three absorption bands observed at 2187, 2114 and 2080 cm^{-1} are in agreement with the presence in **1** of μ_2 - and μ_3 -cyanide bridges. In contrast, for compound **2**, only one absorption band is observed at 2110 cm^{-1} . It is also well known that IR spectroscopy can be used as a diagnostic tool for identifying the coordination mode of the bpy ligand [23]; chelate coordination mode usually splits the strong $\gamma(\text{CH})$ absorption observed as an in-

tense and sharp band at 757 cm^{-1} in the free bpy in an asymmetric doublet. The presence of such doublet on the spectrum (764(s) and 729(m) cm^{-1}) clearly indicates that the bpy ligands present their usual chelating coordination mode. Finally, the 1,3-diaminopropane ligand is easily characterized by the presence on the IR spectrum of bands due to ν_{NH} stretching vibrations of the NH_2 groups at 3302 and 3245 cm^{-1} and to the ν_{CH} stretching vibrations of the CH_2 groups around 2900 cm^{-1} [19,24].

2.2. Crystal structures of **1** and **2**

Both compounds **1** and **2** crystallize in the monoclinic space group $P2_1/n$. ORTEP plots and perspective views are shown in Figs. 1–5; selected inter-atomic distances and angles for compounds **1** and **2**, and pertinent crystal data are listed in Tables 1–3, respectively.

$[\text{Cu}^{\text{II}}(\text{bpy})\text{Cu}^{\text{I}}(\text{CN})_3]_n$ (**1**): The asymmetric unit of compound **1** consists of two Cu atoms, one bpy unit and three CN ions, all in general positions (Fig. 1, Table 1). The two non-equivalent copper ions strongly differ in their environments. Thus, the Cu1 ion, presumably a Cu^{I} centre, presents a CuC_4 coordination involving four carbon atoms from four cyano ligands; the environment is pseudo-tetrahedral as clearly shown by the respective C–Cu–C angles (in the range 102.3–118.3°, with an average value of 109.5°). The C1 carbon atom acts as an almost symmetrical bridge towards two Cu1 ions with Cu1–C1 bond distances of 2.160(9) and

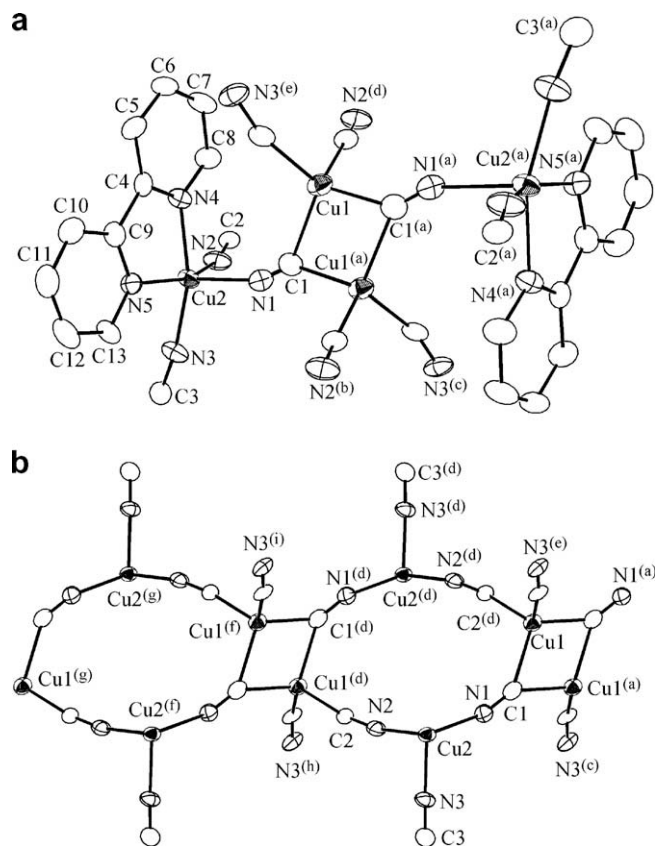


Fig. 1. ORTEP views of compound **1** showing: (a) the atom labelling scheme and the Cu^{I} and Cu^{II} environments and (b) the μ_2 - and the μ_3 -cyanide bridges (the bpy ligands are omitted for the sake of clarity). The shortest Cu...Cu distances (Å) are: Cu1...Cu1^(a) = 2.536(1), Cu1...Cu2 = 4.863(1), Cu1...Cu2^(e) = 4.963(1) and Cu1...Cu2^(d) = 5.012(1). Symmetry transformations used to generate equivalent atoms: (a) $-x, -y, -z$; (b) $-1 + x, y, z$; (c) $-1/2 + x, 1/2 - y, -1/2 + z$; (d) $1 - x, -y, -z$; (e) $1/2 - x, -1/2 + y, 1/2 - z$; (f) $1 + x, y, z$; (g) $2 - x, -y, -z$; (h) $1/2 + x, 1/2 - y, -1/2 + z$; (i) $3/2 - x, -1/2 + y, 1/2 - z$.

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