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Short communication

Cyanide-bridged mixed-valence copper(II/I) coordination polymers: Unique 7-connected *sev*-type 3D network versus anionic 2D host network encapsulated with cationic complex

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ABSTRACT

Reactions of $CuCl_2$, $K_2[Ni(CN)_4]/K_3[Co(CN)_6]$, and 5-amino-1H-tetrazole led to cyanide-bridged mixed-valence Cu(II/I) complexes, $[Cu(H_2O)_3Cu_3(CN)_5]$ (**1**) and $[Cu(H_2O)_4][Cu_4(CN)_6]$ (**2**).The uncommon semi-closed $\{Cu_2(CN)_3\}$ dimmers in **1** are bridged by μ_3-C,C,N cyanide ligands to afford rare 1D centipedal-like chain motifs, which are further bridged by μ_2-C,N and metalloligand "CN–Cu(4)–CN" to finish sophisticated zeolite-like 3-D structure. Topologically, **1** is the first example of uninodal 7-connected *sev*-like cyanide-bridged network. Compound **2** consists of two-dimensional honeycomb-related anionic layers $[Cu_4(CN)_6]^{2-}$, within which the $[Cu(H_2O)_4]^{2+}$ cations are intercalated into alternate interlamellar space. Compound **1** shows antiferromagnetic couple arising from pure ground-state configuration of Cu(II) mediated by diamagnetic bridges –CN–Cu^I–CN — . The inclusion compound **2** shows blue photoluminescence originated from Cu(I) center to the unoccupied π* orbital of the cyanide ligand (MLCT) charge transfer.

Rational design and construction of metal cyanide compounds has become a particularly important area of research because of their potential applications as materials for catalysis, inorganic–organic zeolites, high-*Tc* molecular based magnets, and high-temperature superconductors [1–4]. The ability of the cyanide groups to connect transition metal ions in variety of bridge fashion has afforded a plethora of homo- and heterometallic cyanide-bridged assemblies [5–7]. Among them, the monometallic copper-containing cyanide-complexes represent a particular and interesting case. The increased tendency of Cu(II) metal ions to be reduced by cyanide anions, in aqueous solution, accompanied by the oxidation of cyanide to cyanogen [8], afforded versatile $[Cu(I)(CN)_m]^{n-}$ fragments ($m = 2$–4 and $n = m-1$) with linear, trigonal-planar or tetrahedral geometries. At present, there are two main classes of copper cyanide compounds: (i) extended copper(I) networks; (ii) mixed-valence copper(I)/copper(II) complexes with different dimensionalities and attractive solid-state architectures [9,10]. Mixed-valence species are obtained either as cyanide-bridged copper(I)/copper(II) systems [11,12] or as copper(I)/copper(II) clathrates, in which mononuclear cationic copper(II) complexes are trapped by two- or three-dimensional Cu(I) cyanide networks [13–15]. Among them, most of the cyanide-bridged mixed-valence Cu(II)/Cu(I) coordination polymers have been obtained, in which Cu(II) cations decorated with polydentate aliphatic/aromatic amine ligands (L) [16]. The architectures and topologies of these cyanide-bridged systems are strongly influenced by the nature of the ligand L (density, volume, rigidity, etc.). In addition to their attractive architectures, it is of interest to study coupling interaction between the copper (II) ions through long diamagnetic bridges $\{Cu^{II}–(NC–Cu^{I})_n–NC–Cu^{II}\ (n = 1, 2)\}$. 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, some studies on cyanide-bridged mixed-valence Cu(II/I) compounds showed non-negligible exchange interactions between second nearest-neighbor paramagnetic metal ions [17]. Herein we report the synthesis, structures and properties of two mixed-valence Cu(II/I) complexes $[Cu(H_2O)_3Cu_3(CN)_5]$ (**1**) and $[Cu(H_2O)_4][Cu_4(CN)_6]$ (**2**). Compound **1** was identified a unique 3-D 7-connected *sev*-like zeolite framework constructed by trinuclear nodes and μ_2-C,N and metalloligand "CN–Cu(4) –CN" linkers. The coordinated water molecules binding to Cu(II), forming a distorted square pyramidal geometry due to the Jahn–Teller effect. The weak antiferromagnetic magnetic exchange interactions of **1** has been justified toarising from pure ground-state configuration of Cu(II) mediated by –NC–Cu^I–CN– diamagnetic bridges. Compound **2** exhibited honeycomb-like $[Cu_4(CN)_6]^{2-}$ sheet accommodating $[Cu(H_2O)_4]^{2+}$ cation complexes showing photoluminescence.

Complex **1** crystallizes in the monoclinic space group $P2_1/n$ (Table S1), and the asymmetric unit contains three crystallographically independent Cu(I) centers, one Cu(II) atom, five cyanide ligands, three water molecules, as shown in Fig. 1a. All of the atoms localize in general

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positions. The Cu(1) atom is tetrahedral geometry and thus monovalent, coordinated by two different μ_3-cyanide and two μ_2-cyanide ligands. The Cu(1)—L (L = C or N) bonds are in the range of 1.915(14)–2.431(17) Å, and the L–Cu(1)—L angles are between 93.9(5)–120.9(6)°. The Cu(2) atom shows disordered trigonal environment, coordinated by two μ_3-cyanide and one μ_2-cyanide ligands. The Cu(2)—L (L = C or N) bonds are in the range of 1.930(15)–1.961(14) Å, and the L –Cu(2)—L angles are between 110.9(6)–123.8(6)°. The Cu(3) atom also shows disordered trigonal environment, but coordinated by one μ_3-cyanide and two μ_2-cyanide ligands. The Cu(3)–C bonds are in the range of 1.887(13)–2.308(15) Å, and the C–Cu(3)–C angles are between 109.4(6)–138.6(6)°, suggesting more distorted than Cu(2). The Cu(4) atom has a square-pyramidal geometry and is assumed to be divalent, coordinated by two μ_2-cyanide ligands (Cu–N = 1.959(11)—1.969(13)Å) and three water molecule (Cu–O = 2.013(17)–2.371(16) Å). The L–Cu(4)—L (L = N or O) angles are in the range of 85.5(7) — 173.8(7)°, thus suggesting a disordered pyramidal geometry. This copper atom shows classic Jahn-Teller distortion, with the significantly long Cu(4)–O(3W) distance of 2.371(16)Å (Table S2). In **1**, cyanide ligands show two (μ_3,η^2) and (μ_2,η^2) different coordination fashions. Interestingly, there exist semi-closed $\{Cu_2(CN)_3\}$ dimer units with Cu…Cu distances of 2.687(3) and 2.640(3) Å, which are shorter than the sum of the Van der Waals radii of two copper atoms (2.80 Å), suggesting an effective intermetallic interaction. To the best of our knowledge, semi-closed $\{Cu_2(CN)_3\}$ dimer is an uncommon feature compared with reported $\{Cu_2(CN)_2\}$ "square" motifs [15b]. Additionally, semi-closed subunits are mutually linked to produce unique 1D centipedal-like chain substructure (Fig. 1b). These centipedal-like chains are further connected by μ_2-cyanide and metalloligands "CN–Cu(4)–CN" to form complicated zeolite-like three-dimensional (3-D) network (Fig. 1c, Fig. S1). In order to simplify network topology, we consider trinuclear SBUs acts as a node and μ_2-C,N cyanides and metalloligands "CN–Cu(4)–CN" as linkers (Fig. S2). Thus, the whole network can be simplified as unusual 7-connected uninodal net with a short *Schläfli* symbol $\{4^{17}.6^4\}$ [18]. This network is identified by the code *sev* in the RCSR database, which is constructed from single trinuclear SBUs that are coordinated by eight cyanide bridging ligands. Six of the linkers form single bridges to six neighboring trinuclear SBUs, while the remaining two form a double bridge to a single trinuclear SBUs (Fig. 1d).

In fact, we are not aware of any other example of such connectivity in reported cyanide-bridged structures. Only a few cyano-bridged Cu(II/I) mixed-valence complexes have been reported so far. For example, similar polymer $\{[Cu_3(CN)_4(H_2O)_3](H_2O)_2\}_n$ [15b] also shows complicated 3-D network with different topology, in which novel 1-D water tapes consisting of cyclic pentamers were found in this structure. Compound $[Cu(tn)_2][Cu_2(CN)_4]$ [13] (tn = 1,3-diaminopropane) is a 2-D sheet formed by 18-membered "$[Cu^I(CN)]_6$" planar metallocycles. Compounds of $[Cu(en)_2(H_2O)][Cu_2(CN)_4]$ [16d] and $[Cu(pn)_2][Cu_2(CN)_4]$ [14] (en = ethylenediamine; pn = 1,2-propanediamine) consist of a 3-D diamond-related anionic framework, encapsulated $[Cu(en)_2(H_2O)]^{2+}$ and $[Cu(pn)_2]^{2+}$ cations. The $\{[Cu(H_2O)(NH_3)_4][Cu_3(CN)_5]\cdot H_2O\}_n$ [15c] has cage-like 3D framework encapsulated $[Cu(H_2O)(NH_3)_4]^{2+}$ and crystallization water molecules. For compound $\{(CH_3)_4N[Cu(H_2O)(NH_3)_4][Cu_4(CN)_7]\}_n$ [15a], two different cationic units $[Cu(H_2O)(NH_3)_4]^{2+}$ and $[N(CH_3)_4]^+$ are surrounded by an anionic 3D host lattice $[Cu_4(CN)_7]^{3-}$.

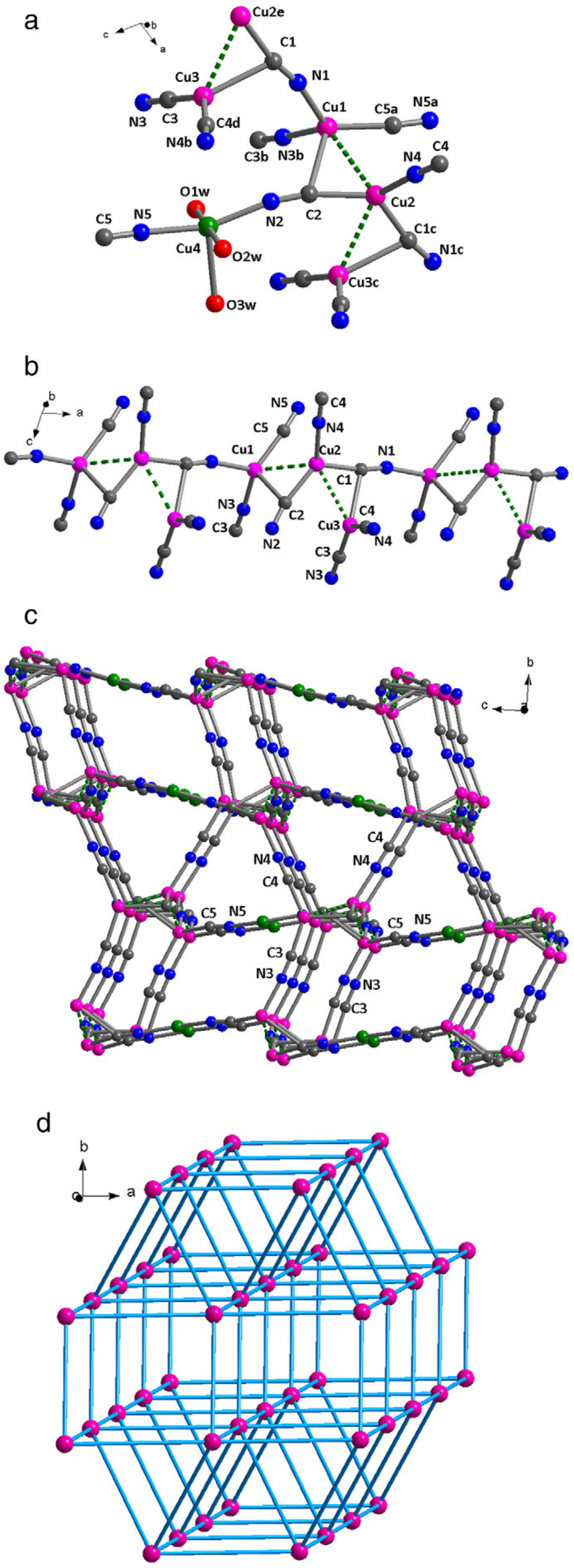

Fig. 1. View of coordination environment of copper atoms(a). The 1D centipedal-like chain motifs (b). The overall 3D net formed by the crosslinking of the 1D centipedal-like chains through C(3)N(3), C(4)N(4), C(5)N(5). The terminal water molecule ligands omitted for clarity. (Cu(I) atoms are shown as pink and Cu(II) atom as green color) (c). Schematic representation of the underlying 7-connected uninodal*sev*-like network topology in compound **1** (Pink spheres represent the trinuclearSBUs) (d).