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A novel three-dimensional coordination polymer constructed with mixed-valence dimeric copper(I,II) units†

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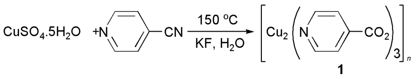
A novel three-dimensional coordination polymer with a mixed-valence localized copper(I,II) dimeric unit, $[\mathrm{Cu_2(4\text{-}pya)_3}]_n$ (4-pya = 4-pyridinecarboxylate), was hydrothermally synthesized *via* a simultaneous *in-situ*a redox and hydrolysis reaction of Cu(II) and 4-cyanopyridine and crystallographically characterized to be a twofold interpenetrated three-dimensional coordination network with a cubic $[\mathrm{Cu_{16}(4\text{-}pya)_{12}}]$ building unit.

The connection of metal-organic coordination networks based on complexes of transition metals and multifunctional bridging ligands has proven to be a fertile field due to the intriguing network topologies and potential functions as new classes of materials.[1] The hydro(solvo)thermal method has been proved to be a promising technique in the preparation of highly stable, infinite metal–ligand frameworks[2] together with many interesting phenomena[3] such as a redox process of copper, ligand oxidative coupling, hydrolysis and substitution. Nevertheless, it is still a challenge when we hope to control the final products, especially for those mixed-valence $\mathrm{Cu^ICu^{II}}$ compounds which are of great biological importance and electronic properties.[4] This may be the reason why few mixed-valence Cu(I/II) coordination polymer species have been isolated to date. Two recently reported interesting examples, $[\mathrm{Cu_4(tp)_3(4,4'\text{-}bpy)_2}]$ and $[\mathrm{Cu_2(ipO)(4,4'\text{-}bpy)}]$ (4,4′-bpy = 4,4′-bipyridine, tp = terephthalate) are both generated under hydrothermal reactions of Cu(II) with mixed ligands.[5] Moreover, several coordination polymers were also reported to incorporate discrete single Cu(I) and Cu(II) atoms separated by organic spacers.[6] We are investigating the synthesis of mixed-valence Cu(I/II) coordination polymers by hydrothermal method.[3d,e,5b] Derived from the known reactions towards mixed-valence copper(I,II) coordination polymers, it may be expected to generate the target products by utilizing a simple kind of ligand containing both a pyridyl group and a carboxylate group through the *in-situ* redox reaction of Cu(II)-pyridyl and the stabilization of $\mathrm{Cu(I,II)_2}$-carboxylate coordination. Fortunately, we isolate a novel mixed-valence Cu(I,II) coordination polymer with localized dimeric $\mathrm{Cu^ICu^{II}}$ units, namely $[\mathrm{Cu_2(4\text{-}pya)_3}]$ (4-pya = 4-pyridinecarboxylate) (**1**), which was generated simply from 4-cyanopyridine under hydrothermal conditions. Cyanopyridine-like ligands and their hydrolysate derivatives (3- or 4-pyridinecarboxylates) have been widely used for hydrothermal synthesis of coordination polymers of Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II),[3a,b,7,8] to the best of our knowledge, this is the first time its mixed-valence Cu(I,II) coordination polymer has been successfully isolated.

The hydrothermal reaction of copper(II) salt with 4-pyCN, and water in a molar ratio 1 : 1 : 555, at 150 °C (48–72 h) led to the formation of dark blue **1** (Scheme 1).† KF was added acting as a mineraliser to get larger crystals. The IR spectrum of **1** clearly indicates the absence of characteristic peaks for sulfate groups and for cyano groups, the presence of strong peaks at 1622, 1396 and 1380 cm^{-1} suggests the formation of carboxylate groups during the reaction. The 4-pyridinecarboxylate group evidently results from the hydrolysis of 4-pyCN. Part of 4-pyCN may act as a reducing reagent to promote the formation of mixed-valence dimeric $\mathrm{Cu^ICu^{II}}$ units.

Single-crystal X-ray analysis‡ has revealed that there are two crystallographically independent metal atom centres bridged by triple μ-carboxylate groups in the crystal structure (Fig. 1). Cu1 is coordinated to three carboxylate oxygen atoms and two pyridyl nitrogen atoms from five different 4-pya ligands in a slightly distorted square pyramidal geometry. The metal atom (Cu1) is slightly deviated from the basal plane (0.113 Å). Cu2 is in greatly distorted tetrahedral geometry coordinated by three carboxylate oxygen atoms and one pyridyl nitrogen atom from four different 4-pya ligands, showing the typical character of monovalent Cu.

Most of the striking features of **1** are listed below. Firstly, a well-localized dimeric carboxylate-bridged $[\mathrm{Cu^ICu^{II}(4\text{-}pya)_3}]$ unit was clearly shown in **1**, which we believe is the first time this has been found in mixed-valence Cu(I,II) coordination polymers with no other ancillary ligand. Of the reported related compounds with dimeric $[\mathrm{Cu_2}]^{3+}$ units,[3d,e,4a,5a] the copper atoms are all coordinated in a square-pyramidal geometry, showing a fully delocalised state. The Cu(I)–Cu(II) distance in **1** is 2.9558(13) Å, which is similar to that (2.9306(9) Å) found in a thiolate-bridged, fully delocalized mixed-valence dicopper(I,II) complex,[4c] but greatly longer than those (2.5–2.7 Å) found in $\mathrm{Cu_A}$ centres in cytochrome *c* oxidase and nitrous oxide



Scheme 1

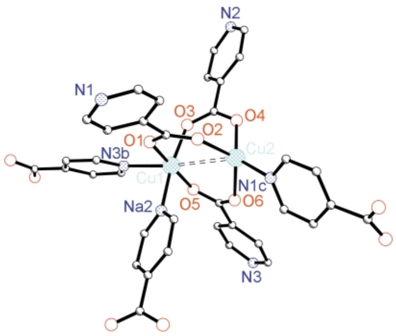


Fig. 1 The coordination environment of the copper atoms in **1**. Selected bond distances (Å): Cu(1)–O(5) 1.954(3), Cu(1)–O(1) 1.958(3), Cu(1)–O(3) 1.990(3), Cu(1)–N(2a) 2.055(3), Cu(1)–N(3b) 2.266(3), Cu(1)···Cu(2) 2.9558(13), Cu(2)–N(1c) 1.968(4), Cu(2)–O(4) 1.975(3), Cu(2)–O(2) 2.138(4), Cu(2)–O(6) 2.224(3), N(1)–Cu(2d) 1.968(4), N(2)–Cu(1e) 2.055(3), N(3)–Cu(1f), 2.266(3).

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† Electronic supplementary information (ESI) available: synthesis and data for **1**. See http://www.rsc.org/suppdata/cc/b2/b210914j/

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reductase containing bis(cysteinate)-bridged fully spin-delocalised dicopper(1.5) units[4a] and those (2.402(1)–2.443(2) Å) found in synthesized delocalised mixed-valence [Cu_4(tp)$_3$(4,4′-bpy)$_2$],[5a] [Cu_4(tp)(ophen)$_4$],[3d] [Cu_4(tp)(obpy)$_4$],[3d] [Cu_4(dpdc)(ophen)$_4$][3e] (4,4′-bpy = 4,4′-bipyridine, tp = terephthalate, dpdc = diphenyl-4,4′-dicarboxylate, ophen = 2-hydroxy-1,10-phenanthroline, obpy = 6-hydroxy-2,2′-bipyridine) and [Cu_2(PXDK)(THF)$_4$](BF_4)[4a] (H_2XDK = *m*-xylylenediamine bis(Kemp's triacid imide)). Secondly, **1** is a three-dimensional coordination network with cubic Cu_{16}(4-pya)$_{12}$ building unit (Fig. 2), quite different from another reported coordination polymer with dimeric $[Cu_2]^{3+}$ unit, in the latter, a pair of parallel Cu_2(tp)(4,4′-bpy) coordination layers pillared by tp generate a 2D bilayered coordination polymer, and adjacent pillared double-layered sheets are polycatenated and extended into a 3D notwork.[5a] While within each cubic unit in **1**, each corner is occupied by a Cu^ICu^{II} dimer, and each dimer acts as a 6-connector to link six ones through interdimer three carboxylate groups and three pyridyl groups into a distorted three-dimensional cubic network. The whole structure of **1** is a twofold-interpenetrating network (Fig. 3), which may play a vital role in stabilizing the mixed-valence localized Cu(I,II) dimeric units. The topology of **1** can be described as a twofold-interpenetrated α-Po network by simplifying the 6-connector dimer to the middle point of the Cu(1)–Cu(2) vector. There is extensive weak C–H···O hydrogen-bonding between the interpenetrated nets. The shortest distances between the carbon atoms of pyridyl groups and carboxylate oxygen atoms are 3.348–3.679 Å. Thirdly, **1** is the first example of mixed-valence Cu(I,II) coordination polymers constructed by only one kind of ligand. Moreover, the 4-pyridinecarboxylate derived from 4-cyanopyridine is a polar ligand, therefore, a polar coordination polymer results. It should also be noted that the structure of **1** is quite different from that of another byproduct [Cu(4-pya)$_2$]·$2H_2O$, of which adjacent Cu atoms are linked to each other *via* the *syn–anti* bridging carboxylate groups to form infinite chains along the *a* axis. In the *bc* plane, each Cu atom is linked to four adjacent Cu atoms through the 4-pya groups to form a rhombohedral grid structure. These grids are further linked by the carboxylate bridges along the *a* axis to form a 3D framework structure.[8c]

Magnetic studies on **1** also support its novel mixed-valence formulation. The value of the magnetic moment at room temperature is 1.85 μ_B per [Cu_2] formula unit, consistent with one unpaired electron per Cu_2 unit with $g = 2.14$. Upon lowering the temperature, the magnetic moment (μ_{eff}) gradually decreases from 1.85 μ_B at 300 K to 1.62 μ_B at 2.0 K (Fig. S1). A plot of $1/\chi_M$ *vs.* T obeys the Curie–Weiss Law [$\chi_M = C/(T - \theta)$] at 10 kOe with a Weiss constant, $\theta = -1.63$ K, and a Curie constant, $C = 0.544$ cm^3 mol^{-1} K, indicates a weak antiferromagnetic coupling between the $S = 1/2$ spins of Cu_2 units through the 4-pya bridges (Fig. S2). The $M(H)$ data (Fig. S3) shows a linear behavior from 0 to 20 kOe. It then starts to reduce the slope and reaches a value of 0.996 Nβ at 50 kOe, which is very near to the saturated value 1 Nβ per [Cu_2] formula unit with $S = 1/2$.

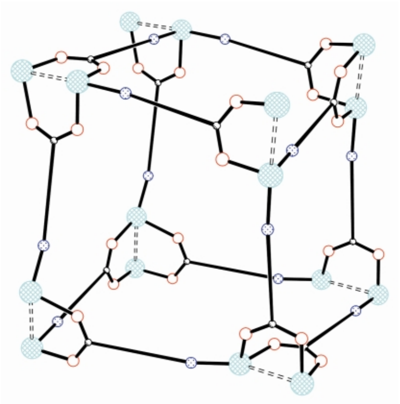

Fig. 2 Perspective view of the cubic-like Cu_{16}(4-pya)$_{12}$ unit in **1**. The pyridyl groups of the 4-pya ligands are shown as bold lines for clarity.

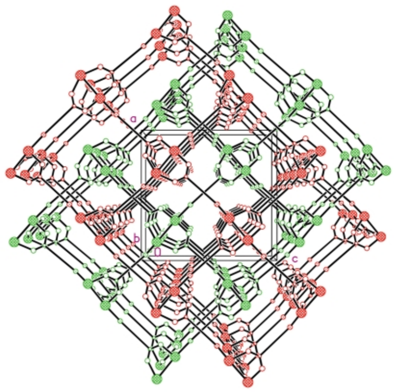

Fig. 3 Schematic view of the 3D twofold interpenetrating network along *b*-axis in **1**.

In summary, we provide here a new possible strategy for the construction of mixed-valence Cu(I/II) coordination polymers *via* a simultaneous *in-situ* redox and hydrolysis reaction. We are actively moving this synthesis strategy towards other related cyanopyridine derivatives.

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Notes and references

‡ *Crystal data* for **1**: $C_{18}H_{12}Cu_2N_3O_6$, *Mr* = 493.39, orthorhombic, space group $Pna2_1$ (no. 33), $a = 14.148(7)$, $b = 9.007(5)$, $c = 14.649(7)$ Å, $V = 1866.6(16)$ Å^3, $Z = 4$, $Dc = 1.756$ g cm^{-3}, $\mu = 23.20$ cm^{-1}. Data collection ($2.68 < 2\theta < 30°$) was performed at 293 K on a Rigaku CCD diffractometer (Mo-Kα, $\lambda = 0.7107$ Å). The structure was solved using direct methods and refined with full-matrix least-squares (SHELX-97),[9] giving a final R_1 value of 0.0446 for 262 parameters and 4165 unique reflections with $I > 2\sigma(I)$ and wR_2 of 0.1144 for all 4377 reflections for **1**, the Flack parameter is 0.537(17). CCDC reference number 197092. See http://www.rsc.org/suppdata/cc/b2/b210914j for crystallographic data in CIF or other electronic format.

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