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Two mixed-valence copper(I,II) imidazolate coordination polymers: metal-valence tuning approach for new topological structures†

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A new metal-valence tuning synthetic approach has been utilized to generate two new mixed-valence Cu(I,II) coordination polymers $Cu_2(im)_3$ and $Cu_3(im)_4$ (Him = imidazole), which are an unprecedented uninodal 4-connected 4.8^5 topological net and a 4-connected (4,4) net, respectively.

Extended framework solids are of current interest and importance because they may offer new materials with a range of potentially useful properties, as well as beautiful molecular topological nets.[1]

Despite the simple formulations, the rigid nature and the predictable (local) coordination geometry, imidazolate (im) as an exo-bidentate ligand has afforded a variety of two-dimensional (2D) to 3D coordination polymers with bivalent metal ions,[2] in which most of them were characterized by powder X-ray diffraction, implying a challenge in growing single-crystals of such complexes. All these networks are 4-connected nets based on metal nodes and im linkers with 1:2 metal–im ratios. On the other hand, linear im–metal(I)–im geometry observed in Ag(im)[3] could be expected for copper(I). We speculated that the integration of both bivalent and univalent metal ions with the bent im ligand may offer a new opportunity to construct novel 4-connected topological nets. Encouraged by several recent reports that Cu^{II} could be reduced to Cu^{I} under basic hydrothermal conditions,[4] we designed and tuned different conditions to attain a series of copper imidazolates. Hydrothermal reaction of cupric salt with Him ligand in a molar ratio 1:2 with addition of concentrated aqueous ammonia at 120 °C led to the formation of blue single crystals of $Cu(im)_2$.[2b] With step-by-step increasing of the temperature and amount of aqueous ammonia we observed reduction of Cu^{II} ions into Cu^{I} ones in different degrees. Dark-green $Cu_2(im)_3$ (**1**) were produced with the lower molar ratio (2:3) of Cu^{II} and Him in the presence of an increased amount of aqueous ammonia at 130 °C, whereas mauve $Cu_3(im)_4$ (**2**) were obtained with a further lower molar ratio (Cu:Him = 3:4) in an increased amount of aqueous ammonia at 140 °C. The phase-pure or almost phase-pure products were yielded under the above conditions, whereas mixtures of **1** and **2** resulted at intermediate conditions. Aqueous ammonia in this reaction maybe acts not only as the base but also the reducing agent,[5] and temperature should also an important factor in controlling the reduction of Cu^{II} ions. Magnetic measurements confirmed the Cu^{I} and Cu^{II} ions are in 1:1 and 2:1 ratios in **1** and **2**, respectively.†

Single-crystal X-ray analysis‡ has revealed that there are four copper atoms and six im groups in a crystallographically independent unit in the crystal structure of **1** (Fig. 1*a*). The bivalent Cu1 and Cu2 ions are coordinated in highly flattened tetrahedral geometries [Cu–N 1.954(3)–1.974(3) Å, *trans* N–Cu–N 134.1(1)–152.5(1)°], which are similar to the $Cu(im)_2$ polymorphs.[2a,b] Cu3 and Cu4 are in typically linear coordination environments [Cu–N 1.872(3), 1.884(3) Å; N–Cu–N 175.2(1), 177.3(1)°]. To our knowledge, no structurally characterized example of a linearly coordinated Cu^{I} ion by im groups has been documented to date. The coordination axes of the two Cu^{I} centers are approximately perpendicular to each other (torsion angles N–Cu–Cu–N 82.4 and 84.6°) with short contacts between Cu3 and Cu4 (2.7293(6) and 2.8144(5) Å) without a direct ligand bridge. Such short intermetallic $Cu^{I}\cdots Cu^{I}$ contacts, close to the van der Waals radius sum of the copper atom (2.8 Å), extend through the *a*-axis into infinite Cu^{I} chains (Cu–Cu–Cu 174.63(2)°) (Fig. S1†).

The most striking feature of **1** is the 3D network which can be rationalized to be an unprecedented, uninodal 4-connected topological net when Cu^{II} ions are treated as nodes and im as well as im–Cu^{I}–im fragments as linkers (Fig. 1*b*,*c*). This net has short and long Schläfli vertices symbols of 4.8^5 and $4.8_2.8_4.8_6.8_4.8_6$ as the shortest circuits of the network are 4-membered $Cu^{II}{}_4(im)_4$ and different types of 8-membered $Cu^{II}{}_8Cu^{I}{}_4(im)_{12}$ fragments. It is worthy of note that some of the 8-membered circuits $Cu^{II}{}_8Cu^{I}{}_4(im)_{12}$ are catenated by other 8-membered circuits (Fig. 2), illustrating that this net is an unusual self-entanglement one, since only a very limited self-entangled nets have been reported to date.[6] If the short Cu···Cu contacts are regarded as one kind of linker, this net is transformed into a 4-connected net with complex vertex symbols, and no longer a self-penetrating one.

Crystal structure of **2** shows three crystallographically unique copper atoms and two im groups, in which one Cu^{II} atom, located at an inversion center, adopts a square coordination geometry (Cu–

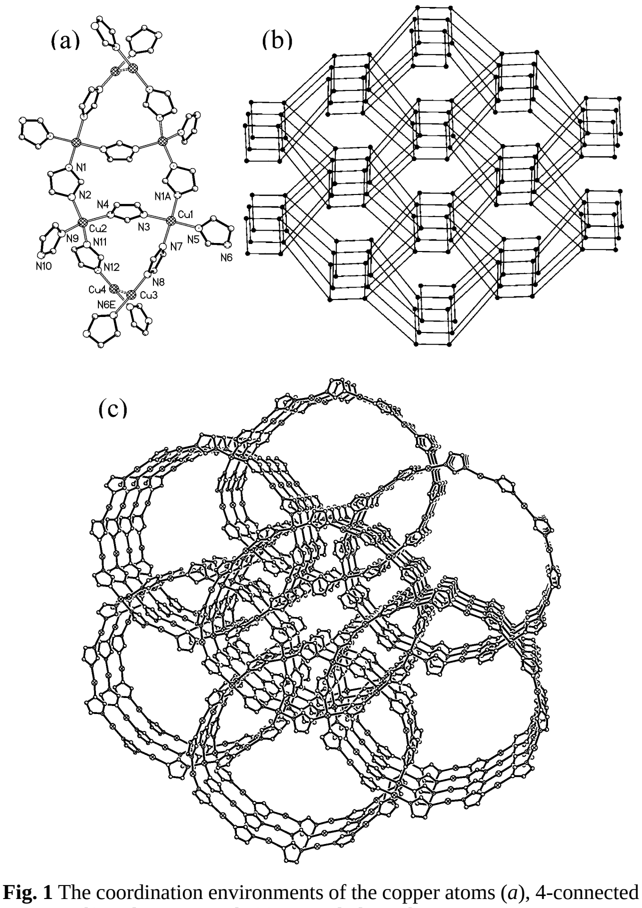

Fig. 1 The coordination environments of the copper atoms (*a*), 4-connected 4.8^5 net (*b*) and 3D network (*c*) viewed along the *a*-axis in **1**.

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† Electronic supplementary information (ESI) available: Synthesis and additional plots for **1** and **2**. See http://www.rsc.org/suppdata/cc/b4/b401691b/

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N 1.981(4)–2.002(4) Å) which are similar to those in the blue polymorph of Cu(im)$_2$.[2a,b] The two independent Cu$^{\mathrm{I}}$ atoms, also located at inversion centers, both assume linear coordination geometry (Cu–N 1.864(4)–1.871(4) Å). The whole network exhibits the well-known 4-connected 2D (4,4) topology with Cu$^{\mathrm{II}}$ atoms as square nodes and im–Cu$^{\mathrm{I}}$–im fragments as linkers (Fig. 3). The 2D networks are stacked in an ABCABC… fashion to form a distorted 4-connected NbO net (Fig. S2†) if Cu$^{\mathrm{I}}\cdots$Cu$^{\mathrm{I}}$ contacts (Cu2–Cu3, 3.36 Å) are taken into account as linkers and the Cu$^{\mathrm{I}}$ atoms act also as 4-connected nodes. Similar to **1**, there are infinite linear Cu$^{\mathrm{I}}$ chains (Cu–Cu–Cu 180°, N–Cu–Cu–N 59.7°) in **2** running along the *b*-axis (Fig. S1†), although the intermetallic distances are much longer.

Also interestingly, two unusually short C–H$\cdots\pi$ hydrogen bonds (H$\cdots\pi$ 2.24 and 2.50 Å, C–H$\cdots\pi$ 160 and 146°) (Fig. 4) between 2D layers are found in **2**, which dominate the molecular packing of **2**. Although C–H$\cdots\pi$ interaction has been shown to play a critical role in supramolecular chemistry,[7] a statistical search[8] of the CCDC database for edge-to-face aromatic/aromatic interactions in general revealed most C–H$\cdots\pi$ contacts to be d = 2.79 Å (d represents H$\cdots\pi$ distance), and only one example of the H$\cdots\pi$ distance as short as 2.24 Å has been found in arenediazonium tetraphenylborate salt [ArN$_2$$^+BPh_4$$^-$].[9]

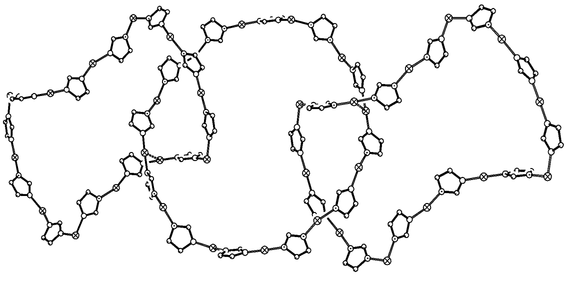

Fig. 2 The catenation of 8-membered Cu$^{\mathrm{II}}_8$Cu$^{\mathrm{I}}_4$(im)$_{12}$ circuits in **1**.

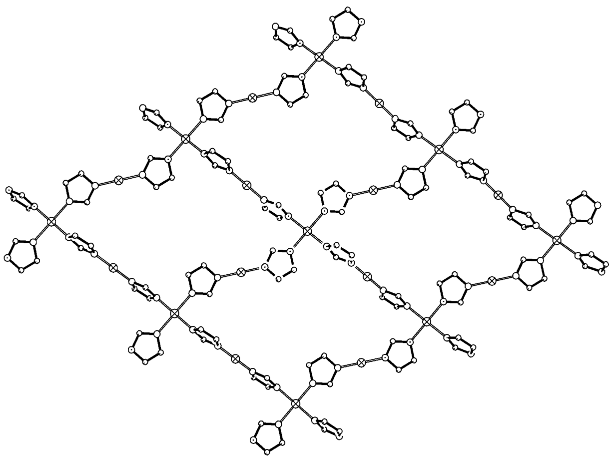

Fig. 3 The (4,4) 2D network in **2** viewed along the *b*-axis.

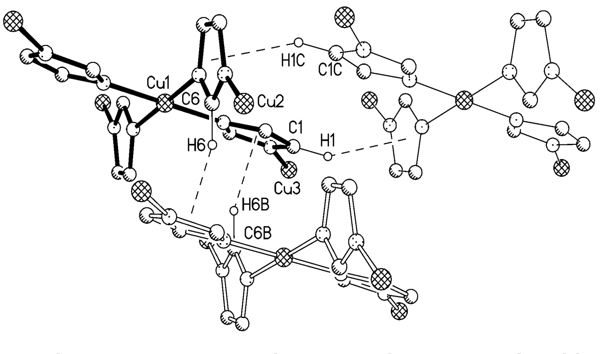

Fig. 4 The C–H$\cdots\pi$ interactions between 2D layers in **2**. Selected bond contacts (Å) and angles (°): H6$\cdots\pi$ 2.24; C6–H6$\cdots\pi$ 160; H1$\cdots\pi$ 2.50; C1–H1$\cdots\pi$ 146. Symmetry codes: A) −x, −y+1, −z+1; B) −x, −y, −z+1.

In summary, we have successfully established a controlled synthetic approach through precise manipulation of the reaction conditions to obtain two mixed-valence Cu(I,II) imidazolate coordination polymers, which exhibit topological diversity as a consequence of the variation of Cu$^{\mathrm{II}}$/Cu$^{\mathrm{I}}$ ratios.

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Notes and references

‡ *Crystal data* for **1** (C$_9$H$_9$Cu$_2$N$_6$): monoclinic, space group $P2_1/n$, M_r = 328.30, a = 5.5376(3), b = 28.164(2), c = 14.6134(9) Å, β = 91.337(1)°, V = 2278.5(2) Å^3, Z = 8, ρ_{calcd} = 1.914 g cm^{-3}, μ = 3.717 mm^{-1}, F(000) = 1304; R_1 = 0.0424, wR_2 = 0.0804, GOF = 1.055 for all data; *Crystal data* for **2** (C$_{12}$H$_{12}$Cu$_3$N$_8$): triclinic, space group $P\bar{1}$, M_r = 458.92, a = 5.5367(5), b = 6.7153(6), c = 10.0436(9) Å, α = 105.550(2), β = 90.044(2), γ = 90.586(2)°, V = 359.74(6) Å^3, Z = 1, ρ_{calcd} = 2.118 g cm^{-3}, μ = 4.404 mm^{-1}, F(000) = 227; R_1 = 0.0467, wR_2 = 0.1219, GOF = 1.047 for all data. Data collection was performed at 123 K on a Bruker Smart Apex CCD diffractometer (Mo-Kα λ = 0.71073 Å). The structures were solved with direct methods and refined with full-matrix least-squares technique using SHELXTL.[10] Anisotropic thermal parameters were applied to all non-hydrogen atoms. The hydrogen atoms were generated geometrically (C–H 1.083 Å). CCDC reference number 227576 & 227577. See http://www.rsc.org/suppdata/cc/b4/b401691b/ for crystallographic data in .cif or other electronic format.

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