

# An unprecedented two-fold interpenetrated heterometallic 4<sup>6</sup>6<sup>4</sup> network constructed by five-connected copper metal nodes

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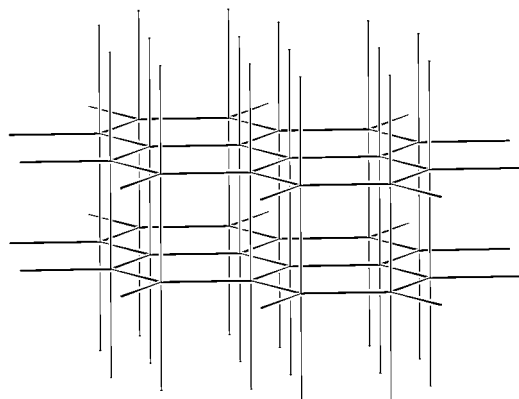
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Hydrothermal reactions making use of dichromate metal anion as a *secondary ligand* yielded a novel three dimensional, bimetallic copper(II)–chromium(VI) network with an unprecedented 4<sup>6</sup>6<sup>4</sup> topology consisting of Cu(II) ions as five-connected nodes; two such networks, completely identical, interlock to generate a two-fold interpenetrated structure.

Self-assembled inorganic/organic frameworks that mimic prototypical structures have received intense attention in the field of coordination chemistry. Synthetic approaches making use of carefully selected, suitable metal centers as nodes and *exobidentate* or multifunctional ligands as connectors have produced numerous fascinating archetypal structures, including diamond (6<sup>6</sup>-α),<sup>1</sup> α-Po (4<sup>12</sup>6<sup>3</sup>),<sup>2</sup> α-ThSi<sub>2</sub> (10<sup>3</sup>-b),<sup>3</sup> SrSi<sub>2</sub> (10<sup>3</sup>-a),<sup>4</sup> PtS (4<sup>2</sup>8<sup>4</sup>),<sup>5</sup> SiO<sub>2</sub> (6<sup>4</sup>8<sup>2</sup>-b),<sup>6</sup> and NbO (6<sup>4</sup>8<sup>2</sup>-a),<sup>7</sup> which have experimentally confirmed the topologies predicted by theory. In certain cases, coordinated systems have generated interesting structures that do not appear to be adopted by simple inorganic compounds, as in the case of the 'dense' net (7<sup>5</sup>9).<sup>8</sup> These inorganic/organic frameworks often contain large open spaces that may be subject to interpenetration. The interlocking networks may or may not be identical. To date, the highest degree of catenation that has been reported is eleven-fold.<sup>9</sup> All of these extraordinary structures are of fundamental importance in structural design and in the understanding of structure–property correlations. Considering the existing coordination systems, one notes that while numerous monometallic structures have been prepared, there has been little progress concerning the synthesis of heterometallic frameworks. With the premise that metal anion functional groups such as CrO<sub>4</sub><sup>2-</sup>, MoO<sub>4</sub><sup>2-</sup>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> and Mo<sub>2</sub>O<sub>7</sub><sup>2-</sup> can form effective M–O–Cr or M–O–Mo bonds,<sup>10</sup> where M is typically a late transition metal, we have successfully applied a synthetic strategy to make use of these metal–anion functional groups as *secondary ligands* in the assembly of heterometallic networks. In this communication, we report a two-fold interpenetrated bimetallic network containing Cu<sup>2+</sup> metal centers and bridging Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> metal anions. The structure can be classified as a 4<sup>6</sup>6<sup>4</sup> topological type built upon pure five-connected nodes,<sup>11</sup> as defined by Wells (Scheme 1).<sup>12</sup> To the best of our knowledge, this structure represents the

first example of coordination polymers possessing such a topology.

Cu(4,4'-bpy)<sub>1.5</sub>Cr<sub>2</sub>O<sub>7</sub>·H<sub>2</sub>O **1** was prepared in single-crystal form by the hydrothermal reaction of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, 4,4'-bpy, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and deionized water in the ratio of 1 : 1 : 0.5 : 5555 at 150 °C for 3 days.† A dark-red single crystal suitable for single-crystal X-ray diffraction was isolated.‡ The coordination environment of Cu in **1** is shown in Fig. 1. Each copper metal has a distorted octahedral coordination. The apical positions are occupied by one coordinated water (O8) and one dichromate oxygen (O6<sup>i</sup>), while the equatorial positions are occupied by three nitrogen atoms (N1, N2 and N3) from different 4,4'-bpy ligands with roughly identical Cu–N bond lengths (2.009–2.033 Å). The remaining equatorial position is occupied by another oxygen (O1) from the second dichromate group. The Cu–O bond distances for the apical oxygen atoms (Cu–O6<sup>i</sup> = 2.330 and Cu–O8 = 2.511 Å) are significantly longer than the equatorial Cu–O bond length of 1.972 Å, liable to Jahn–Teller distortion of Cu(II) (d<sup>9</sup>). The coordination environments around Cu–O–Cr and the Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> group are consistent with those reported in a comparable dichromate compound.<sup>13</sup> Each Cu center in the framework acts as a five-connected node by connecting the three pyridine nitrogen atoms from the 4,4'-bpy at the equatorial positions to form a 2D Cu–bpy (6,3) network and by further bonding to the oxygen atoms of the Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> metal anions to give rise to a unique network with an unprecedented 4<sup>6</sup>6<sup>4</sup> topology (Fig. 2). The coordination of the Cu(II) in this structure is quite different from those in the two well known Cu–bpy compounds, the six-connected Cu(II) in Cu(4,4'-bpy)SiF<sub>6</sub>,<sup>14</sup> and the three-connected Cu(II) in Cu(4,4'-bpy)NO<sub>3</sub>·1.5H<sub>2</sub>O.<sup>15</sup> As shown in Fig. 2, the single 4<sup>6</sup>6<sup>4</sup> network of **1** contains large one-dimensional open channels parallel to the *a*-axis. The cross-section of the channel window is *ca.* 11.2 × 22.0 Å. Note that the Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> anions protrude into the channel, causing a slight distortion of the N2–Cu–N3 bond angle of 170.22(19)°. This results in a narrow 'neck' at the middle of each channel with a shortest O···O distance of *ca.* 4.4



Scheme 1 4<sup>6</sup>6<sup>4</sup> net.

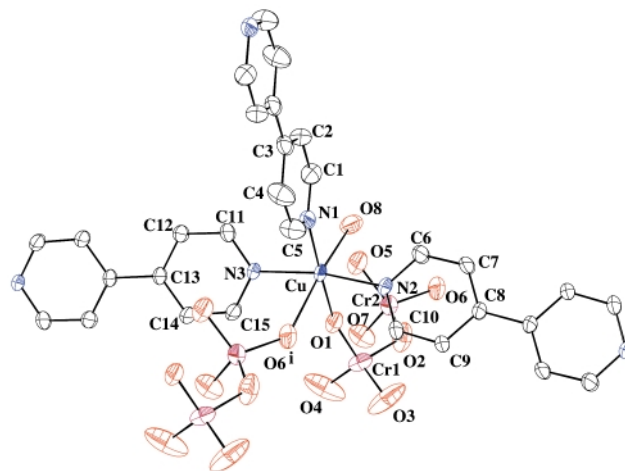
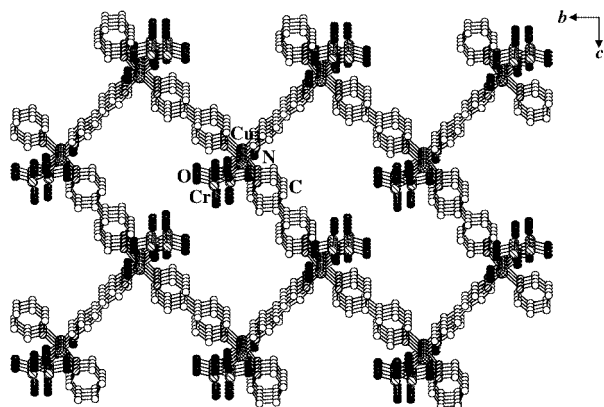
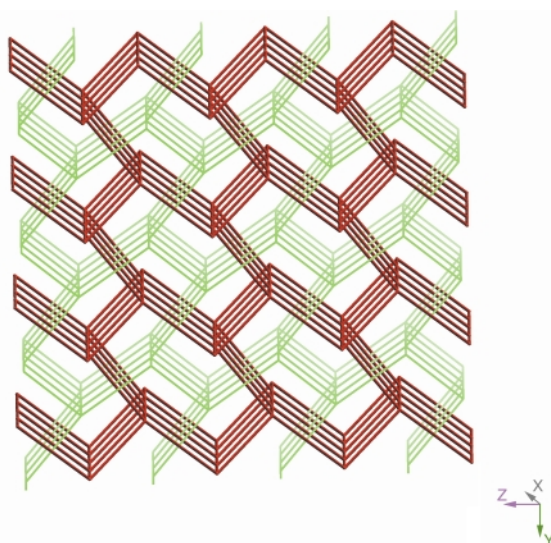


Fig. 1 The coordination environment of Cu in **1** (ORTEP drawing with ellipsoids at 50% probability).



**Fig. 2** A view along the crystallographic  $a$ -axis showing a single  $4^66^4$  3D network of **1**. The cross-shaded circles represent Cu atoms; large singly shaded circles are Cr atoms; and small singly shaded, open and solid circles are N, C, and O atoms, respectively.



**Fig. 3** A view along the  $a$ -axis showing two identical  $4^66^4$  nets built upon five-connected copper nodes. These two 3D nets interlock to generate a two-fold interpenetrated structure of **1**.

Å. The two shortest Cu–Cr distances in **1** are 3.543(14) and 5.1629(18) Å, respectively. A two-fold interpenetrating framework is generated by accommodating two identical  $4^66^4$  networks into the structure (Fig. 3). As clearly illustrated in Fig. 3, pure five-connected copper atoms constitute the nodes of this structure. Note that this  $4^66^4$  net is topologically analogous to the inorganic network  $B_2$  in  $AlB_2$  (see Scheme 1).<sup>16</sup>

In conclusion, we have shown that the inorganic metal anion  $Cr_2O_7^{2-}$  can act as an effective secondary ligand in constructing a bimetallic structure with an unprecedented  $4^66^4$  topology built upon five-connected  $Cu^{2+}$  metal centers. The structure has the same topology as that of the inorganic network  $B_2$  in  $AlB_2$ . The design and synthesis of novel bimetallic structures using other metal–anion secondary ligands and metal centers other than  $Cu(II)$  are currently under investigation.

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## Notes and references

† Preparation of  $Cu(4,4'-bpy)_{1.5}Cr_2O_7 \cdot H_2O$  **1**: hydrothermal reaction of  $Cu(NO_3)_2 \cdot 3H_2O$  (0.0242 g, 0.1 mmol), 4,4'-bpy (0.0156 g, 0.1 mmol),  $K_2Cr_2O_7$  (0.0143 g, 0.05 mmol) and 10 mL deionized water in the ratio of 1:1:0.5:5555 for 3 days at 150 °C followed by slow cooling to room temperature over an 8 hour period produced block-like dark-red crystals of **1** in about 30% yield and an unidentified brown powder. Reactions which attempted to form a single phase were not successful. When the ratio of  $K_2Cr_2O_7 : Cu(NO_3)_2 \cdot 3H_2O$  was reduced from 0.5:1 to 0.25–0.125:1, only an orange solution resulted. Column-like pink crystals were collected after evaporation of this solution. The structure of these crystal was determined to be  $[H_2-4,4'-bpy]Cr_2O_7$ .<sup>17</sup>

‡ Crystal data for **1**:  $Cu(4,4'-bpy)_{1.5}Cr_2O_7 \cdot H_2O$ , MW = 531.83, monoclinic, space group  $P2_1/c$  (No. 15),  $a = 8.176(2)$ ,  $b = 14.718(3)$ ,  $c = 15.952(3)$  Å,  $Z = 4$ ,  $V = 1880.4$  Å<sup>3</sup>,  $D_c = 1.879$  g cm<sup>-3</sup>, crystal size  $0.15 \times 0.15 \times 0.10$  mm,  $\mu(Mo-K\alpha) = 2.306$  mm<sup>-1</sup>. The intensity data were collected with an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). 3687 unique reflections of which 2240 with  $I > 2\sigma(I)$ ;  $R_1[I > 2\sigma(I)] = 0.0538$ ,  $wR_2$  (all data) = 0.0883, GOF = 1.182. The structure was solved by direct methods (SHELXS-86) and refined by full-matrix least-squares methods (SHELXL-97). All non-hydrogen atoms were refined anisotropically. CCDC 159168. See <http://www.rsc.org/suppdata/cc/b1/b102155a/> for crystallographic data in .cif or other electronic format.

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