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Synthesis and structural characterization of the 3-D coordination polymer $[Cu_6(CN)_6(C_4N_3H_{13})]$

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The complex $[Cu_6(CN)_6(C_4N_3H_{13})]$ with short metal–metal separations has been hydrothermally synthesised and structurally characterised by single crystal X-ray crystallography.

In the coordination chemistry of late transition metals, cyanide is used as a bridging ligand to link metal atoms into coordination polymers.[1–6] Because of its flexible coordination ability to connect metal centres, the materials obtained often exhibit a variety of interesting properties and structural chemistry. Thus, it is of significance for building up various multidimensional solids.[7–13] The new materials can exhibit mineralomimetic structures[14,15] and form various types of host–guest systems.[16–18] We investigated the H_2O–$Cu(NO_3)_2$–$Na_4[Fe(CN)_6]$–$C_4N_3H_{13}$ (diethylene triamine) system by a hydrothermal method and obtained novel 3-D coordination polymer $[Cu_6(CN)_6(C_4N_3H_{13})]$ **1** with short metal–metal separations. We report here on the synthesis and structural characterization of this compound.

We prepared compound **1**[†] with a mixture of sodium benzenetetracarboxylate, $Cu(NO_3)\cdot 2H_2O$ (2.50 g), diethylene triamine ($C_4N_3H_{13}$, 1.0 ml), $Na_4[Fe(CN)_6]\cdot 10H_2O$ (1.50 g) and H_2O (22 ml) (pH 9) in a 30 cm^3 Teflon-lined reactor. The solution was sealed and heated to 160 °C for 72 h under autogenous pressure. The resulting brown crystals were isolated (yield of 15% based on the tridentate amine) by filtration and washing with distilled water. The IR spectra show the presence of C≡N (2108, 2090 cm^{-1}) and the XPS spectra show a typical peak of Cu^{I}.[19] The chemical shift of Cu $2p_{3/2}$ is 934.1 eV. EPR measurements exhibited no significant peaks. IR spectra (ν/cm^{-1}): 3330 (s), 3285 (s), 3218 (s), 2905 (s), 2108 (s), 2090 (vs), 1565 (vs), 1440 (s), 1425 (s), 1375 (m), 1347 (m), 1160 (m), 1060 (m), 1010 (s), 940 (s), 790 (m), 585 (m), 490 (m). Found (%): C, 18.72; H, 2.02; N, 19.58; Cu, 59.70. Calc. for $Cu_6C_{10}N_9H_{13}$ (%): C, 18.75; H, 2.05; N, 19.69; Cu, 59.52.

Note that we used a Cu^{II} salt as a reactant, but Cu^{I} ions were got in compound **1**. The Cu^{I} cations obtained in the product might come from the reduction of Cu^{II} by CN$^-$, an organic amine or even Fe^{II}.

Figure 1 shows a displacement ellipsoid plot (30% probability level) of compound **1**, and depicts the atom-numbering scheme. The crystallographic independent unit of compound **1** consists of six CN$^-$, one $C_4N_3H_{13}$ and six Cu^{I}; it contains one tetra-copper chain [Cu(1), Cu(2), Cu(3), Cu(4)] one bi-copper group [Cu(5), Cu(6)], six CN$^-$ anions and one diethylene triamine unit ($C_4N_3H_{13}$). The metal atoms exhibit diverse bond connection modes. Cu(1) is linked by Cu(2), C(1), N(2A), C(4), N(3B); Cu(2) by Cu(1), Cu(3), C(1), C(4), C(5); Cu(3) by Cu(2), Cu(4), C(6), N(8), N(7); Cu(4) by N(1C), N(9), Cu(3); Cu(5) by Cu(6), C(2), N(5), N(6D) and Cu(6) by Cu(5), N(4E), C(3), C(2). The organic ligand $C_4N_3H_{13}$ coordinates the metal atoms Cu(3) and Cu(4). The metal–metal separations (Å): Cu(1)–Cu(2) 2.6179(13), Cu(2)–Cu(3) 2.8476(13), Cu(3)–Cu(4) 2.8235(13), and Cu(5)–Cu(6) 2.5767(12) are obviously shorter than the sum of the van der Waals radii 2×1.54 Å,[20] implying

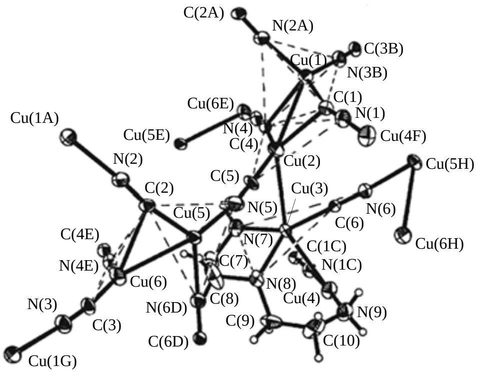

Figure 1 Molecular structure of $[Cu_6(CN)_6(C_4N_3H_{13})]$. Selected bond lengths (Å) and angles (°): Cu(1)–C(1) 1.923(6), Cu(1)–N(3B) 1.941(5), Cu(1)–N(2A) 1.972(5), Cu(1)–C(4) 2.499(6), Cu(2)–C(5) 1.882(6), Cu(2)–C(4) 1.900(6), Cu(2)–C(1) 2.341(6), Cu(3)–C(6) 1.853(6), Cu(3)–N(7) 2.025(5), Cu(3)–N(8) 2.139(5), Cu(4)–N(1C) 1.831(6), Cu(4)–N(9) 1.895(6), Cu(5)–C(2) 1.919(6), Cu(5)–N(5) 1.942(6), Cu(5)–N(6D) 1.962(5), Cu(6)–C(3) 1.870(6), Cu(6)–N(4E) 1.909(6), Cu(6)–C(2) 2.399(6), C(5)–Cu(2)–C(4) 142.0(3), C(5)–Cu(2)–C(1) 104.8(2), C(4)–Cu(2)–C(1) 108.9(2), C(6)–Cu(3)–N(7) 145.6(2), C(6)–Cu(3)–N(8) 128.9(2), N(7)–Cu(3)–N(8) 85.2(2), N(1C)–Cu(4)–N(9) 173.2(3), C(2)–Cu(5)–N(5) 118.0(2), C(2)–Cu(5)–N(6D) 126.3(2), N(5)–Cu(5)–N(6D) 114.9(2), C(3)–Cu(6)–N(4E) 141.0(2), C(3)–Cu(6)–C(2) 108.0(2), N(4E)–Cu(6)–C(2) 100.0(2).

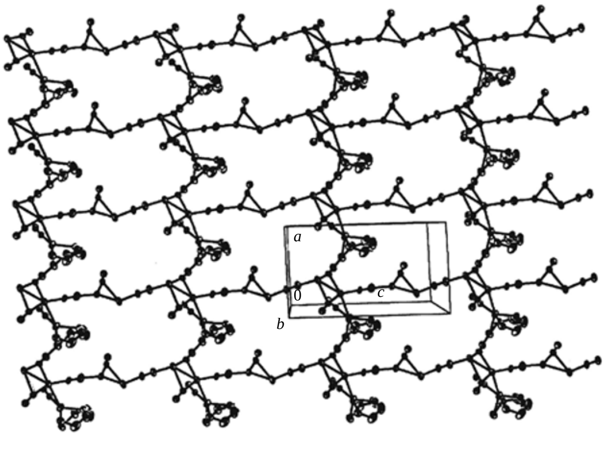

Figure 2 One layer of the compound $[Cu_6(CN)_6(C_4N_3H_{13})]$ along the crystallographic *b* axis.

[†] *X-ray structure analysis.* Crystals of $[Cu_6(CN)_6(C_4N_3H_{13})]$ are monoclinic, space group $P2_1/c$, a = 7.813(2), b = 16.254(3), c = 13.959(3) Å, β = 91.23(3)°, V = 1772.4(6) Å^3, Z = 4, d_{calc} = 2.400 g cm^{-3}, μ = = 7.082 mm^{-1}, F(000) = 1240, crystal size of 0.24×0.32×0.52 mm. Data collection was performed at 293.2 K on a Simens P4 four-circle diffractometer (MoKα, λ = 0.71073 Å) in the range 1.92° < θ < 24.99° using a ψ scan technique. The structure was solved by a direct method and refined using a full-matrix least-square technique (SHELXS-97), giving a final value of R_1 = 0.0389 for 226 parameters and 3115 unique reflections with $I > 2\sigma(I)$ and wR_2 = 0.0943 for all 4228 reflections.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 151125. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2004.

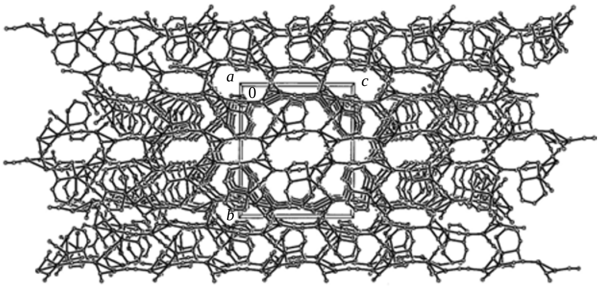

Figure 3 The packing of the compound [$Cu_6(CN)_6(C_4N_3H_{13})$].

that short Cu–Cu interactions occur in the structure. The six CN^- anions bridge cooper atoms with two types of bond modes. [C(3), N(3)]; [C(5), N(5)]; [C(6), N(6)] groups exhibit end-on μ_2-coordination, and [C(1), N(1)]; [C(2), N(2)]; [C(4), N(4)] groups, end-on μ_3-coordination. From the point of view of a polyhedron of copper atoms, this structure is unusual: Cu(1) displays a distorted square coordination with four cyanide ligands and Cu(2), Cu(3), Cu(5) and Cu(6) take trigonal co-ordinations distorted from planarity [Cu(2) sum of bond angles of 355.7°, Cu(3) sum of bond angles of 359.7°, Cu(5) sum of bond angles of 359.2°, and Cu(6) sum of bond angles of 349°]; and Cu(4) exhibits a linear coordination. As compared with the result reported by C. Happenstein,[21] this supramolecular organization is quite different; it might be caused by special short metal–metal contacts.

Figure 2 shows that [$Cu_6(CN)_6(C_4N_3H_{13})$] groups connect each other into polymeric chains along the crystallographic *a* axis, and along the crystallographic *c* axis, the chains further extend to polymeric layers. The packing of the layers along the *b* axis forms a novel 3-D structure (Figure 3). Figure 4 shows that the neutral species [$Cu_6(CN)_6$] gives the 3-D skeleton in the structure.

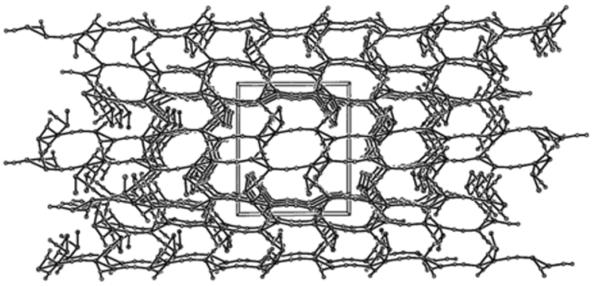

Figure 4 The packing of the neutral species [$Cu_6(CN)_6$].

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