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An unprecedented 1D ladder coordination polymer based on a pentanuclear copper(II) 2,4,6-tris(dipyridin-2-ylamino)-1,3,5-triazine building block†

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Copper(II) nitrate reacts with the rigid polydentate triple-connecting dpyatriz ligand in acetonitrile to an unprecedented infinite molecular ladder in which five-coordinated copper pseudo-dimers are bridged by nitrate anions and the coordination polymer chains are linked by hexacoordinated copper ions leading to the formation of large guest cavities.

The preparation of polymeric complexes can be achieved by using judiciously designed polydentate ligands.[1] The growing interest in the field of coordination polymers is motivated by the ability of metallo-ligand coordination to provide a simple route to the controlled assembly of one-, two- or three-dimensional networks.[2] Many advanced 2D and 3D materials have been prepared in this way with potential applications in catalysis, separation, gas storage and molecular recognition.[3] However, only a few examples of an infinite 1D molecular ladder have been reported so far.[1]

The novel inorganic–organic polymer reported here is formed from copper(II) nitrate and the multidentate trinucleating ligand 2,4,6-tris(dipyridin-2-ylamino)-1,3,5-triazine, dpyatriz (Fig. 1).

Reaction of $Cu(NO_3)_2 \cdot 3H_2O$ in acetonitrile with dpyatriz in acetonitrile yields light blue crystalline needles of $[Cu_5(NO_3)_{10}(dpyatriz)_2(CH_3CN)_2] \cdot 7CH_3CN$ (**1**)‡ whose crystal structure was determined by X-ray diffraction (Fig. 2).§ The pentanuclear unit is constituted by four pentacoordinated copper ions and one hexacoordinated copper ion, which is located on an exact, crystallographic inversion center. The central ion Cu(1) is in an octahedral environment formed by two crystallographically related pairs of N-coordinating 2-pyridyl moieties belonging to two different dpyatriz ligands and two acetonitrile molecules. The CuN distances (Cu(1)–N(21) 2.015(4) Å, Cu(1)–N(31) 2.002(5) Å and Cu(1)–N(80) 2.425(6) Å are typical for Jahn–Teller distorted octahedral environments. The N–Cu–N angles are close to 90° varying from 85.21(17)° to 94.79(17)°. The other Cu ions, Cu(2) and Cu(3), are five-coordinated with one didentate dipyridylamine unit from a dpyatriz ligand and three nitrate anions. The parameter τ is 0.04 for Cu(2) and 0.14 for Cu(3),[4] indicating an almost perfect square pyramidal geometry with O(99) and O(910) being the axial ligands, respectively. The Cu–N distances of 1.986(4) (Cu(2)–N(41)) and 1.989(4) Å (Cu(2)–N(51)) can be considered as normal, as well as the Cu(2)–O(91) and the Cu(2)–O(95) distances (1.974(4) and 1.978(4) Å, respectively). The oxygen atom of the axially coordinated nitrate is at a larger distance (Cu(2)–O(99) 2.253(4) Å). The angles around Cu(2) in the basal plane of the square pyramid range from 87.71(18) to 90.67(17)°. In addition, two other nitrate oxygens, O(92) and O(96), are semicoordinated to the copper centre (Cu(2)–O(92) 2.774(5) Å and Cu(2)–O(96) 2.719(5) Å.

This pentanuclear copper complex constitutes the recurring unit of the coordination polymer. The units are assembled by means of didentate nitrate bridges between two pentacoordinated copper ions. This leads to pseudo-isolated dimeric copper units. The Cu(2)···Cu(3)′ separations within the linear chains are 5.6331(17) Å. The central copper ions are thus connecting two coordination polymer chains to form a 1D molecular ladder[5] as evidenced in Fig. 3. The ladder runs in the direction of the crystallographic *b*-axis with the steps alligned in the [101] diagonal, a likely reason for the non-merohedral twinning of the crystal (see experimental section). This particular self-assembly architecture is due to the 'T-shape' that the ligand adopts upon coordination.[6] This unusual molecular network presents large rectangular guest cavities with dimensions of 10 × 5.5 Å, which are occupied by several acetonitrile molecules. In total, the

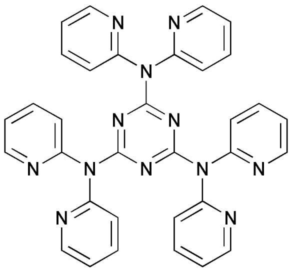

Fig. 1 2,4,6-Tris(dipyridin-2-ylamino)-1,3,5-triazine (dpyatriz).

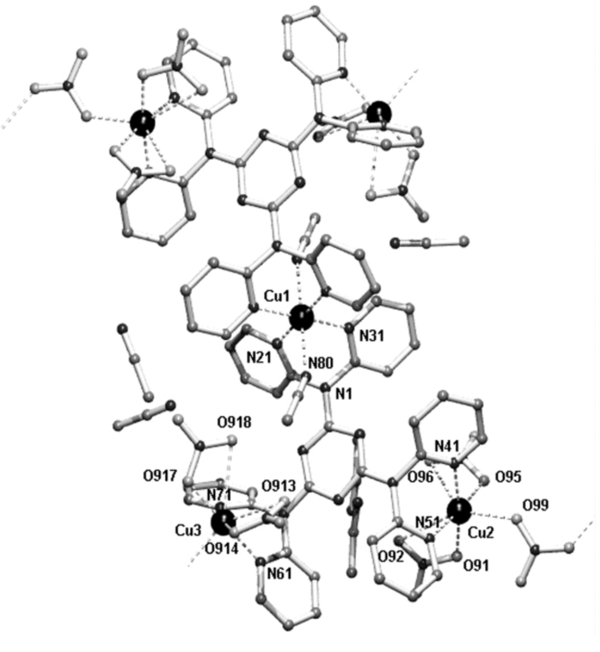

Fig. 2 Pentanuclear copper(II) 2,4,6-tris(dipyridin-2-ylamino)-1,3,5-triazine (dpyatriz) complex **1**.

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† Electronic supplementary information (ESI) available: additional characterization data for **1** (μ_{eff} *vs.* *T* and *B* curves, TGA, XRD). See http://www.rsc.org/suppdata/cc/b2/b203394a/

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uncoordinated solvent molecules cover 25% (652 Å^3) of the unit cell volume.

The diffuse reflectance spectrum of compound **1** exhibits a very broad absorption in the visible region centered between 14 200 cm^{-1} and 16 500 cm^{-1}, which is consistent with an overlap of absorption bands of a five-coordinated copper(II) chromophore with a square pyramidal geometry and a six-coordinated copper(II) chromophore with an axially elongated octahedral geometry.[7] Besides the d–d bands, the spectrum displays a ligand-to-metal charge transfer transition (LMCT) at 36 000 cm^{-1}.

Thermogravimetry analysis (TGA)[8] of **1** shows a 11.1% loss in weight which exactly corresponds to seven acetonitrile molecules.[¶] The X-ray powder diffraction (XRD)[8] of the resulting solvent-free compound displays a pattern which differs from the simulated pattern for complex **1**.[‖] A TGA experiment[8] on this acetonitrile-free crystalline material shows a decrease of 18.8% in weight. This decrease is ascribed to the loss of water molecules rapidly absorbed by the material after removal of the acetonitrile molecules. This is confirmed by the IR spectrum displaying a broad band at 3400 cm^{-1} which is not observed for **1**. Furthermore, the elemental analysis of air-dried **1** reveals the absence of acetonitrile and the presence of nine water molecules.[‡] These experiments tend to support the idea that the coordination polymer structure is rigid enough not to collapse when the solvent is removed. It seems that the cavities can be emptied and re-filled.

The molar magnetic moment of **1**[**] remains almost constant down to 25 K, with a slight decrease from 4.24 μ_B at 200 K to 4.18 μ_B at 25 K. It then drops markedly down to 3.85 μ_B at 2 K. The value at 200 K is consistent with the presence of five Cu(II) ions (spin-only value would be 3.87 μ_B for $g = 2$), while the drop at low temperatures indicates a weak antiferromagnetic component.[8] In view of the structure, the data was fit to an expression contemplating two identical magnetically coupled (according to the Hamiltonian $H = -J\, S_A S_B$) Cu(II) dimeric units and a paramagnetic Cu(II) ion.[9] The exchange integral J was found to be -0.94 cm^{-1}, in agreement with the magnetisation *vs.* field profile at 10 K which is a straight line, with an almost constant effective magnetic moment of 4.12 μ_B, indicating dominant Curie behaviour with a possible antiferromagnetic exchange component manifested at very low temperature. Indeed weak axial coordination of the nitrate bridges is expected to yield very small spin density in the apical position of the Cu(II) ions.[10] Since no other magnetic pathway exists and the Cu···Cu distance is large (5.6331(17) Å) only very weak coupling can be expected. The Landé factors are 2.20 and 2.00, respectively, which agrees well with the EPR spectra of **1** in the solid state (one broad EPR signal at $g = 2.12$) and in acetonitrile solution (g values at 2.17 and 2.05, respectively).[††] In addition, these magnetic measurements show that, both in the solid state and in solution, apparently the same types of copper atoms are detected. Complex **1** seems to exist in solution, but the presence of the 1D ladder coordination polymer is not evidenced.

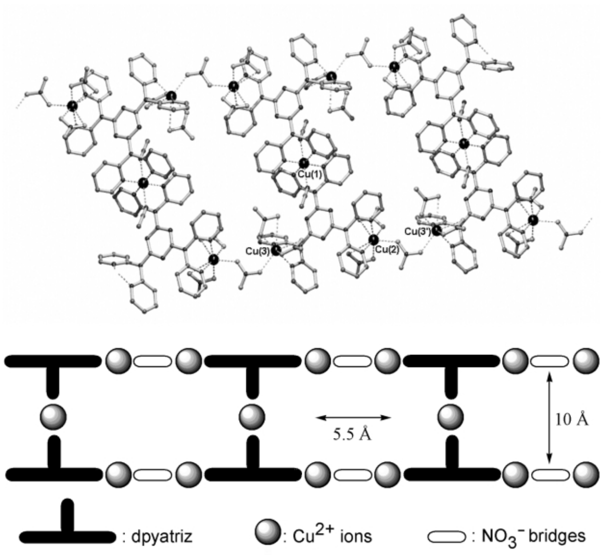

Fig. 3 Repeating unit of the coordination polymer and schematic representation of its 1D ladder structural architecture.

In conclusion, the structure reported here reveals an exciting new route to the preparation of 1D non-interpenetrated molecular ladders comprising large cavities. The possibility to use this coordination polymer in guest–host molecular recognition is currently being addressed. The complexation of the trinucleating dpyatriz with other metals, and the use of the coordination compounds obtained in catalytic oxidations are under investigation.

Notes and references

[‡] A solution of dpyatriz (200 mg, 0.34 mmol) in acetonitrile (40 mL) was added dropwise to a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (247 mg, 1.02 mmol) in acetonitrile (40 mL). 194.1 mg of air-sensitive blue crystalline compound formed after 3 days which was isolated and dried (0.08 mmol, 48%) (Found: C, 35.33; H, 2.94; N, 21.34. Calc for $C_{70}H_{54}Cu_5N_{36}O_{30} \cdot 9H_2O$: C, 35.63; H, 3.08; N, 21.37%).

[§] *Crystal data* for **1**: $C_{70}H_{54}Cu_5N_{36}O_{30} \cdot 7(\underline{C}_2H_3N)$, $M = 2484.57$, blue needle 0.30 × 0.03 × 0.03 mm, triclinic, $P\bar{1}$ (no. 2), $a = 12.052(2)$, $b = 14.0863(18)$, $c = 16.425(4)$ Å, $\alpha = 79.047(11)$, $\beta = 73.946(15)$, $\gamma = 82.334(11)°$, $V = 2621.2(9)$ Å^3, $T = 150$ K, $Z = 1$, μ(Mo-Kα) = 1.096 mm^{-1}, analytical absorption correction (0.83–0.97 transmission), non-merohedrical twin with a 180° rotation around hkl = (101) as twin operation, twin ratio 0.252(1) : 0.748(1), 56827 reflections collected, 12741 unique ($R_{int} = 0.08$), 8894 observed ($I > 2\sigma(I)$), 687 parameters, $R_1 = 0.0649$ ($I > 2\sigma(I)$), $wR_2 = 0.1610$ (all data), $S = 1.112$. CCDC reference number 183664. See http://www.rsc.org/suppdata/cc/b2/b203394a/ for crystallographic data in CIF or other electronic format.

[¶] Thermogravimetric measurements were carried out with a Setaram TAG 24 apparatus coupled to a Setaram universal controller G11, in the temperature range 300–400 K under ambient atmosphere. The experimental uncertainty in temperature was ±0.5 K.

[‖] X-Ray powder patterns were recorded at room temperature using a Philips PW 1730 X-ray generator working with Cu-Kα radiation ($\lambda = 1.514$ Å) coupled with a laboratory-made counter diffractometer.

[**] Variable-temperature magnetic measurements were carried out in the range 2–200 K using a Quantum Design MPMS-5S SQUID magnetometer in fields of 0.05–5 T. Corrections for diamagnetic portions of the complex, deduced from Pascal's tables, and for the sample holder were applied.

[††] X-Band EPR spectra were recorded on a JEOL electron spin resonance spectrometer equipped with an Esprit 330 data system at room temperature and at 77 K, with dpph as an internal reference ($g = 2.0036$).

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8 See Electronic Supplementary Information (ESI†).
9 Least-squares fit of the experimental susceptibility to the expression $\chi = C/T + 2 \times (2N_A g^2 \beta^2)/[k_B T(3 + \exp(-J/k_B T))]$ + TIP was performed with a fixed TIP of 300 × 10^{-6} cm^3 mol^{-1}. N_A, β and k_B have their usual meaning. Best fit was reached for $C = 0.377(1)$ cm^3 mol^{-1} K, $g = 2.20(1)$ and $J = -0.94(1)$ cm^{-1}.
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