Letter

Novel zigzag 1D coordination polymer from copper(II) chloride and *N,N′*-{2,4-di[(di-pyridin-2-yl)amine]-1,3,5-triazine}ethylenediamine exhibiting ferromagnetic interactions

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Copper(II) chloride reacts with the polydentate 1,3,5-triazine containing ligand opytrizediam in methanol–THF to form a unique infinite zigzag coordination polymer in which trinuclear copper complexes are bridged by chloride anions, giving rise to five-coordinated ferromagnetically coupled copper pseudo-dimers.

The molecular self-assembly of coordination polymers is a potential route to novel one-, two- and three-dimensional networks.[1] The preparation of polymeric complexes can be accomplished by using rationally designed polydentate ligands.[2] Many advanced 2D and 3D materials have been generated in this way with encouraging applications in catalysis, separation, gas storage and molecular recognition.[3] However, fairly few examples of infinite 1D molecular zigzag polymeric chains have been reported so far.[4]

The new inorganic-organic zigzag polymer reported here is formed from copper(II) chloride and the multidentate polynucleating ligand *N,N′*-{2,4-di[(di-pyridin-2-yl)amine]-1,3,5-triazine}ethylenediamine, opytrizediam (Fig. 1).[5]

Reaction of $CuCl_2 \cdot 2H_2O$ in methanol with **1** in methanol–THF yields light green parallelepipeds of $[Cu_3Cl_5(opytrizediam)(MeOH)](Cl) \cdot 6.1CH_3OH \cdot C_4H_8O$ (**2**) whose crystal structure was determined by X-ray diffraction (Fig. 2). The trinuclear unit consists of one central hexacoordinated copper ion Cu(2) and two pentacoordinated copper ions, Cu(1) and Cu(3), which are involved in the self-assembly of the coordination polymer by means of chloride bridges. The middle ion Cu(2) is in a distorted octahedral geometry with N(27) in an axial position. The other axial position is occupied by a weakly bonded methanol molecule with a Cu–O distance of 2.664(5) Å. The equatorial plane is formed by three N-coordinating 2-pyridyl moieties belonging to two didentate dipyridylamine units from **1**, leading to a ligand bend, and one chloride ion. The in-plane Cu–N distances of 2.060(2) [Cu(2)–N(25)], 2.008(2) [Cu(2)–N(26)] and 2.037(3) [Cu(2)–N(28)] Å can be considered as normal, as well as the Cu(2)–Cl(3) distance of 2.2787(8) Å. The nitrogen atom of the axially coordinated pyridine is at a larger distance [Cu(2)–N(27) 2.244(2) Å]. The angles around Cu(2) in the equatorial plane range from 86.43(10)° to 91.10(8)°. The other Cu ions, Cu(1) and Cu(3), are square-pyramidal five-coordinated with one didentate dipyridylamine unit and two cis chloride anions in the basal plane, and one axial semi-coordinated chloride atom. The Cu–N distances [Cu(1)–N(23) = 2.035(2), Cu(1)–N(24) = 2.025(2), Cu(3)–N(29) = 2.012(2) and Cu(3)–N(210) = 2.038(2) Å], as well as the Cu–Cl distances [Cu(1)–Cl(1) = 2.3061(7), Cu(1)–Cl(2) = 2.2541(7), Cu(3)–Cl(4) = 2.3061(7) and Cu(3)–Cl(5) = 2.2557(7) Å] can be regarded as normal. The angles around Cu(1) and Cu(3) in the basal plane are close to 90°, varying from 87.18(9)° to 93.25(3)° for Cu(1) and from 86.44(9)° for N(29)–Cu(3)–N(210) to 93.84(3)° for Cu(3). The angles to the axial chlorides are distorted with

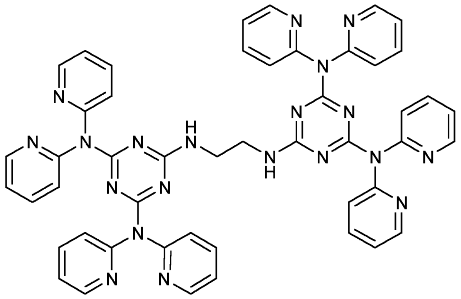
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Fig. 1 *N,N′*-{2,4-Di[(di-pyridin-2-yl)amine]-1,3,5-triazine}ethylenediamine (**1**, opytrizediam).

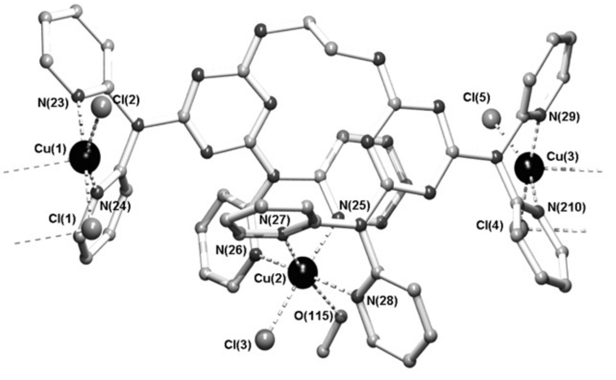

Fig. 2 Trinuclear copper(II) *N,N′*-{2,4-di[(di-pyridin-2-yl)amine]-1,3,5-triazine}ethylenediamine (opytrizediam) complex **2**. Hydrogen atoms, uncoordinated solvent molecules and a non-coordinated chlorine ion have been omitted for clarity.

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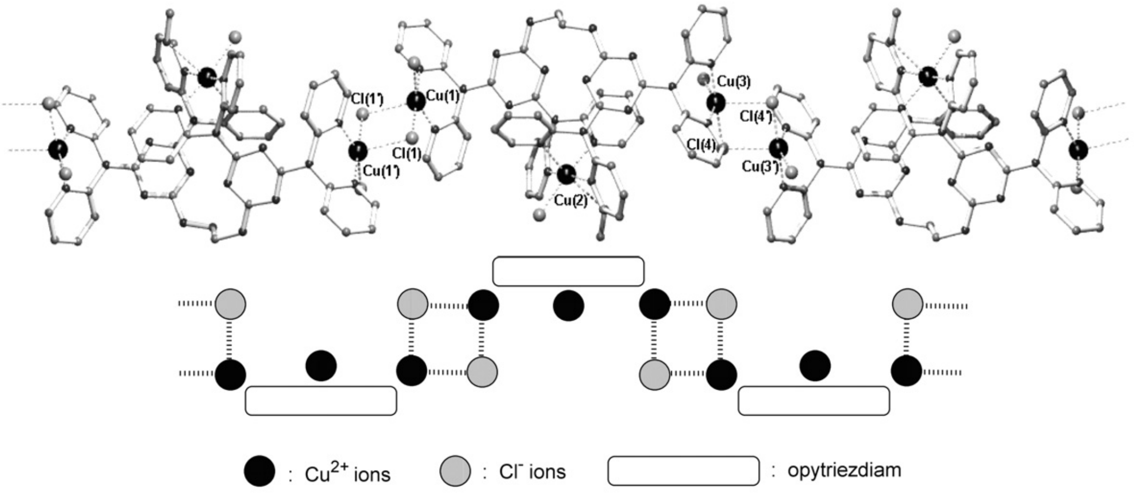

Fig. 3 Repeating unit of the coordination polymer and schematic representation of its 1D zigzag structural architecture.

maxima of 106.04(3)° and 109.97(3)° for Cu(1) and Cu(3), respectively, resulting in τ parameters[6] of 0.38 and 0.39. In addition, an uncoordinated chloride atom and several methanol and THF molecules are present in the crystal lattice, connected by hydrogen bonds. In total, the uncoordinated solvent molecules cover 29% (1016 Å^3) of the unit cell volume.

This trinuclear copper complex constitutes the repeating unit of the coordination polymer. The monomeric units are assembled by means of two asymmetric chloride bridges [Cu(1)–Cl(1) = 2.3061(7), Cu(1)–Cl(1)′ = 2.6950(7) Å and Cu(3)–Cl(4) = 2.3061(7), Cu(3)–Cl(4)′ = 2.6703(7) Å] between two pentacoordinated copper ions, resulting in two slightly different pseudo-isolated dimeric copper entities. The two chloride bridges are located on two independent inversion centres of space group $P\bar{1}$. The Cu(1)···Cu(1)′ and Cu(3)···Cu(3)′ separations within the linear zigzag chains are 3.6635(4) and 3.6769(3) Å, respectively (Fig. 3).

The existence of three different Cu(II) sites for **2** is revealed in its solid-state EPR spectra. At liquid nitrogen temperature, three separate resonances are observed, respectively at g = 2.0866, 2.1256 and 2.2179. The first signal is likely ascribed to Cu(2) because of its octahedral coordination environment, while the two higher g values are assigned to Cu(1) and Cu(3). At room temperature, the three signals are broader, and because of their overlap it is difficult to determine separate g values. Magnetic susceptibility measurements have been performed on crystals of **2** (m = 12.09 mg) at 5 kG in the temperature range 2–300 K. The effective magnetic moment μ_{eff} per trinuclear unit (see Fig. 4) remains almost constant at 3.28 μ_B from 300 K down to *ca.* 75 K. This value is in accordance with the spin-only value expected for three uncoupled $S = \frac{1}{2}$ spin centres, that is 3.00 μ_B. Below 75 K, μ_{eff} increases to a maximum of 3.53 μ_B at 5 K and then decreases smoothly. This behaviour derives from the presence of a ferromagnetic component owing to the chloro-bridged pseudo-dimers. The decrease of μ_{eff} at very low temperatures is likely due to zero-field splitting of the triplet ground state $S = 1$ of these pseudo-dimers. The susceptibility data down to 5 K were fitted to a model assuming one monomeric Cu(II) centre obeying the Curie law and two exchange-coupled Cu(II) dimers described by the isotropic Heisenberg–Dirac–van Vleck Hamiltonian $\hat{H} = -J_i\hat{S}_i\cdot\hat{S}_i$, $J_i(i = 1$ or 3) representing the singlet-triplet gaps of the two Cu(II) dimers.[7] Thus, compound **2** is considered as an assembly of isolated, non-interacting monomer and dimers, in agreement with the large separations arising from the opytrizediam ligands. In the fitting procedure, the g parameters were fixed to the values obtained from EPR spectroscopy, while a fixed TIP of 60×10^{-6} cm^3 mol^{-1} per Cu(II) was considered. An excellent fit (full line in Fig. 4) was obtained for $J_1 = 6.4(1)$ and $J_3 = 15.6(1)$ cm^{-1}. In magnetization measurements at 2 K, a saturation value of 3.45 $N_A\beta$ is reached at 70 kG. The shape of the magnetization curve confirms the presence of ferromagnetic interactions.

A correlation between J and the Φ/R_0 ratio has been reported (Φ being the bridging Cu–Cl–Cu angle and R_0 the Cu–Cu separation) for dinuclear dichloro-bridged square-pyramidal Cu(II) complexes with square pyramids sharing a base-to-apex edge and having parallel basal planes,[8] such as for compound **2** (Fig. 5). Following these correlations, an overall ferromagnetic behaviour can be expected for ratios between 32° and 35°. The Φ/R_0 ratios for **2** are 34.8 [Cu(3)] and 35.6 °·Å^{-1} [Cu(1)], which is in agreement with two different positive singlet-triplet energy gaps. DFT calculations for the present geometry indeed yield small positive coupling constants.[9] The ferromagnetic coupling arises from superexchange pathways involving doubly occupied d_{z^2} and d_{xz} orbitals. The only antiferromagnetic pathway in such dimers having a centre of symmetry, arising from the direct interaction between semi-occupied copper $d_{x^2-y^2}$ orbitals, is minimized in this range of Φ/R_0 ratios. **2** represents one of the very few ferromagnetically coupled di-μ-chloro copper dimers bearing organic *N*-donor ligands. A more thorough examination of the magnetic properties of such compounds, contemplating the zero-field splitting of the triplet ground state of the pseudo-dimers, will be presented in a forthcoming full paper.

In conclusion, a unique 1D zigzag coordination polymer has been synthesized by self-assembly of copper(II) chloride and

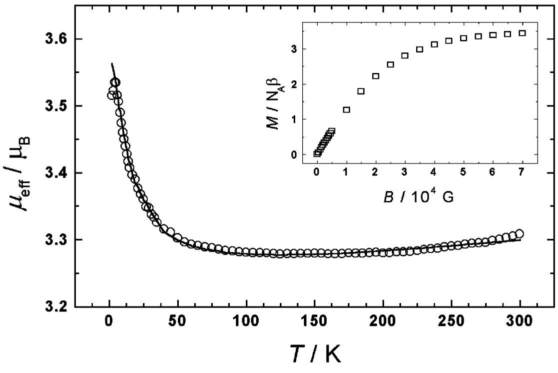

Fig. 4 Temperature dependence of the effective molar magnetic moment of **2**. The inset shows the field dependance of the magnetization at 2 K.

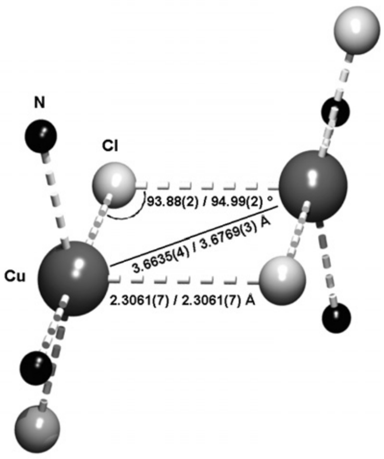

Fig. 5 Pseudo-dimeric copper unit of complex **2**.

the new opytrizediam (**1**) polynucleating ligand. The polymeric material reported shows ferromagnetic properties inherent to the geometry of its copper pseudo-dimer entities. The complexation of the polydentate ligand **1** with other metals, and the use of the coordination compounds obtained in catalytic oxidations, are under investigation.

Experimental

Preparation of $[Cu_3Cl_5(opytrizediam)(MeOH)](Cl)\cdot 6.1CH_3OH\cdot C_4H_8O$

The ligand opytrizediam was prepared according to the reported method.[5] A suspension of opytrizediam (100 mg, 0.11 mmol) in methanol (15 mL) was added dropwise to a solution of $CuCl_2{\cdot}2H_2O$ in methanol (15 mL). Single crystals of **2** suitable for X-ray analysis were obtained as light green parallelepipeds by slow diffusion between two layers of the methanol solution (5 mL) and tetrahydrofurane (5 mL) at room temperature for several days. Yield: 81%. Anal. calcd for $C_{48}H_{46}Cl_6Cu_3N_{20}O_4$: C, 42.07; H, 3.38; N, 20.44%. Found: C, 42.02; H, 3.41; N, 20.21%. IR (neat, cm^{-1}): 3332, 1604, 1367, 1056, 1021, 439.

Measurements

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 ($g = 2.0036$).

Variable temperature magnetic measurements were carried out in the range 2–300 K using a Quantum Design MPMS-7XL SQUID magnetometer in fields of 0.05–7 T. Corrections for diamagnetic portions of the complex, deduced from Pascal's tables, and for the sample holder were applied.

Table 1 Summary of crystal data and refinement parameters for complex $[Cu_3Cl_5(opytrizediam)(MeOH)](Cl)\cdot 6.1CH_3OH\cdot C_4H_8O$ (**2**)[a]

Empirical formula	$C_{57}H_{66}Cl_6Cu_3N_{20}O_6$ *
Formula weight	1530.62 *
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
a/Å	13.9278(1)
b/Å	16.1724(1)
c/Å	16.4180(1)
α/°	92.1781(3)
β/°	104.2578(3)
γ/°	103.0907(3)
V/Å^3	3473.76(4)
Z	2
μ/mm^{-1}	1.2 [*]
Measured reflections	77969
Unique reflections	15852
Observed reflections	12950
R_{int}	0.047
R $[I > 2\sigma(I)]$	0.0439
wR $[I > 2\sigma(I)]$[b]	0.1280

[a] * derived values do not contain the contribution of the diffuse solvent molecules. [b] $w = 1/[\sigma^2(F_o^2) + (0.0763P)^2 + 2.6452P]$ where $P = (F_o^2 + 2F_c^2)/3$

X-Ray crystallography

A green, block-shaped crystal of $[Cu_3Cl_5(opytrizediam)(MeOH)](Cl)\cdot 6.1CH_3OH\cdot C_4H_8O$ (**2**) with approximate dimensions $0.30 \times 0.15 \times 0.15$ mm^3 was mounted and data collection was carried out on a Nonius Kappa CCD diffractometer at 110 K, using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). An absorption correction was not considered necessary. The structure was solved by automated Patterson methods (DIRDIF97[10]) and refined with SHELXL97[11] against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters, hydrogen atoms were refined as rigid groups. Besides the localized methanol and THF solvent molecules, the structure contains heavily disordered, diffuse methanol molecules. Their contribution to the structure factors was secured by back-Fourier transformations as implemented in the CALC SQUEEZE routine of the program PLATON[12] (75 electrons per unit cell in solvent accessible voids of 336.1 Å^3 per unit cell). The asymmetric unit thus contains 1 weakly coordinated MeOH, 4 localized non-coordinated MeOH, 1 localized non-coordinated THF, and 2.1 diffuse, non-localized MeOH. Details of the crystal parameters, data collection and refinement for the compound are summarized in Table 1.

CCDC reference number 188817. See http://www.rsc.org/suppdata/nj/b2/b206344a/ for crystallographic data in CIF or other electronic format.

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