A 1D coordination polymer of copper(II) with three different bridging anions: synthesis, crystal structure and magnetic behaviour

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Reaction of $Cu(ClO_4)_2 \cdot 6H_2O$ with *N*,*N*′-dipropylethane-1,2-diamine (dpren, L), sodium oxalate and sodium azide in a 2 : 2 : 1 : 1 molar ratio results in a 1D coordination polymer of general formula $[L(H_2O)CuOxCu(H_2O)L]^{2+}$, bridged through alternate azide and perchlorate anions, which, on mutual interaction with neighbouring 1D chains through H-bonding *via* interchain free perchlorate anions, produces a sheet-like structure. A low temperature magnetic measurement of the complex shows the existence of strong antiferromagnetic interactions between the copper(II) ions. Least-squares fitting of the experimental magnetic susceptibility data using a modified Bleaney–Bowers equation for a dinuclear copper(II) system leads to the parameters $J = -331.3\ cm^{-1}$ and $g = 2.05$. The complex has also been characterised by X-ray single-crystal structure analysis and IR spectroscopy.

Crystal engineering of multinuclear metal complexes has been a subject of great interest for chemists during the last few decades.[1] Efforts have been made to design and construct polynuclear solids with specific networks and having interesting properties, in areas such as nonlinear optics,[2] molecular recognition,[3] design of porous solids with novel inclusion properties,[4] electrical conductivity,[5] new sensor materials, *etc.* Such progress makes possible the rational design and synthesis of molecules with one-, two- or three-dimensional networks. Moreover, the advent of molecular-based magnets[6] has enriched this field. Recently, construction of multinuclear metal complexes using multi-bridging synthons has become a fascinating frontier area in chemistry. From the magnetic point of view, both azide and oxalate bridging ligands can transmit electronic effects between paramagnetic centres and the azide ligand very efficiently forms such complexes, some of which show spontaneous magnetisation at T_c below 16 and 40 K.[7]

With the aim of combining oxalate and azide superexchange pathways in the same compound, Vicente *et al.*[8] designed a strategy to link $[(L)M–Ox–M(L)]^{2+}$ structural units in the presence of azide anions to generate a 1D polymer with two different bridging ligands in an alternate fashion. Following the same strategy, we have chosen $[(H_2O)(L)Cu–Ox–Cu(L)(H_2O)]^{2+}$ (L = *N*,*N*′-dipropylethane-1,2-diamine) as our starting material. The basis for taking this diamine in which both donor nitrogens are bonded to hydrogen is to observe its role in alternate chain formation and to form hydrogen bonds through both the donor nitrogens of the diamine. Using the same synthetic procedure, we have obtained a one-dimensional coordination polymer $[(\mu\text{-}ClO_4)_{1/2}(H_2O)(L)Cu^{II}–Ox–Cu^{II}(L)(H_2O)(\mu\text{-}N_3)_{1/2}]_n(ClO_4)_n$ with three different bridging anions; this chain, *via* weak interactions (H-bonding) with free ClO_4^- and amine hydrogens of neighbouring chains, produces a sheet-like structure. Although a few examples of alternating chains with two different bridging anions have been reported to date,[9,10] to our knowledge, alternating chains with three different types of bridging anions repeated in a periodic fashion have yet to be reported. In the present paper we report the synthesis, X-ray single-crystal structure and magnetic properties of this novel 1D coordination polymer in which three different bridging anions are repeated periodically.

Experimental

Materials and methods

High purity (98%) *N*,*N*′-dipropylethane-1,2-diamine (L) was purchased from Lancaster Chemical Company Inc. and used as received. All other reagents were of analytical grade.

Elemental analyses (carbon, hydrogen, nitrogen) were performed using a Perkin–Elmer 240 elemental analyser and Cu(II) content was estimated titrimetrically. IR spectra (4000–600 cm^{-1}) were taken in Nujol and hexachlorobutadiene mulls using a Jasco FT-IR (model 300E). The magnetic susceptibilities were measured on a Quantum Design MPMS-5XL 5T SQUID at 1000 Oe applied field. Diamagnetic corrections were made using Pascal's constants.[11]

Synthesis

N,*N*′-Dipropylethane-1,2-diamine (2 mmol) was added slowly to an aqueous solution (10 cm^3) of $Cu(ClO_4)_2 \cdot 6H_2O$ (2 mmol) with constant stirring. An aqueous solution (5 cm^3) of sodium oxalate (1 mmol) was added to the resulting blue solution and the mixture stirred for 0.5 h. Then sodium azide (1 mmol) dissolved in water (10 cm^3) was poured very slowly into the solution, which was then filtered. The green filtrate was allowed to crystallise slowly in a $CaCl_2$ desiccator. After a few days shining blue single crystals were obtained, yield 70%. Anal. found: C, 30.36; H, 5.78; Cu, 17.60; N, 12.99; calc. for $C_{36}H_{88}N_{11}Cu_4Cl_3O_{24}$: C, 30.28; H, 5.75; Cu, 17.91%; N, 12.80%. IR: ν(C–O) 1648, $\nu(N_3)$ 2039, $\nu(ClO_4)$ 1098–984 cm^{-1}.

Crystal data collection and refinement

Suitable single crystals of the complex were mounted on an AFC7S diffractometer. The lattice constants and the crystal

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Table 1 Crystal data and details of the structure determination for $[(\mu\text{-ClO}_4)_{1/2}(\text{H}_2\text{O})(\text{L})\text{Cu}^{\text{II}}\text{-Ox-Cu}^{\text{II}}(\text{L})(\text{H}_2\text{O})(\mu\text{-N}_3)_{1/2}]_n(\text{ClO}_4)_n$

Formula	$C_{36}H_{88}N_{11}Cu_4Cl_3O_{24}$
FW	1419.72
Crystal system	Monoclinic
Space group	$P2/a$
Z	1
a/Å	11.798(7)
b/Å	9.585(7)
c/Å	14.167(3)
α/°	90
β/°	110.95(2)
γ/°	90
U/Å^3	1496.2(14)
T/K	293
μ(Mo-Kα)/mm^{-1}	1.6
R^a	0.0988
$R_w{}^a$	0.2598
No. meas. reflect.	5766
No. indep. reflect. (R_{int})	5412(0.138)

^{a} $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$; $R_w = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

orientation matrix were determined by least squares refinement. Crystal data and refinement details are given in Table 1. Intensity data were collected using graphite monochromated Mo-Kα radiation ($\lambda = 0.710\,69$ Å) with $\omega - 2\theta$ scans. Three standard reflections measured at regular intervals during the X-ray exposures indicated no significant variation in the intensities. All the data were corrected for Lorentz and polarisation effects.[12] Empirical absorption corrections based on ψ-scans were applied for the crystal. The structure was solved by the Patterson method followed by successive Fourier synthesis and refined through full-matrix least-squares calculations (SHELXL 93).[13] Anisotropic thermal parameters were assigned to all non-H atoms.

The coordinates of the Cl(1) and N(3) atoms show that they are in special positions. Due to symmetry constraints they have two positions in the unit cell (the number of general positions for the space group $P2/a$ is four). So they automatically have 50% occupancy. Analysis of difference Fourier peaks showed that the peak, N(3), at a distance 0.8 Å from Cl(1), could not be incorporated in the ClO_4 moiety and moreover N(4)–N(3)–N(4)* (* = symmetry related) gave us the geometry of an azide. Thus, the solution of the structure led to an azide in the proximity of the perchlorate. We thus had to model the structure as disordered. The best refined model gave 50 : 50 occupancy of azide : perchlorate. As stated earlier, the Cl(1) and N(3) atoms have 50% occupancy and ClO_4 is disordered with azide. So the occupancies of all atoms in the perchlorate and azide moieties are halved. This means that N(3) and Cl(1) have 0.25 and O(11), O(12), N(4) have 0.5 occupancies. Thus, the unit cell contains one perchlorate and one azide bridging anion. Selected bond lengths and angles are presented in Table 2 and hydrogen bonds are listed in Table 3.

Table 2 Selected bond lengths (Å) and bond angles (°) for $[(\mu\text{-ClO}_4)_{1/2}(\text{H}_2\text{O})(\text{L})\text{Cu}^{\text{II}}\text{-Ox-Cu}^{\text{II}}(\text{L})(\text{H}_2\text{O})(\mu\text{-N}_3)_{1/2}]_n(\text{ClO}_4)_n$

Cu–O(W)	2.448(7)	Cu–O(1)	1.982(4)
Cu–O(2)	1.992(4)	Cu–N(1)	1.989(5)
Cu–N(2)	2.005(5)	Cu–N(4)	2.666(12)
Cl(1)–O(11)	1.433(13)	Cu–O(12)	2.654(15)
N(1)–Cu–N(2)	87.5(2)	Cu–O(12)–Cl(1)	124.68(8)
O(1)–Cu–O(2)	84.23(19)	O(11)–Cl(1)–O(12)	107(10)
O(1)–Cu–N(2)	94.2(2)	O(1)–Cu–N(1)	177.4(2)

CCDC reference number 440/260. See http://www.rsc.org/suppdata/nj/b1/b100468i/ for crystallographic in .cif format.

Results and discussion

Structure description

The structure solution reveals that the unit cell contains three types of bridging anions: two oxalate, one perchlorate and one azide, which link the four copper atoms of the unit cell. This composition leads to the only possible structure, which is that the copper atoms are bridged alternately by oxalate, end-to-end azide and perchlorate anions to form a polymeric 1D chain $-ClO_4-Cu-Ox-Cu-N_3-Cu-Ox-Cu-$. A ZORTEP[14] drawing of the chain with atom labelling scheme is shown in Fig. 1. In this chain the $Cu(L)^{2+}$ [L = *N*,*N*′-dipropylethane-1,2-diamine] fragment is linked to the next unit by means of a bridging oxalate to form a dimeric unit. One of the copper atoms of this dimeric unit is bridged by an end-to-end azide and the other copper atom is bridged by a ClO_4^- anion in *trans* configuration. This bridging mode leads to a unique polymeric 1D zigzag chain along the *a* axis.

The coordination environment of the copper atom is best described as a distorted octahedron. The two oxygen atoms of

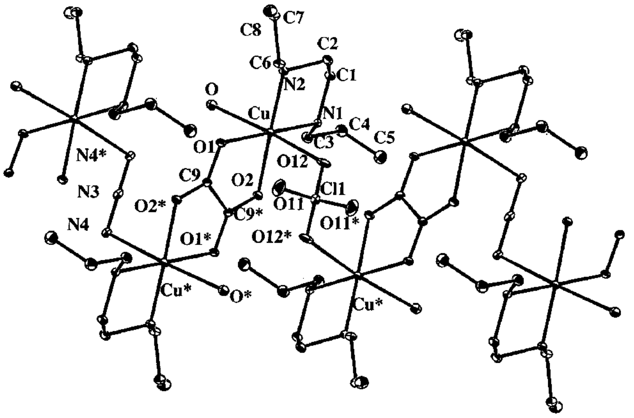

Fig. 1 ORTEP diagram of the 1D chain in $[(\mu\text{-N}_3)_{1/2}(\text{H}_2\text{O})\text{Cu-Ox-Cu}(\text{H}_2\text{O})(\mu\text{-ClO}_4)_{1/2}]_n(\text{ClO}_4)_n$ with atom labelling scheme showing 50% probability thermal ellipsoids for all non-hydrogen atoms.

Table 3 Hydrogen bond parameters (in Å and °) for $[(\mu\text{-ClO}_4)_{1/2}(\text{H}_2\text{O})\text{Cu-Ox-Cu}(\text{H}_2\text{O})(\mu\text{-N}_3)_{1/2}]_n(\text{ClO}_4)_n$. Symmetry codes: (*i*) 3/2 − *x*, *y*, 2 − *z*; (*ii*) 1/2 + *x*, 2 − *y*, *z*; (*iii*) − 1/2 + *x*, 2 − *y*, *z*.

D–H···A	D–H	H···A	D···A	∠D–H···A
N(1)–H(1)···O(2)^{i}	0.911(7)	2.491(6)	3.284(7)	145.8(5)
N(1)–H(1)···O(1)^{ii}	0.911(7)	2.464(7)	3.333(7)	159.8(5)
O–H(1W)···O(21A)^{iii}	0.91(6)	2.17(6)	3.078(14)	174(8)
O–H(1W)···O(21B)^{iii}	0.91(6)	1.96(6)	2.860(12)	169(8)
N(2)–H(2)···O(22A)^{iii}	0.910(8)	2.316(15)	3.114(15)	146.3(7)
N(2)–H(2)···O(22B)^{iii}	0.910(8)	2.122(14)	2.986(14)	158.2(7)

the oxalate bridge and two nitrogen atoms of the amine ligand define the equatorial plane around both copper atoms of the dimeric subunit. The coordinated water molecules are placed in two axial coordination sites *trans* to each other and perpendicular to the Cu–Ox–Cu plane. The octahedral coordination around one copper is completed by one of the nitrogen atoms of the bridging azide ligand and around the other copper atom by one of the oxygen atoms of the bridging perchlorate anion.

As usual, the Cu(Ox)Cu fragment is almost planar; the maximum deviation of any atom from the plane is less than 0.029(5) Å. The deviations of the amine nitrogens [N(1) and N(2)] from this plane are 0.003(5) and 0.189(6) Å, respectively, indicating that these also lie approximately in this plane. The bond distances and angles of the $[LCu–Ox–CuL]^{2+}$ dimeric subunit are close to the expected values; the Cu–O(water), Cu–N(4)(azide) and Cu–O(12)(perchlorate) distances are 2.448(7), 2.666(12) and 2.654(15) Å, respectively. The Cu–N(4)–N(3) angle is 99.52(9)° and the Cu–N_3–Cu torsion angle is −133.6(9)°, whereas the Cu–O(12)–Cl(1) angle is 124.7(8)° and the Cu–O(12)–Cl(1)–O(12)* angle is −55.7(8)°. Consequently, the Cu–Ox–Cu mean planes are not parallel and the dihedral angle between two consecutive mean planes is 83.7(8)°, *i.e.* almost perpendicular to each other.

The Cl(1) atom of the coordinated perchlorate occupies a special position; the O(11) atom and its symmetry related counterpart O(11)* occupy approximately equivalent positions as do the end atoms of the azide ligand, namely N(4) and N(4)*. So the azide and perchlorate ligands are disordered with an occupancy ratio of 0.5 : 0.5. The oxygen atoms O(21) and O(22) of the free perchlorate are distributed over two positions with site occupancies of 0.6 : 0.4.

The O(1) and O(2) atoms of the oxalate ligand are engaged in two distinct, strong H-bonding interactions [N(1)–H(1)···O(1)/(O2) 3.28(7)/3.33(7) Å, ∠N(1)–H(1)···O(1)/(O2) 145.80(5)/159.8(5)°]. Interchain hydrogen bonding interactions *via* free perchlorate anions [O–H(water)···O(21A)/O(21B) 3.08(14)/2.86(12) Å, ∠O–H(water)···O(21A)/O(21B) 174(8)/169(8)° and N(2)–H(2)···O(22A)/(O22B) 3.11(15)/2.98(14) Å, ∠N(2)–H(2)···O(22A)/(O22B) 146.30(7)/158.20(7)°] results in an infinite sheet in the *ac* plane (Fig. 2).

Another interesting feature is that, according to Vicente *et al.*,[8] the tmeda (*N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine) ligand yielded a hexanuclear complex, whereas *N*,*N*-diethylethane-1,2-diamine (deen) produced an alternating chain. On the basis of these two results they concluded that the presence of coordinated water in the tmeda complex inhibited the incoming bridging ligand (azide) from coordinating the copper(II) and terminated the growth of the polymer. On the other hand, in the case of the deen complex, no water was coordinated to copper(II), as a result of which, the bridging azido readily coordinated copper(II) favouring polymer formation. However, with the same synthetic procedure we have obtained a polymeric structure using the dpren ligand, although both the copper centres have water in their coordination sphere. Thus, the presence or absence of water in the coordination sphere does not seem to be the key factor for the formation of an alternating chain. There must be an another factor, which controls the polymer formation. We did not find any inter- or intrachain H-bonding interactions in the CCDC data of the tmeda complex,[8] whereas in our case, there are both types of interactions. Thus, we can safely conclude that the formation of hydrogen-bonding networks in our complex is the key factor and may be crucial for the formation of a 1D coordination polymer as a way to maximise hydrogen-bonding interactions in the solid state to stabilise the system. This can be also explained by considering steric factors: the NR_2 group in tmeda will produce greater steric hindrance to the approach of the bridging group to Cu than will the NHR group in dpren.

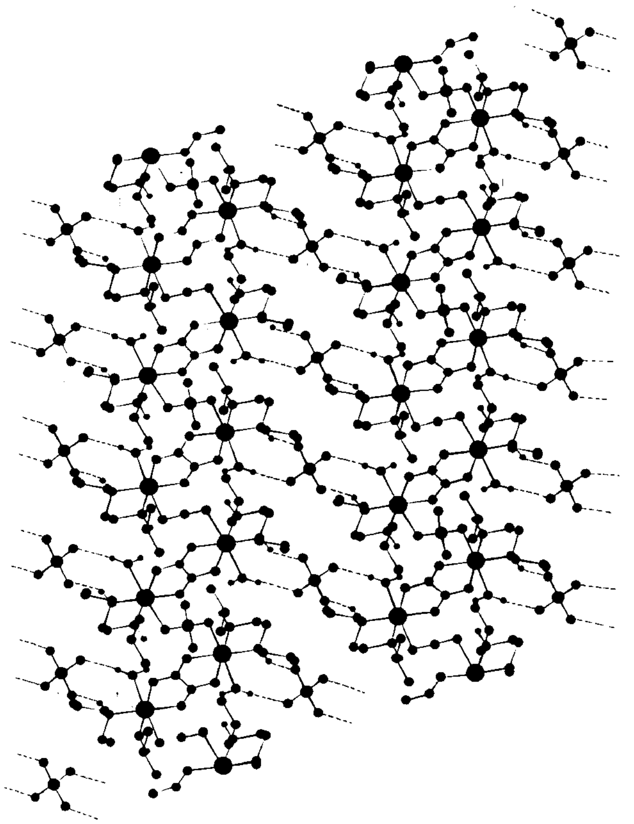

Fig. 2 View of an infinite 2D supramolecule showing the interlayer H-bonding motifs in the *ac* plane.

Another interesting property of our complex is sheet formation; the tmeda and deen[9] complexes did not produce such 2D sheets, though both of them show the presence of free perchlorate in their corresponding structures. This may be due to the terminal ligand (dpren) in which both donor nitrogens are bonded to a hydrogen, which enhances the link-up of neighbouring 1D chains into a sheet-like structure.

Magnetic properties

The molar magnetic susceptibility (for two copper atoms) gradually decreases with decreasing temperature from room temperature to 50 K (Fig. 3) then increases. The molar susceptibility value per two copper atoms is 0.0013 emu mol^{-1} at room temperature, reaching a minimum value of 0.000 15 emu

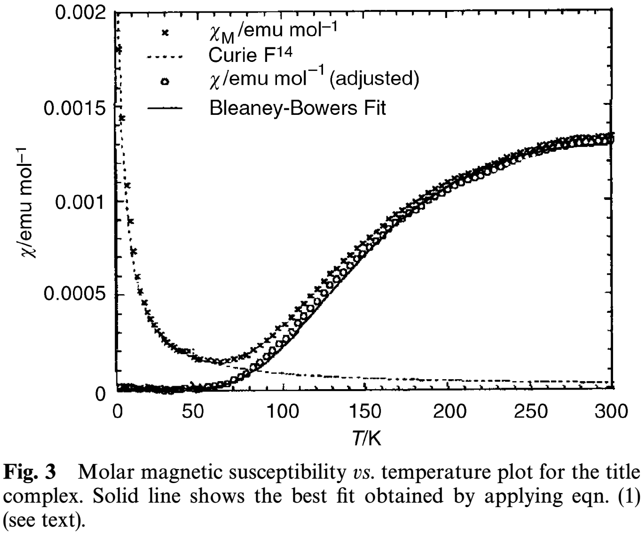

Fig. 3 Molar magnetic susceptibility *vs.* temperature plot for the title complex. Solid line shows the best fit obtained by applying eqn. (1) (see text).

mol^{-1} at 50 K. The magnetic behaviour indicates an antiferromagnetically coupled system. To calculate the coupling parameter we can consider the system as an alternating chain or a dinuclear system. On the basis of the crystal structure, in the $Cu(N_3)Cu$ part of the chain the Cu–N(azide) distance is 2.666(12) Å, even longer than that of the very weakly coupled azido-bridged system.[15] So, the coupling parameter corresponding to the apical azido bridge in our complex can reasonably be expected to be very small. Similarly, in the $Cu(ClO_4)Cu$ fragment of the chain the Cu–O(perchlorate) distance is 2.654(15) Å, which is comparable to that of the weakly coupled perchlorate bridged copper(II) system.[16] Moreover, the environment around each copper(II) is distorted octahedral with four short equatorial and two long axial bond lengths, which clearly indicates that the spin unpaired electron on each copper(II) is located in a $d_{x^2-y^2}$ orbital and the d_{z^2} orbital contains spin paired electrons. As the bridging perchlorate and azide are located in axial positions at copper(II) they should give very small or close to zero contributions to the magnetic coupling parameter. Because these bridging moieties interact with the d_{z^2} orbital (which is not magnetic) of the copper(II) the only possible superexchange pathway in this complex is through the oxalate. The magnetic orbitals ($d_{x^2-y^2}$) of the copper(II) ions interact through the oxalate anion, which binds in the equatorial positions at copper(II). From the analysis of the structural parameters we consider the complex as a magnetically isolated $[LCu(Ox)CuL]^{2+}$ dimer. The χ_M *vs.* T data of the complex are fitted well using the Bleaney–Bowers equation for the magnetic susceptibility of isotropically coupled dinuclear $S = 1/2$ ions,[7] adding an impurity term that is due to the presence of non-coupled monomeric species [eqn. (1)]

$$\chi_M = 2N\beta^2 g^2(1-\rho)[3+\exp(-2J/kT)]^{-1}/kT + N\beta^2 g^2 \rho/2kT + N\alpha \quad (1)$$

using the Hamiltonian $H = -2JS_a S_b$. The results of the best fit, shown as a solid line in Fig. 3, are $J = -331.3\ \text{cm}^{-1}$, $g = 2.05$, $\rho = 0.6\%$ with $R = 1.7 \times 10^{-7}$.

Conclusion

We present here the synthesis, crystal structure and magnetic study of a novel 1D coordination polymer of copper(II) with periodic repetition of oxalate, azide and perchlorate bridging anions. From the foregoing discussion it is found that hydrogen-bonding and steric effects govern the alternating chain formation. The terminal amine ligand and counter anion also play a vital role in 2D sheet formation. The magnetic study shows that the effect of bridging azide and perchlorate is negligible in comparison to the oxalate and the system may be considered as a magnetically isolated oxalato-bridged copper(II) dimer.

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