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Synthesis, crystal structure and magneto-structural correlation of two bi-bridging 1D copper(II) chains†

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Two 1D bi-bridging Cu(II) chains, catena-oxalate-bis[1-(2-aminoethyl)pyrrolidine-copper(II)]-0.5(squarate) perchlorate hydrate (**1**) and catena-pyrazine-oxalate-tetraaquo-dicopper(II) diperchlorate (**2**) have been synthesised and their molecular structures determined by X-ray crystallography. Compound **1** exhibits a polymeric arrangement with a ladder-like structure running parallel to crystallographic axis *a*, in which two $[(Cu(ampy))_2(ox)]$ chains (ampy = 1-(2-aminoethyl)pyrrolidine; ox = oxalate) are linked by squarate groups. The oxalate behaves simultaneously as bis-bridging and bis-monodentate towards four coplanar copper ions, a coordination mode which has never been reported for Cu(II). Compound **2** is characterized by a polymeric array with alternate repetition of bridging oxalate and 'pyz' (pyz = pyrazine). Low temperature magnetic behaviour reveals the existence of a dominant weak antiferromagnetic interaction within **1** whereas in **2** a strong antiferromagnetic interaction is observed. The results obtained experimentally corroborate the structural parameters in both **1** and **2**.

Introduction

The dicarboxylate ligand has been extensively studied in the field of molecular magnetism and in material chemistry on account of its promising application in the area of technology since it exhibits a variety of chelating abilities resulting in dinuclear, tetranuclear, 1D, 2D as well as 3D networks.[1–4] A few of these systems are also useful in material chemistry for solvent exchange due to the presence of open frameworks in their molecular structure. Among the different dicarboxylates, major work has been done with oxalate, coordinating in a bis-bidentate chelating fashion.[5] The magneto-structural correlation of μ-oxalato dinuclear complexes of Cu(II) containing linear polyamine terminal ligands has been studied thoroughly and it has been found that the magnetic interaction between the two Cu(II) centres is antiferromagnetic in nature in almost all the cases. Recently, our laboratory has given attention to designing the molecular system with a polymeric structure with two or three bridging ligands.[6] In the present paper we report the synthesis, crystal structure and low temperature magnetic behaviour of two 1D chains of Cu(II) with oxalate as one of the bridging ligands. The first one (complex **1**) is a ladder-like, one-dimensional compound made by four Cu(II) ions linked by a squarate ligand in a very uncommon μ-1,2,3,4 mode, and these entities are linked by oxalate which behaves simultaneously as a bis-bridging and a bis-monodentate ligand towards four coplanar copper ions, a coordination mode which has never been reported for Cu(II).[7] The latter (**2**) is an alternating chain of Cu(II) with oxalate and pyrazine repeated alternately. An oxalate-bridged dicopper(II) system is again linked by pyrazine to produce the chain. Low temperature magnetic study reveals the existence of antiferromagnetic interaction in both complexes. The coupling parameter through the oxalato pathway compares well with the previous data.

Experimental

Materials

High purity (98%) 1-(2-aminoethyl)pyrrolidine and pyrazine were purchased from the Aldrich Chemical Company Inc. and were used as received. All other chemicals were of AR grade.

Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin-Elmer 240C elemental analyser. The magnetic measurements were carried out on polycrystalline samples using a Quantum Design MPMS SQUID magnetometer (applied field 5 T) working in the temperature region 300–2 K. Diamagnetic corrections were estimated from Pascal's Tables.[8]

Synthesis of complex 1

An aqueous solution of disodium oxalate (10 cm^3) (0.134 g, 1 mmol) was added dropwise to a deep blue methanolic solution (5 cm^3) of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.74 g, 2 mmol) and ampy (0.228 g, 2 mmol) with continuous stirring. To this mixture an aqueous solution (5 cm^3) of sodium squarate was added drop by drop to form a green solution. Thin green single crystals suitable for X-ray diffraction were obtained by keeping the green filtrate in a $CaCl_2$-dessicator for 20 days. Yield 80%. Analytical data: Found: C, 31.57; H, 5.01; N, 9.45. Calc. for $C_{16}H_{28.5}ClCu_2N_4O_{10.25}$: C, 31.81; H, 4.72; N, 9.28%.

Synthesis of complex 2

An aqueous solution (10 cm^3) of sodium oxalate (0.134 g, 1 mmol) was added to a methanolic solution (5 cm^3) of

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† Electronic supplementary information (ESI) available: magnetization curve for **1** between 0 and 5 K and an EPR spectrum for **1**. See http://www.rsc.org/suppdata/dt/b2/b204728b/

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Table 1 Crystal data and refinement details of complexes **1** and **2**

Compound	**1**	**2**
Empirical formula	$C_{16}H_{28.5}ClCu_2N_4O_{10.25}$	$C_6H_{12}Cl_2Cu_2N_2O_{16}$
M	603.46	566.16
T/K	293(2)	293(2)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/m$
a/Å	6.081(3)	10.644(4)
b/Å	13.402(4)	10.254(4)
c/Å	16.185(5)	8.363(3)
α/°	65.85(3)	90.00
β/°	91.23(3)	90.96(2)
γ/°	82.25(3)	90.00
V/Å^3	1188.3(8)	912.6(6)
Z	2	2
D_c/g cm^{-3}	1.687	2.060
μ(Mo-Kα)/mm^{-1}	1.961	2.707
Reflections collected	8216	1890
Unique reflections/R_{int}	5046/0.0826	1135/0.0412
$R1^a$	0.0590	0.0569
$wR2^b$	0.1581	0.1526

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$.

Table 2 Selected bond lengths (Å) and angles (°) for complex **1**

Cu(1)–N(1)	2.003(5)	Cu(2)–N(3)	2.072(5)
Cu(1)–N(2)	2.051(5)	Cu(2)–N(4)	2.011(6)
Cu(1)–O(2)#1	2.017(4)	Cu(2)–O(4)	2.007(4)
Cu(1)–O(6)	1.959(4)	Cu(2)–O(5)	1.960(4)
Cu(1)–O(1)#1	2.350(4)	Cu(2)–O(2)#1	2.398(4)
Cu(1)–O(4)	2.377(4)	Cu(2)–O(3)	2.307(4)
O(1)#1–Cu(1)–O(4)	151.7(1)	O(3)–Cu(2)–O(2)#1	152.4(1)
N(1)–Cu(1)–O(6)	175.3(2)	N(3)–Cu(2)–O(4)	175.9(2)
N(2)–Cu(1)–O(2)#1	178.4(2)	N(4)–Cu(2)–O(5)	173.2(2)
C(4)–O(6)–Cu(1)	130.6(4)	C(3)–O(5)–Cu(2)	132.7(4)

Symmetry transformations used to generate equivalent atoms: #1: 1 + x, y, z.

$Cu(ClO_4)_2 \cdot 6H_2O$ (0.74 g, 2 mmol) and pyz (0.16 g, 2 mmol) with continuous stirring. A sky blue solid compound was separated which was filtered, washed with water and dissolved in a minimum amount of dilute (4N) ammonia solution. The resulting deep blue solution was kept in refrigerator for 7 days to obtain diffraction quality single crystals. Yield 65%. Analytical data: Found: C, 12.58; H, 2.00; N, 4.60. Calc. for $C_6H_{12}Cl_2Cu_2N_2O_{16}$: C, 12.71; H, 2.11; N, 4.94%.

Crystallographic data collection and refinement

Data collections were carried out on a Nonius DIP-1030H system equipped with a graphite monochromator and Mo-Kα radiation (λ = 0.71073 Å). A total of 30 frames was collected, each with a rotation of 6° about ϕ, an exposure time of 20 min, and the detector positioned at 80 mm from the crystal. Data reductions and cell refinements were carried out using the programs Mosflm and Scala.[9] The structures were solved by Patterson and Fourier analyses (SHELXS-97),[10] and refined by the full-matrix least-squares based on F^2 using SHELXL-97.[10] In both crystals, the perchlorate oxygens were found to be disordered over two positions around a Cl–O bond [occupancies 0.71(2)/0.29 and 0.83(3)/0.17 in **1** and **2**, respectively]. The disorder in these anions required the introduction of constraints on bond lengths and angles for optimizing the geometries. In **1** a residual in the Fourier map was assigned to a water oxygen, and owing to the low occupancy (0.25), hydrogen atoms were not associated. All calculations were performed using the WinGX System, Ver 1.64.03.[11] Details of the structural determination and refinement are listed in Table 1.

CCDC reference numbers 185893 and 185894.

See http://www.rsc.org/suppdata/dt/b2/b204728b/ for crystallographic data in CIF or other electronic format.

Results and discussion

The X-ray analysis of both of the complexes disclose 1D coordination polymers comprising a $[CuL_2]_2(ox)$ structural motif; however, the different coordination mode of the oxalate anion towards copper induces different topologies. In complex **1** (L_2 = ampy), $[(CuL_2)_2(ox)]_n$ chains are linked by squarate anions whereas in **2** (L_2 = H_2O) the structural units are connected by pyz ligands.

Structure description of 1

The geometry of the copper ions in **1** is that of a tetragonal octahedron with an N_2O_4 chromophore: in the equatorial plane that comprises the 'ampy' N donors, the oxygens from oxalate and squarate, the coordination distances range from 1.959(4) to 2.072(5) Å, where the Cu–O bond lengths appear slightly shorter than those of Cu–N (Table 2). The axial sites are occupied by oxalate oxygens with weaker Cu–O distances [2.307(4)–2.398(4) Å]; the relative O–Cu–O bond angles, of about 152°, indicate severe distortions from the ideal octahedral geometry (Fig. 1). It is worthwhile to observe that, making allowance for the e.s.d.s, the oxalate C=O distance involved in metal bridging appears slightly longer [O(2) 1.267(7), O(4) 1.259(7) Å] when compared with the other two [O(1) 1.233(7), O(3) 1.230(7) Å]. In fact, the oxalate behaves simultaneously as a bis-bridging [through O(4) and O(2)] and bis-monodentate [O(3) and O(1)] ligand towards four coplanar copper ions, a coordination mode which has never been reported for the copper ion. The X-ray structural determination evidences a polymeric arrangement with a ladder-like motif running parallel to crystallographic axis a, in which two $(Cu(ampy))_2(ox)$ chains are linked by squarate species that feature the rungs (Figs. 1 and 2). This framework (Fig. 2) appears to be composed of empty boxes, of dimensions 7.00 × 6.08 Å, which corresponds to the shorter Cu–Cu separation across the squarate and oxalate, respectively, while 3.470(2) represents the distance between Cu(1) and Cu(2) bridged by the dicarboxylate anion. The squarate, located on a symmetry centre, has a fourfold coordination mode [Cu–O of 1.959(4), 1.960(4) Å] and its orientation is such that it makes an angle of 43.5° (mean value) with the equatorial copper planes. The dihedral angle between the squarate and the dicarboxylate anion is 80.2(2)°.

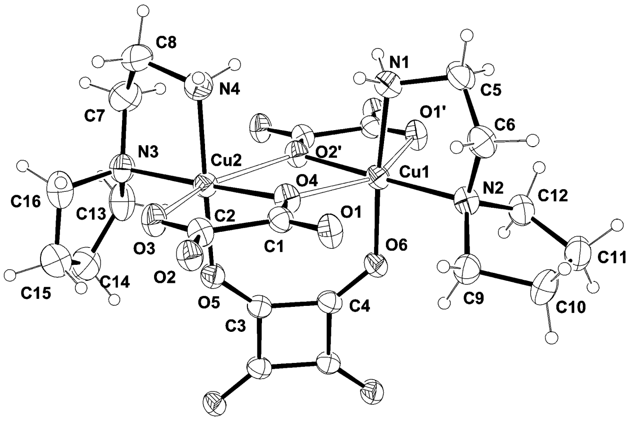

Fig. 1 ORTEP drawing (ellipsoids at 30% probability level) of the dicopper core inside the polymeric structure of **1**. Open bonds indicate longer axial distances.

The present complex, besides the tetranuclear species $[(tren)_4Cu_4(squarate\text{-}\mu_4)]^{6+}$ [where tren = tris(2-aminoethyl)amine],[12] is the only one with squarate displaying four comparable, *i.e.* short, Cu–O linkages. Moreover, a search in the Cambridge Database (CSD)[13] for angles subtended by the oxygen of squarate reveals a wide range of values, from 109 to 153°. As a

Table 3 Selected bond lengths (Å) and angles (°) for complex **2**

Cu–O(1)	2.008(3)	Cu–O(2)	1.994(4)
Cu–N(1)	2.287(6)		
O(1)–Cu–O(1)#1	83.46(18)	O(1)–Cu–N(1)	87.26(15)
O(2)–Cu–O(2)#1	94.4(3)	O(2)–Cu–N(1)	101.34(19)
O(1)–Cu–O(2)	169.2(2)	C(2)–O(1)–Cu	111.4(3)
O(1)#1–Cu–O(2)	90.31(19)		

Symmetry transformations used to generate equivalent atoms: #1: *x*, −*y*, *z*.

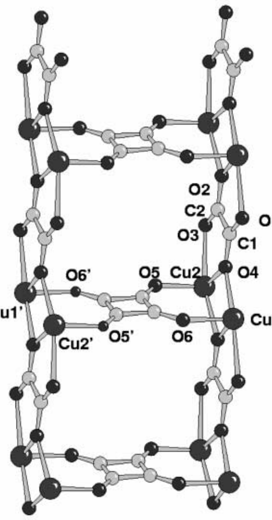

Fig. 2 Schematic drawing of the ladder-like polymer built up by oxalate and squarate coordinated to copper ions for complex **1**. (For the sake of clarity the ampy ligands are omitted).

comparison, the present ones [132.7(4), 130.6(4)°] are close to those found (130.1–133.4°) in the 3D network of $[(\text{squarate})_4\text{Cu}_4(\text{H}_2\text{O})_8]_n$,[12] which comprises three crystallographically independent squarates presenting a μ$_4$-coordination. The perchlorate anions are packed among the polymers, weakly interacting (at *ca.* 3.0 Å) with the 'ampy' nitrogens.

Structure description of complex 2

The polymer of **2** evidences a staircase arrangement with the oxalate anion that, acting as a bis-chelating ligand, coordinates two $\text{Cu(H}_2\text{O)}_2$ units and the resulting fragments are connected through 'pyz' ligands (Fig. 3, Table 3). In the oxalato complex chemistry,[14] the adoption of the present coordination mode to form five-membered rings with the metal centres is extensively predominant in the literature.[13] As illustrated in Fig. 3, the coordination geometry of the copper ion is square pyramidal (SP). The basal sites are occupied by the chelating oxalate oxygens and two water molecules with the metal displaced by 0.163 Å from the basal plane towards the apical 'pyz' N donor. The Cu–O bond lengths of 2.008(3) and 1.994(4) Å are significantly shorter than the apical Cu–N bond distance [2.287(6) Å]. In the crystal the copper ions and the 'pyz' N atoms are located on a mirror plane thus bisecting the polymer elongated in the direction of the *c* axis. The chain motif is specified by a dihedral angle of 74.2(2)° formed by the pyz ring and the oxalate plane. The Cu–Cu distance spanned by the 'pyz' is 7.341 Å, while the copper ions bridged by oxalate are 5.233 Å apart. The shortest distance between metals pertaining to different chains is 5.760 Å. The coordinated water molecule is involved in a hydrogen bonding interaction (2.87 Å) with a perchlorate oxygen.

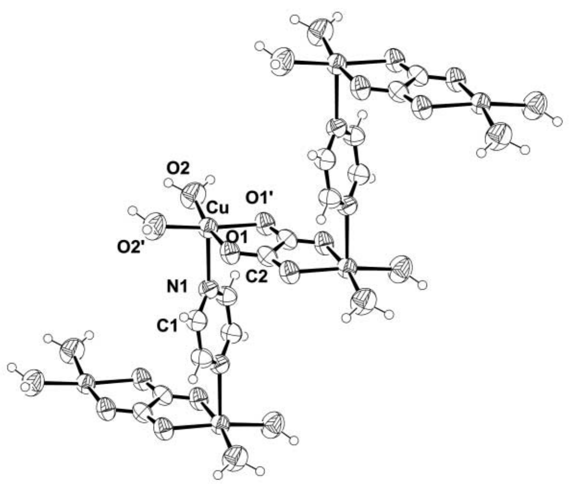

Fig. 3 Staircase arrangement of the complex **2** with copper ions and pyz nitrogens located on a mirror plane (thermal ellipsoids at 50% probability level).

Magnetic properties

Complex 1. The magnetic behaviour of compound **1** is illustrated in Fig. 4 by means of a plot of $\chi_M T$ and χ_M (inset) *vs.* the temperature in the range 2–300 K. At room temperature the $\chi_M T$ value is 5.08 cm^3 mol^{-1} K for 12 Cu ions (see below for the fit). This corresponds to 0.423 cm^3 mol^{-1} K per Cu(II) ion, a typical value for a quasi-isolated copper ion. Upon cooling from room temperature, the $\chi_M T$ product decreases continuously to 50 K and then in a more abrupt form to 2 K, thus indicating small global antiferromagnetic interactions between the Cu(II) ions. The same character is shown by the χ_M curve (inset of Fig. 4). At room temperature χ_M is 0.0172 cm^3 mol^{-1}. Upon cooling from room temperature, χ_M increases to a maximum of 0.322 cm^3 mol^{-1} at 7 K. After this maximum, there is a pronounced decrease up to 2 K (χ_M = 0.0477 cm^3 mol^{-1}). A maximum in this low temperature region indicates that the antiferromagnetic coupling is very small. For fitting, it is important to consider all possible coupling parameters. A scheme of 12 copper ions is given in Fig. 5. J_1 and J_2 will be the coupling parameters through the squarato bridging ligand and J_3 through the oxalato bridging ligand. In this kind of coupling mode it is not possible to fit with an equation derived by Kambe's method. Thus, it has been made by the irreducible tensor operator formalism (ITO) using the CLUMAG program.[15] In order to avoid over-parametrization in the fitting curve the diagonal coupling constant ($J_{14} = J_{23}$ and $J_{28} = J_{46}$) has been assumed to be zero. In the case of $J_{14} = J_{23}$ this hypothesis is consistent with literature data (*trans*-O,O-squarato).[16–18] On the other hand, taking into account that the EPR measurements indicate a g_{average} = 2.14, the *g* value variation has been

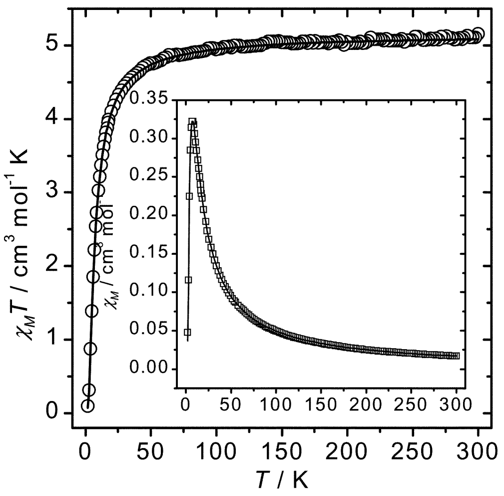

Fig. 4 Plot of $\chi_M T$ *versus* *T* data for complex **1** with the solid lines showing the best fit obtained (inset: plot of χ_M *versus* *T* data).

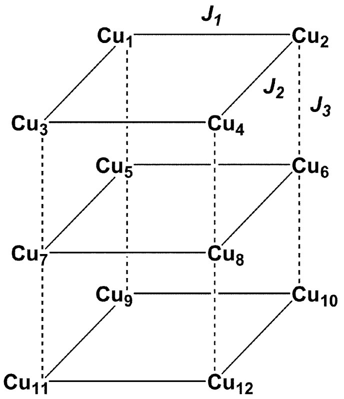

Fig. 5 Scheme of 12 copper atoms to fit the magnetic data of **1** with different coupling parameters through different pathways. To simplify the figure, only one J_1, one J_2 and one J_3 have been indicated.

limited to between 2.11 and 2.15. For fitting the one-dimensional systems, 12 copper ions are considered, according to Fig. 5, to obtain reasonable dimensions of the matrix to be diagonalized. The least-squares fitting procedure led to $J_1 = -7.9$ cm^{-1}; $J_2 = -3.8$ cm^{-1}; $J_3 = 0.96$ cm^{-1} and $g = 2.14$ with an agreement factor of $R = 2.4 \times 10^{-6}$ {R is defined as $\Sigma[(\chi_M)_{obs.} - (\chi_M)_{calc.}]^2/\Sigma[(\chi_M)_{obs.}]^2$}. Taking into account the small J values (in agreement with the structural factors) there is a possible correlation between them. For this reason, any over-parametrization could give worse results. In fact, the introduction of TIP does not significantly modify the results. After several fitting procedures, it is possible to conclude that the uncertainty in the J values is within 5–10%.

To complete and corroborate the susceptibility data, a magnetization experiment at 2 K between 0 and 5 T was performed (Fig. 6). The simulation was made using the MAGPACK program[19] employing the coupling parameters found from the $\chi_M T$ curve, and gives the straight line shown in Fig. 7. The correspondence between experimental and calculated points is good. It must be stressed that the $M/N\beta$ value without antiferromagnetic coupling for Cu(II) ions should be approximately 1.2 (for $g = 2.14$) (Brillouin formula).

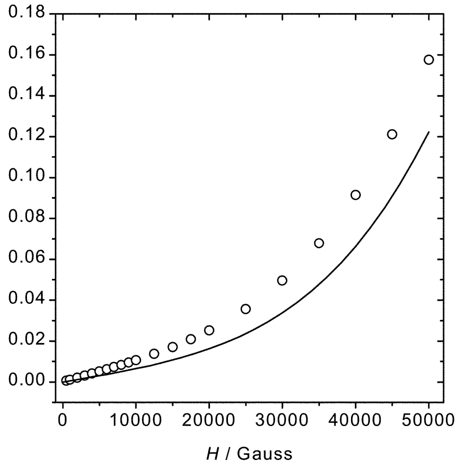

Fig. 6 Plot of the reduced magnetization ($M/N\beta$) for one coper(II) ion (open points). The solid line represents the simulation with the fitted J and g parameters (see the text for the program used).

The EPR spectra of complex **1** do not change with temperature (from r.t. to 4 K). They show the typical axial pattern with $g_{\|} = 2.28$ and $g_{\perp} = 2.07$ ($g_{average} = 2.14$), with the unpaired electrons in the $d_{x^2-y^2}$ orbital according to the square-pyramidal geometry.

Complex 2. Magnetic studies in the 300–2 K temperature range reveal that the molar magnetic susceptibility for compound **2** is 0.00149 cm^3 mol^{-1} at room temperature and decreases to reach a minimum at *ca.* 50 K (1.1×10^{-4} cm^3 mol^{-1}) and then suddenly increases with lowering temperature to 0.0018 cm^3 mol^{-1} at 2 K. The $\chi_M T$ value is 0.447 cm^3 mol^{-1} K at room temperature and rapidly decreases lowering the temperature to 0.01 cm^3 mol^{-1} K at 75 K and 0.00378 cm^3 mol^{-1} K at 2 K (Fig. 7). The χ_M curve is typical for a very strong antiferromagnetic coupling with a small amount of monomeric copper(II) impurities, manifested at low temperature. The $\chi_M T$ curve is also indicative of this strong antiferromagnetic coupling.

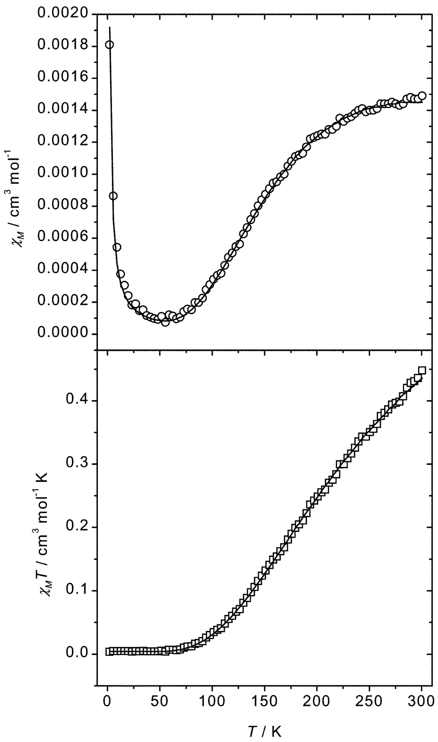

Fig. 7 Plot of χ_M *versus* T data for complex **2** (upper part) with the solid lines showing the best fit obtained (below: plot of $\chi_M T$ *versus* T data).

Taking into account the structure, we can interpret the magnetic results based on dinuclear Cu(II)–oxalato complexes linked by pyrazine bridging ligands. As indicated in the structural part, the pyrazine bonds to copper(II) through the d_{z^2} orbital (long distance). The SP (square-pyramidal) character of copper(II) ions is 100%. Thus, the magnetic orbital is centred exclusively in the $d_{x^2-y^2}$ magnetic orbital. This feature gives a strong antiferromagnetic coupling between two consecutive copper(II) ions linked by the oxalato ligand and almost nil (zero) coupling between two consecutive copper(II) ions linked by the pyrazine ligand. Thus, even if structurally the compound **2** is a chain, from a magnetic point of view it can be considered as a dinuclear complex linked by pyz, assuming that this coupling will be non-existent. The singlet–triplet energy gap (J) was deduced from least-squares fit of the experimental data to the temperature for isotropic exchange in the copper(II) dimer, according to the Bleaney–Bowers equation modified according to Kahn [eqn. (1)] to take into account some paramagnetic impurities, always visible when the antiferromagnetic coupling is very strong.

$$\chi_M = \frac{2Ng^2\beta^2}{kT}\left[3+\exp(-J/kT)\right]^{-1}(1-\rho)+\frac{Ng^2\beta^2}{2kT}\rho \quad (1)$$

The Hamiltonian employed is $H = -JS_1S_2$. The symbols have their usual meanings, and ρ is the percentage of non-coupled impurity. The best fits, shown as the solid line in Fig. 7, afforded the parameter values $J = -336.1\ \text{cm}^{-1}$; $g = 2.15$; $\rho = 0.4\%$ and $R = 1.2 \times 10^{-6}$ $\{R$ is defined as $\Sigma[(\chi_M)_{obs.} - (\chi_M)_{calc.}]^2/\Sigma(\chi_M)_{obs.}{}^2\}$. The J value is large as in preceding planar μ-oxalato copper(II) complexes.[20] X-Band EPR spectra of polycrystalline samples at room temperature show the typical axial pattern with $g_{\parallel} = 2.29$ and $g_{\perp} = 2.07$, this pattern is indicative of a $d_{x^2-y^2}$ ground state, as shown by the structure. The intensity of the spectrum diminishes with lowering the temperature. At 4 K the signal is very weak, but the g values are practically the same. This lowering is indicative of the strong antiferromagnetic coupling.

Magneto-structural correlations

Complex 1. *(a) Squarato pathway.* The number of tetrameric metal complexes with the four metal cations being bridged by a single squarato ligand in a μ-1,2,3,4-coordination mode is very rare.[12,21] The most typical coordination modes are μ-1,2 (*cis*) and μ-1,3 (*trans*). The *trans* coordination gives a very small coupling, close to zero.[16,17] The *cis* coordination gives a small antiferromagnetic coupling (close to $-10\ \text{cm}^{-1}$).[17] Julve *et al.* have reported a complete study of the coupling constant considering different possible geometries for each Cu(II) ion in a μ-1,2,3,4 tetranuclear compound. When the copper(II) has TBP (trigonal bipyramidal) geometry the J constant could reach *ca.* $-20\ \text{cm}^{-1}$, while for SP this coupling constant is considerably reduced, to approximately half (16/9 according to their calculations).[12] In these calculations, the authors assume the planarity of the squarato ligand giving, thus, only a J value. In the present case, this is not true. The planes of the copper(II) ions are slipped two by two, owing to a shift of the squarate with regard to the planarity. This feature (Fig. 8) gives two different J values (J_1 and J_2 as considered in the fit). The J_2 value corresponds to the coupling between the copper(II) ions through O(1) and O(2) atoms. The magnetic orbitals are not well placed to have a good overlap between the $d_{x^2-y^2}$ orbitals of each Cu(II) centre, such as in the case of the Cu ions through J_1 (which are well aligned to give a very good overlap). Thus, it is logical in the two different J values found in the fit procedure that J_2 is the lower.

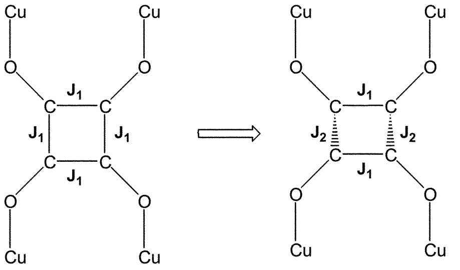

Fig. 8 Schematic representation of how two different coupling parameters J_1 and J_2 are originated in complex **1** (see the text).

(b) Oxalato pathway. The great majority of the μ-oxalato-bridged copper(II) complexes that have been characterized structurally belong to the μ-1,2,3,4 mode. As is well-known, this coordination geometry is advantageous to give strong antiferromagnetic interactions through the multi-atom bridge (J close to $-400\ \text{cm}^{-1}$). The number of axial–equatorial μ-oxalato-bridged copper(II) systems with five-coordinated terminal copper atoms is scarce. The present complex **1** is one of them. It has been stressed that the weakest interactions are found for the complexes with nearly SP copper(II) coordination geometry, whereas the interaction becomes stronger as the predominance of TBP character increases.[22,23] As recently reported it is possible to find weak ferromagnetic exchange coupling in the SP cases (SP geometry). The smallest interactions occur when one of the copper-bridge distances is long (the oxalato bridge is asymmetrically coordinated). In this case, the magnetic orbitals of the two metal centres are parallel to each other and perpendicular to the plane of the bridging oxalate anion. For this orientation, the overlap between the magnetic orbitals through the bridge is very poor, and consequently the magnetic coupling is very weak and is of antiferro- or ferro-magnetic nature. This is the case for complex **1**. The value of the ferromagnetic coupling observed in compound **1** is similar to those for previously reported asymmetric bis-chelating oxalato in other copper(II) dimers or chains.[23]

Complex 2. Many papers have been devoted to magneto-structural correlations in oxalato complexes. When the Cu(II) ions are in the SP geometry, the greatest J values are found in planar μ-oxalato complexes. The deviation of this geometry towards TBP gives a small overlap in the $d_{x^2-y^2}$ magnetic orbitals and, thus, decreases the antiferromagnetic coupling. On the other hand, when one looks at the height of the copper atom above the basal plane this indicates that the geometry around the copper ions has somewhat deviated from the ideal 'magnetic' geometry. In compound **2** the SP character is 100%, according to the Addison parameter, and the deviation of the copper ions is (0.16 Å) from normal between the values found in the literature for these planar oxalato complexes.[24] Thus, the antiferromagnetic coupling should be very strong. In fact, one of the strongest antiferromagnetic complexes reported so far is $[Cu_2(tmen)_2(H_2O)_2(C_2O_4)](ClO_4)_2\cdot 1.25H_2O$ (tmen = tetramethylethylenediamine), where $J = -385\ \text{cm}^{-1}$.[24a] The deviation of the copper(II) ions from the basal plane (0.1548 Å) is almost the same in comparison to complex **2**. The Cu–O(oxalato) distances are 1.981 Å in the complex reported by Julve *et al.*[24a] and 2.008 and 1.994 Å in **2**. These slightly greater distances may be the origin of the lower antiferromagnetic coupling. Taking into account the shape of the curve, owing to the strong antiferromagnetic coupling, trying to introduce the main-field approximation in the Bleaney–Bowers formula to calculate a possible coupling between Cu–pyrazine–Cu failed. The results are the same, without improving the fit. This feature is logical taking into account that this possible J', if any, must be very close to zero.

Concluding remarks

We have presented here the synthesis, crystal structure and low temperature magnetic studies along with the magneto-structural correlation of two new bi-bridging copper(II) chains. Complex **1** is a ladder-like chain composed of empty boxes of dimensions 7.00 × 6.08 Å with a novel mode of bridging oxalate acting simultaneously as a bis-bridging and bis-monodentate ligand towards four coplanar copper ions, a coordination mode which has never before been reported for copper(II) ion. Complex **2** consists of Cu(II) coordination polymers with alternate repetition of pyrazine and oxalate. Both of the complexes have been characterized by low temperature magnetic studies. Fitting of the temperature dependent susceptibility data reveals the existence of a very strong antiferromagnetic interaction through oxalate pathway in **2**. On the other hand, the oxalate pathway in **1** mediates a very weak ferromagnetic interaction whereas squarate plays as an antiferromagnetic coupler to induce in the molecule weak antiferromagnetic properties. The coupling parameters in both the complexes have correlated with their structural parameters.

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