Magneto-structural correlations in a new oxalato-bridged Cu(II) alternating-exchange spin-chain compound

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Abstract
A new oxalato-bridged copper(II) compound, $Cu(ox)(pyOH) \cdot H_2O$ (ox = oxalate,
pyOH = 3-hydroxypyridine), has been synthesized and characterized by x-ray diffraction and
magnetic susceptibility measurements. The Cu(II) ions are bridged by oxalate molecules with
two different arrangements alternating along a chain parallel to the b-axis. To the best of our
knowledge, this is the first example of a metal–oxalate chain with such a combination of oxalate
bridges. Due to the specific structural properties, the magnetic susceptibility was analysed in the
framework of an alternating-exchange spin-chain. From a least-squares fit, an antiferromagnetic
coupling constant $J_1 = (442 \pm 5)$ K and an alternation parameter $\alpha = 0.13 \pm 0.06$ were
derived, which classify $Cu(ox)(pyOH) \cdot H_2O$ as a strongly dimerized spin-chain compound. It is
argued that the strength of the magnetic coupling is mainly determined by the displacement of
the Cu(II) ions out of the basal plane of the local Cu environment.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Quantum magnets of restricted dimensionality are of continuing high interest due to the wealth of exciting and unexpected phenomena originating from the interplay of low dimensionality (low-D), competing interactions and strong quantum fluctuations. Owing to their relative simplicity and their model character, much attention has been devoted to one-dimensional (1D) systems such as the uniform or the alternating-exchange $S = 1/2$ Heisenberg chains, the $S = 1$ Haldane chain or even- and odd-leg ladder systems, see e.g. [1, 2] for a review. In the search for new low-D quantum magnets, one focus is directed towards substances with moderate or intermediately strong exchange interactions J between the magnetic ions, i.e. J values ranging from a few Kelvin up to several tens of Kelvin, enabling investigations to be performed in large effective magnetic fields $g\mu_B H/J$ by using accessible laboratory magnets.

Good candidates for a systematic investigation of the properties of low-D quantum magnets are metal–organic compounds [3–5] where the dimensionality and magnitude of the magnetic interactions can be tuned by choice and arrangement of the organic ligands, see e.g. [6, 7]. Magnetic exchange inside metal–organic dimers or 1D magnetic interactions can be found in crystals which are composed of chains of metals, bridged by carboxylate groups of organic molecules and which contain additional large organic ligands as spacers to separate the chains [8–14]. Molecules such as betaine b $= (CH_3)_3NCH_2COO$, with one carboxylate group and a large chemically inactive tail, may combine the bridging and spacer functions in one entity. A typical example is the antiferromagnetic chain in 3b·$MnZnCl_4$ [15].

More flexibility in designing magnetic chain structures, however, would enable the combination of two different organic molecules, a large molecule as spacer (to separate the chains) and a small dicarboxylate or diamine, for instance, to

bridge the metal ions. As it happens, the oxalate molecule has turned out to be an especially suitable bridging unit for mediating magnetic interactions. There are several compounds with oxalate metal chains known as 1D ferro- or antiferromagnets. Most of them are of the composition $[M(ox)L_2]_n(H_2O)_x$ with $M = Co^{2+}$, Ni^{2+}, Cu^{2+}, ox = oxalate $(C_2O_4)^{2-}$ and the ligands L = 3-hydroxypyridine [16, 17], isoquinoline [17], aminopyridine [18, 19] or even just water [20]. In theoretical studies [9, 21], the correlation between magnetic interaction and the structural configuration of the magnetic ions has been investigated and classified. According to Cano *et al* [9], oxalato-bridged Cu^{2+} ions exhibit basically four different configurations of the singly occupied molecular orbitals (SOMOs): 'coplanar', 'perpendicular', 'parallel' and 'trigonal–bipyramidal'. In the materials cited above, there are many examples of the 'parallel' configuration, but only two examples of the 'coplanar' arrangement, one with Ni^{2+} and one with Co^{2+} [18].

We have synthesized a new compound of composition $Cu(ox)(pyOH)·H_2O$ with ox = oxalate and pyOH = 3-hydroxypyridine. It has a Cu:pyOH ratio of 1:1 unlike the 1:2 ratio of the already known $Cu(ox)(pyOH)_2$ system [16]. Both crystal structures contain chains of oxalato-bridged copper ions but exhibit very different magnetic properties.

2. Experiment

2.1. Synthesis and crystallographic characterization

Crystals of $Cu(ox)(pyOH)·H_2O$ were grown from aqueous solution as the by-product of the synthesis performed along the route described by Castillo *et al* [16]. A mixture of commercial pyOH and freshly made $K_2Cu(ox)_2·2H_2O$ in the ratio 3:1 was dissolved in pure water. On evaporation of the solvent, two different phases crystallized, blue isometric crystals of $Cu(ox)(pyOH)_2$, which have already been described [16] and light-green platelets with dimensions of typically $0.1 \times 2 \times 3$ mm³ of $Cu(ox)(pyOH)·H_2O$, which we found to be a new phase.

The crystal structure of $Cu(ox)(pyOH)·H_2O$ was determined by single crystal x-ray diffraction, using a four-circle diffractometer from Oxford Diffraction with a charge coupled device (CCD) detector. Experimental details and structural data have been published previously by some of the present authors [22]. A description of the structural features, important for the interpretation of magnetic properties, is included in section 3.1.

2.2. Magnetic measurements

The magnetic measurements were performed on single crystalline $Cu(ox)(pyOH)·H_2O$, employing a quantum design superconducting quantum interference device (SQUID) magnetometer in the temperature range 2–300 K and in fields of up to 5 T. Single crystals of the above 1:1 phase were separated from other materials of different appearance, including the 1:2 phase and a phase of unknown composition. A bundle of well-shaped single crystals with a total mass of 7.89 mg was selected for the

experiments. These crystallites, randomly oriented, were immersed in a small amount of paraffin inside the sample holder. Due to this procedure, the individual crystals were unable to move, leading to a significant increase of the signal-to-noise ratio.

3. Results

3.1. Crystal structure

The crystals of $Cu(ox)(pyOH)·H_2O$ are monoclinic, space group $P2_1/c$ (No. 14), with lattice constants $a = 12.915$ Å, $b = 9.162$ Å, $c = 8.247$ Å, $\beta = 98.49°$. The crystal structure is built up from oxalato-bridged copper ions, hydroxypyridine molecules and crystal water. Each Cu^{2+} ion has a slightly distorted bipyramidal coordination, formed by the nitrogen atom from a hydroxypyridine molecule and five oxygen atoms from three different oxalate molecules, cf figures 1–3.

The basal plane of the bipyramid is formed by the nitrogen atom and three oxygen atoms (O1A, O2A and O1B) with copper–ligand distances in the range of 1.98–2.01 Å, see [22] for details of the crystal structure. The apical positions are occupied by oxygen atoms (O2B, O2B′) at larger distances of 2.35 and 2.41 Å [22]. Each of these apical oxygen atoms is shared by two Cu polyhedra, thus providing a quasi-2D connectivity of the structure, as shown in figure 1. The hydroxypyridine rings lie above and below the 2D layers, separating these layers by the length of the *a*-axis.

In considering the bond strength, however, there are direct bonds only between copper and the four atoms in the basal plane of the bipyramid, forming –Cu-oxalate-Cu-oxalate– chains along the *b*-axis, cf figure 1. Due to the lack of such direct bonds perpendicular to the basal plane, the inter-chain coupling via the apical oxygen atoms along the *c*-axis is expected to be very small. This is corroborated by magneto-structural investigations on a group of hydroquinone-based Cu(II) compounds, where a similar behaviour was discovered [6].

The new and important structural feature of $Cu(ox)(pyOH)·H_2O$ manifests itself in the alternation of two centrosymmetric oxalate molecules **ox-A** and **ox-B** which are symmetrically non-equivalent. Both molecules bridge pairs of copper ions in a bisbidentate mode, but the oxalate molecule shows different orientations relative to the bipyramid basal plane. For **ox-A**, the bridging oxalate molecule joins corners of a bipyramid basal plane, leading to a configuration where the two basal planes of the Cu bipyramids and the **ox-A** molecule lie in a common plane, see figure 2. This corresponds to the 'coplanar' configuration according to the classification given by Cano *et al* [9].

The **ox-B** molecule is orientated perpendicular to the two neighbouring copper basal planes and its carboxyl groups each connect a corner of a basal plane with its apex, see figure 3. The two pyramidal bases are parallel to each other (as in the case of **ox-A**) but are in different planes, corresponding to the 'parallel' configuration due to Cano *et al* [9].

If the coordination of the central metal ion were to be ideally octahedral, then these two types of oxalate bridges would be indistinguishable as each square section of the
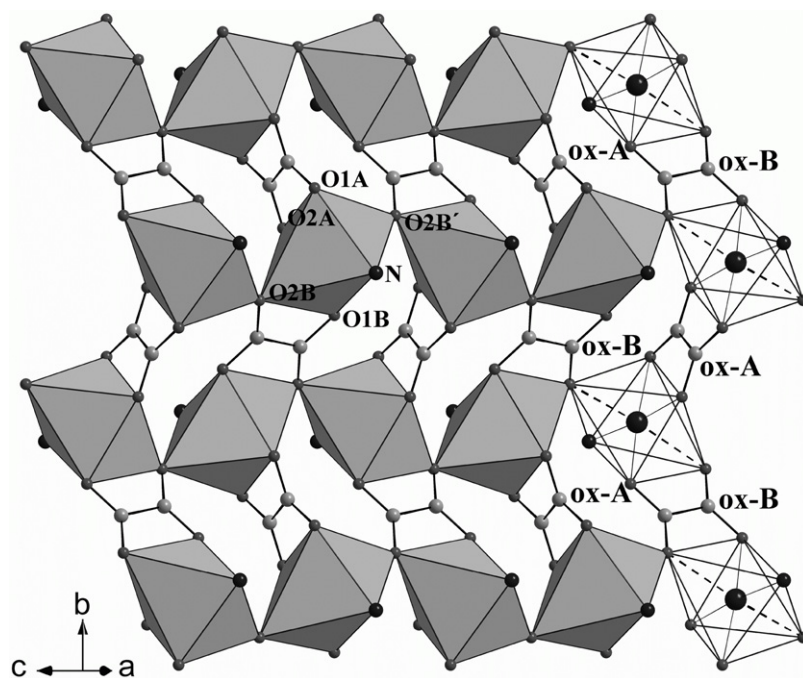
Figure 1. Two-dimensional network of oxalato-bridged Cu^{2+} ions in $Cu(ox)(pyOH) \cdot H_2O$. The copper coordination sphere is a slightly distorted $CuNO_5$ octahedron. The apical positions are occupied by the oxygen atoms O2B and O2B′. The basal plane of the bipyramid is formed by the nitrogen atom (N) and three oxygen atoms (O1A, O2A and O1B). The dashed lines indicate the contacts of the copper ions with two apical oxygen atoms. **ox-A** and **ox-B** are two non-equivalent oxalate molecules. 3-hydroxypyridine and water molecules have been omitted for clarity.
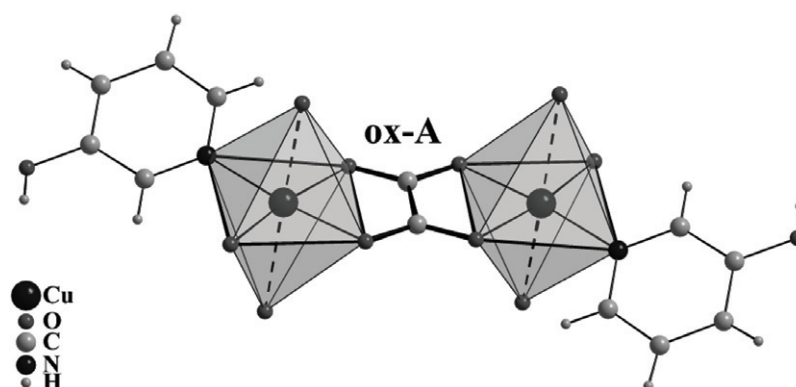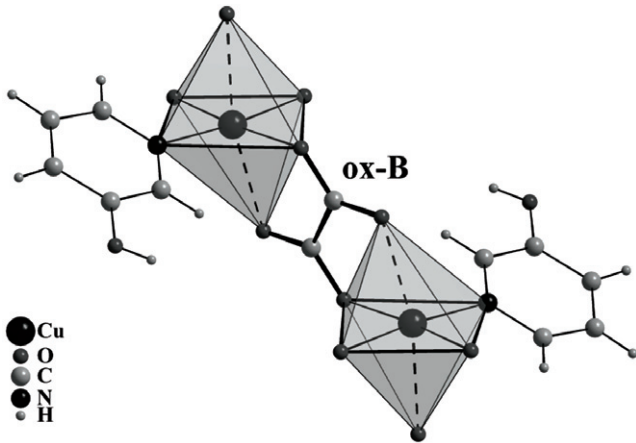

Figure 2. The Cu–oxalate–Cu bridge via **ox-A**, representing a 'coplanar' configuration.

octahedron could be taken as the basal plane. For the d^9 configuration of Cu^{2+}, however, the energies of the $d_{x^2-y^2}$ and the d_z^2 orbitals are significantly different due to the Jahn–Teller effect. In an elongated octahedral ligand field, the single electron occupies the $d_{x^2-y^2}$ orbital. This is the bonding orbital and in this plane there are four short bonds of approximately quadratic copper coordination.

Thus the terms 'coplanar', 'parallel' or 'perpendicular' characterize the relative orientations of the $d_{x^2-y^2}$ orbitals of the bridged copper ions. Depending on the case, none (**ox-A**) or two (**ox-B**) of the oxygen atoms of the oxalate bridge are orientated towards the antibonding d_z^2 orbital. This is the origin of the large differences in magnetic interaction strength found in oxalato-bridged binuclear copper complexes [9, 21], which

is high for 'coplanar', intermediate for 'perpendicular' and low for 'parallel' complexes.

The previously discovered copper oxalate chains with aromatic ligands [16–20] belong mainly to the 'parallel' topology case and reveal weak antiferromagnetic or even ferromagnetic interactions. Only one example is known with the 'perpendicular' topology, namely 2-amino-4-methylpyridine, which has two non-equivalent oxalate bridges. The magnetic properties of this system were modelled by an alternating Heisenberg chain with $J_1 = 96$ K and $J_2 = 84$ K [16]. The case of 3-aminopyridine ($J_1 = 64$ K, $J_2 = 2$ K) [18] does not seem to fit into this scheme at first glance because the copper coordination is nearly ideally octahedral. The special magnetic properties of 3-

Figure 3. The Cu–oxalate–Cu bridge via **ox-B**, representing a 'parallel' configuration.

Figure 4. Temperature dependence of the molar magnetic susceptibility χ_{mol} of a bunch (total mass $m = 7.89$ mg) of randomly oriented single crystals of $Cu(ox)(pyOH) \cdot H_2O$ (open squares) in the temperature range 2–300 K in a magnetic field of 1 T. The solid line is a least-squares fit according to [23]. For details see the text. Inset: inverse susceptibility in the low-temperature range.

aminopyridine, however, are explained by disorder of several elongated Jahn–Teller states which results in a mixing of different bridging topologies [18].
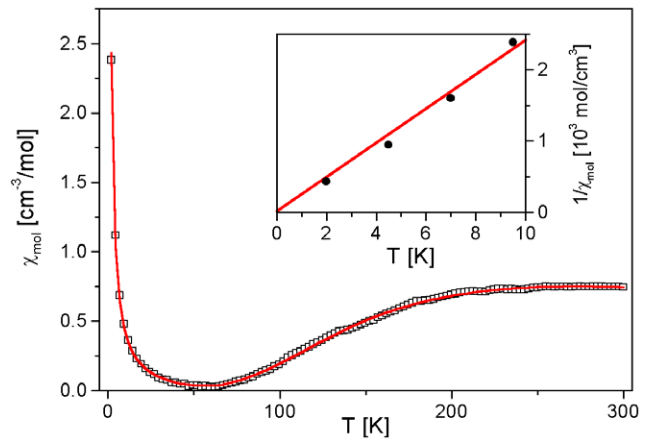
The crystals of $Cu(ox)(pyOH)_2$ reveal 1D ferromagnetic interactions with $J = -1.9$ K [16]. There are two hydroxypyridine molecules attached to each copper ion instead of one, which surround the chains on four sides, leading to large chain separations with a shortest inter-chain Cu–Cu distance of 8.74 Å. All oxalate molecules, and hence all Cu–ox–Cu bridges, are equivalent and adopt the 'parallel' configuration consistent with the observed weak ferromagnetic interaction.

In contrast to the magnetic properties of $Cu(ox)(pyOH)_2$, the newly discovered phase of $Cu(ox)(pyOH) \cdot H_2O$ exhibits two different exchange paths alternating along the *b*-axis. This feature, along with the presumably very small inter-chain coupling along the *c*-axis, as described above, suggests a description of the magnetic properties in terms of an alternating-exchange spin-chain. An exchange anisotropy due to a Dzyaloshinskii–Moriya interaction between two neighbouring Cu^{2+} ions is not expected, because the two centrosymmetric oxalate molecules ox-A and ox-B both exhibit a centre of inversion symmetry. However, the existence of a staggered *g*-tensor along the *b*-axis cannot be excluded.

3.2. Magnetic properties

The open squares in figure 4 display the molar magnetic susceptibility χ_{mol} of $Cu(ox)(pyOH) \cdot H_2O$ in the temperature range 2 K $\leqslant T \leqslant$ 300 K measured in a field of 1 T. These data are corrected for a temperature-independent diamagnetic contribution of paraffin and the diamagnetic core contributions of $Cu(ox)(pyOH) \cdot H_2O$ estimated according to [24].

At around 270 K, a broad maximum in $\chi_{mol}(T)$ is visible, characteristic for a low-D spin system, where $\chi_{mol}(T)$ is governed by short-range spin correlations. Below 270 K, the susceptibility is continuously decreasing down to 60 K. The steep increase at low temperatures is attributed to a Curie-contribution, resulting from uncoupled Cu^{2+}-ions. This is corroborated by plots of the inverse susceptibility of the

data below 10 K in the inset of figure 4, which shows an approximate linear behaviour extrapolating to zero for $T \rightarrow 0$. From the slope of the straight line, a concentration of the uncoupled Cu^{2+} ($S = 1/2$)-ions of $(1.5 \pm 0.2)\%$ is estimated. This small value directly reflects the considerably high quality of our collection of single crystals.

For a quantitative analysis of the $\chi_{mol}(T)$ data, we applied the theoretical results for an antiferromagnetic $S = 1/2$ Heisenberg spin-chain with alternating exchange coupling constants J_1 and J_2 ($= \alpha J_1$), obtained by Johnston *et al* [23]. In [23] quantum Monte Carlo simulations and transfer-matrix density-matrix renormalization group calculations were presented for $\chi(\alpha, t)$ covering wide ranges of normalized temperature $t = T/J$ and alternation parameter α. Two-dimensional (α, t) fits were extracted from the combined theoretical data and used to model experimental susceptibility and specific heat results. The numerical expression for the magnetic susceptibility given there is valid for all values of alternation parameter α including the border cases of isolated dimers ($\alpha = 0$) and the uniform Heisenberg chain ($\alpha = 1$). For this model, the spin $S = 1/2$ Heisenberg Hamiltonian in the following form is used:

$$\hat{H} = J_1 \sum_i (\vec{S}_{2i} \cdot \vec{S}_{2i-1} + \alpha \vec{S}_{2i} \cdot \vec{S}_{2i+1}).$$

Here J_1 and $J_2 = \alpha \cdot J_1$ are the alternating Heisenberg exchange interactions between neighbouring spins along the chain. For $J > 0$, this interaction is antiferromagnetic, whereas $J < 0$ refers to a ferromagnetic coupling. For the alternating Heisenberg chain, the position of the maximum in $\chi_{mol}(T)$ is determined by the dominant coupling constant J_1, cf figure 20 of [23]. The maximum is located at $k_B T_\chi^{max} = 0.64 J_1$, practically independent of the alternation parameter α.

A least-squares fit of the $\chi_{mol}(T)$ data displayed in figure 4 was performed, employing the numerical expression (equation (56)) given in [23] containing three adjustable parameters: the dominant magnetic exchange constant J_1, the

alternation parameter α and the g-factor. A fourth parameter, associated with the Curie contribution of uncoupled $S = 1/2$ spins, was added. The result of this fitting procedure, shown as the straight line in figure 4, nicely describes the experimental data. The following parameters have been derived: $J_1 = (442 \pm 5)$ K, $\alpha = 0.13 \pm 0.06$, i.e. $J_2 = (58 \pm 17)$ K, and a g-factor of 2.19 ± 0.03. In addition, the fit yields a concentration of about 1.5% of uncoupled $S = 1/2$ impurities, consistent with the concentration determined from the slope of $1/\chi_{mol}(T)$ at $T \leqslant 10$ K, as described above. The g-factor revealed from the fit is in accordance with the expectation for randomly oriented single crystals containing Cu^{2+} ions in a distorted octahedral environment [25]. Employing the relation $\Delta(\alpha) \approx (1 - \alpha)^{3/4}(1 + \alpha)^{1/4}J_1$ [23], the zero-field excitation gap is estimated to $\Delta = (410 \pm 20)$ K.

4. Discussion

In view of the structural properties and supported by assessing relative bond strengths, it appears justified to model $Cu(ox)(pyOH) \cdot H_2O$ as a dimerized spin-chain. Along the b-axis of the monoclinic structure, one finds two distinct oxalate bridges, 'coplanar' **ox-A** and 'parallel' **ox-B**, which alternate from bond to bond, resulting in an alternating-exchange spin $S = 1/2$ chain. In [9], Cano *et al* summarize various experimental and theoretical results found for dinuclear oxalato-bridged compounds. For the 'parallel' configuration, they obtained experimental values for the exchange coupling ranging from -2 to 53 K, whereas they listed coupling constants for the 'coplanar' orientation from 430 to 575 K. The same magnitude of the magnetic coupling constants was calculated using density functional theory (DFT) methods on selected oxalato-bridged model systems [9]. Although we are not dealing with isolated dimers but with a dimerized spin-chain (in comparison, a much more complicated magnetic structure), the coupling constants of $Cu(ox)(pyOH)H_2O$, derived from our susceptibility measurements, are comparable to the ones listed in [9].

For a dinuclear oxalato-bridged model compound, Cano *et al* [9] showed that despite the influence of the electronegativity of the terminal ligands and some other structural parameters, the most important effect governing the strength of the magnetic coupling constant J is the displacement h_M of the Cu atoms away from the basal plane of the coordination polyhedra. This displacement h_M is schematically displayed in figure 5. The authors of [9] compared the experimental findings with their theoretical results, calculated for one model substance, and obtained a similar trend for J as a function of h_M for both, but with an offset of approximately 160 K between the theoretical and experimental curves. This offset is larger than the error bars of the experimental results, which are around ± 40 K.

A least-squares-plane was fitted with the four atoms (one nitrogen N, three oxygen O1A, O2A, O1B) forming the basal plane of the bipyramids using the program SHELXL-97 [26]. The given value for h_M is the distance of the Cu^{2+} ion to this plane. For the coplanar **ox-A** bridge in $Cu(ox)(pyOH) \cdot H_2O$, we obtained a displacement out of the
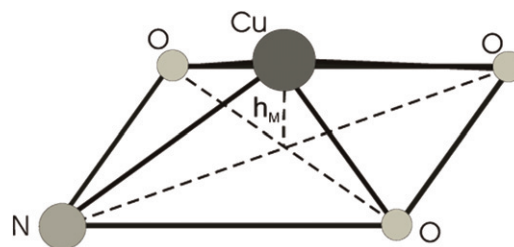
Figure 5. Sketch of the local Cu environment indicating the displacement h_M of the Cu atom away from the basal plane of the coordination polyhedra.

basal plane for the Cu^{2+} ion of $h_M = 0.035$ Å. In contrast to some of the isolated dimer compounds in [22], this is only a moderate displacement. Comparing this displacement with the experimental and theoretical results shown in figure 2 of [9], one expects for $h_M = 0.035$ Å, $J_{theo} = 415$ K and a $J_{exp} = (570 \pm 40)$ K. In fact, the dominant (intra-dimer) coupling $J_1 = (442 \pm 5)$ K of the present dimerized spin-chain $Cu(ox)(pyOH) \cdot H_2O$ is close to these values, lying in between the theoretical and experimental values in [9] for the displacement h_M realized here. This observation suggests that, similar to isolated dimers, the strength of the magnetic couplings in oxalato-bridged coupled dimer systems is mainly determined by the displacement of the Cu^{2+} ion out of the octahedral plane.

5. Summary

Among the polymeric oxalate chains reported up to now, the compound $Cu(ox)(pyOH) \cdot H_2O$ is the first example of a Cu^{2+} oxalate chain with an alternation of 'coplanar' and 'parallel' topologies along the chain leading to an alternating-exchange spin-chain. Due to the presence of a 'coplanar' Cu-coordination, this is also the first time that such a strong antiferromagnetic interaction has been found in a Cu^{2+}-based polymeric oxalate chain. The magnetic behaviour is mainly determined by the displacement of the Cu^{2+}-ions with respect to the basal plane of the local environment.

Acknowledgment

References

[1] Dagotto E and Rice T M 1996 *Science* **271** 618–23
[2] Schollwöck U, Richter J, Farnell D J J and Bishop R F (ed) 2004 *Quantum Magnetism* (*Lect. Notes Phys.* vol 645) (Berlin: Springer)
[3] Day P and Underhill A E 1999 *Phil. Trans. R. Soc.* A **357** 2851–3
[4] Lahti P M (ed) 1999 *Magnetic Properties of Organic Materials* (New York: Dekker)

[5] Miller J S and Drillon M (ed) 2001 *Magnetism: Molecules to Materials* vol 1–3 (Weinheim: Wiley–VCH)

[6] Wolf B, Brühl A, Pashchenko V, Remović-Langer K, Kretz T, Bats J W, Lerner H W, Wagner M, Salguero A, Saha-Dasgupta T, Rahaman B, Valenti R and Lang M 2007 *C. R. Chim.* **10** 109–15

[7] Kretz T, Bats J W, Losi S, Wolf B, Lerner W H, Lang M, Zanello P and Wagner M 2006 *Dalton Trans.* 4914–21

[8] Fitzgerald W, Foley J, McSweeny D, Ray N, Sheahan D, Suresh Tyagi S, Hathaway B and O'Brian P 1982 *J. Chem. Soc., Dalton Trans.* 1117–21

[9] Cano J, Alemany P, Alvarez S, Verdaguer M and Ruiz E 1998 *Chem. Eur. J.* **4** 476–84

[10] Chow M Y, Zhou Z Y and Mak T C M 1992 *Inorg. Chem.* **31** 4900–2

[11] Schreuer J and Haussühl S 1993 *Z. Kristallogr.* **205** 313–5

[12] Tong Y X, Chen X M and Ng S W 1997 *Polyhedron* **16** 3363–9

[13] Wu Y R, Long L S, Huang R B, Zheng L S and Ng S W 2003 *Acta Crystallogr.* E **59** m390–2

[14] Bian G Q, Kuroda-Sowa T, Sugimoto S, Maekawa M and Munakata M 2005 *Acta Crystallogr.* C **61** m144–6

[15] Wiehl L, Schreuer J, Haussühl E, Winkler B, Removic-Langer K, Wolf B, Lang M and Milman V 2006 *J. Phys.: Condens. Matter* **18** 11067–79

[16] Castillo O, Luque A, Julve M, Lloret F and Roman P 2001 *Inorg. Chim. Acta* **315** 9–17

[17] Castillo O, Luque A, Julve M, Lloret F and Roman P 2001 *Inorg. Chim. Acta* **324** 141–9

[18] Castillo O, Luque A, Roman P, Lloret F and Julve M 2001 *Inorg. Chem.* **40** 5526–35

[19] Castillo O, Luque A, Sertucha J, Roman P and Lloret F 2000 *Inorg. Chem.* **39** 6142–4

[20] Garcia-Couceiro U, Castillo O, Luque A, Beobide G and Roman P 2004 *Inorg. Chim. Acta* **357** 339–44

[21] Cabrero J, Ben Amor N, de Graaf C, Illas F and Caballol R 2000 *J. Phys. Chem.* A **104** 9983–9

[22] Wiehl L, Schreuer J and Haussühl E 2006 *Z. Kristallogr. NCS* **221** 35–6

[23] Johnston D C, Kremer R K, Troyer M, Wang X, Klümper A, Bud'ko S L, Panchula A F and Canfield P C 2000 *Phys. Rev.* B **61** 9558–606

[24] Kahn O 1993 *Molecular Magnetism* (New York: VCH)

[25] Ottavianim M F, Montalti F, Turro N J and Tomalia D A 1997 *J. Phys. Chem.* B **101** 158–66

[26] Sheldrick G M 1997 SHELXL-97 *Program for the Refinement of Crystal Structures* (Germany: University of Göttingen)