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New type of metal squarates. Magnetic and multi-temperature X-ray study of di-hydroxy(μ_6-squarato)manganese†

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A new type of crystal packing with μ_6-bridged squarate anions has been found in the structure of $Mn_2(OH)_2(C_4O_4)$ 1 during magnetic and X-ray single crystal diffraction measurements performed over a wide range of temperatures; the unit cell parameters for the crystal remain remarkably unchanged in the interval from 10 to 120 K.

We are currently investigating the use of solvothermal synthesis to generate materials with extended metal–ligand networks,[1] particularly ones displaying cooperative magnetic effects. As part of this study we have prepared $Mn_2(OH)_2(C_4O_4)$ **1** from the hydrothermal reaction of NaOH, $H_2C_4O_4$ and $MnCl_2$ at 220 °C. A study of the magnetic behaviour of this compound‡ is consistent with canted antiferromagnetic ordering below 32 K (Fig. 1). Compound **1** obeys the Curie–Weiss law in the paramagnetic region, and fitting the data in the range $70 \leqslant T/\mathrm{K} \leqslant 300$ gives a Weiss constant of $-52(1)$ K. Below 32 K a very small but significant spontaneous magnetisation of 13 $\mathrm{cm^3\,G\,mol^{-1}}$ is observed, which corresponds to a canting angle $\varphi_\mathrm{m} = 0.03°$ for a two-sublattice model. This type of ordering can be caused by either single ion anisotropy or antisymmetric exchange coupling.[2] The former is a product of the interaction of spin–orbit coupling with a low-symmetry crystal field whilst the latter is also caused by spin–orbit coupling and is due to its modification of the exchange interaction. The weakness of spin–orbit coupling in octahedral high-spin Mn(II) means that canting is rare for this ion in comparison to those such as high-spin Co(II) which display large spin–orbit couplings. Both single-ion anisotropy and antisymmetric exchange have been invoked to account for the observed spin canting in Mn(II) phthalocyaninate[3] and $Mn(CO_3)$[4] respectively. Although the single ion anisotropy for Mn(II) is generally small[5] the distorted Mn environment (see below) and unusual yellow colour of this material are evidence for its existence. Regardless of the magnitude of any single ion anisotropy, the presence of crystallographic inversion centres in the solid state between hydroxy bridged manganese(II) ions means that the axes of anisotropy will be collinear. This precludes single-ion anisotropy as the source of spin canting, unless there is significant structural change accompanying the magnetic phase transition. Therefore it was important to obtain structural data at a temperature as close to the magnetic phase transition as possible. In order to follow possible structural changes during the magnetic phase transition, we collected single crystal X-ray data§ for **1** at 120, 40, 20 and 10 K (well below T_c) using an *Fddd* diffractometer.[6]

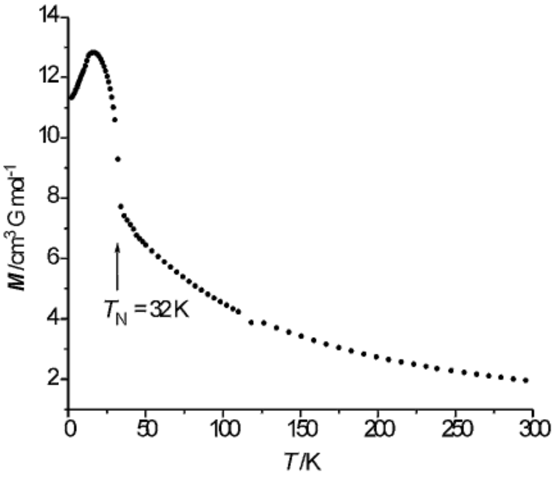

Fig. 1 The static magnetic susceptibility of a powdered sample of **1** in an applied field of 100 G in the temperature range 2 to 300 K.

Squarate complexes of transition metals are well known, not least as materials with unusual magnetic and optoelectronic properties. The new interest in these compounds arose with the development of crystal engineering of organometallic compounds.[7] It was found that the structures of metal squarates contain a complex network of hydrogen bonds, usually there are channels in the structure, $C_2O_4^{2-}$ dianions form stacks and the coordination of the first row transition metals is close to octahedral with squarate ligands in mutually *trans* positions. Depending on the stoichiometry the squarate can be a terminal, μ- or μ_4- bridged ligand. In a recent review,[8] three types of aqua squarates were analyzed and their structural relationship was discussed.

The structure of **1** is remarkably different from those of the aqua squarates, which are chemically closely related to **1**. As in all previously known squarates of Mn the metal center has an octahedral coordination (Fig. 2), but in **1** the octahedron is severely distorted. The coordination mode is unusual: there are not two or four, but three μ-squarate ligands, which are not in the usual mutual *trans* positions but occupy the adjacent vertices (fac) of the octahedron. The squarate dianions occupy special positions in the center of symmetry and adopt the usual geometry for $C_4O_4^{2-}$ with delocalized C–C and C–O bonds and almost perfect $D_{4\mathrm{h}}$ symmetry. The slight difference in C–O bond lengths is the result of different crystal environments and bonding for O(1) and O(2). Indeed, atom O(1) is μ-bridged between two Mn atoms and O(2) is bonded to one Mn atom and accepts a hydrogen bond from the hydroxy group. Therefore each squarate dianion in structure **1** is connected to 6 metal atoms and is a μ_6-ligand. We are not aware of any other observations of such bonding of squarate anions.

In spite of the unusual coordination, the squarate anions in **1** maintain the usual tendency to form stacks. In **1** the stacks are formed along the short *a* axis and the distance between the planes of the anions is about 3.1 Å. The angle between the planes of the anions in adjacent stacks is 35.2º. The Mn(OH) chains are located between the stacks (Fig. 3).

As mentioned above, the aqua squarate complexes of transition metals usually have a number of hydrogen bonds. Complex **1** contains just one independent H atom and the cations and anions have to be linked together by Mn–O bonds.

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† Electronic supplementary information (ESI) available: magnetic susceptibility measurement results; crystal data at various temperatures. See http://www.rsc.org/suppdata/cc/1999/1561

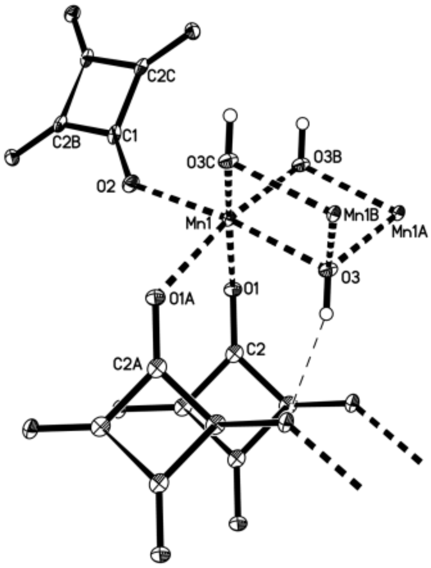

Fig. 2 Fragment of the crystal packing of **1** showing the coordination of the metal atom (thermal ellipsoids are at 70% probability level). Bond lengths (Å) at 10 K: Mn(1)–O(1) 2.3653(9), Mn(1)–O(1A) 2.264(1), Mn(1)–O(2) 2.1374(7), Mn(1)–O(3) 2.1820(7), Mn(1)–O(3B) 2.1132(9), Mn(1)–O(3C) 2.1297(8), O(1)–C(2) 1.2617(9), O(2)–C(1) 1.252(1), C(1)–C(2′) 1.467(1) and C(1)–C(2″) 1.468(1).

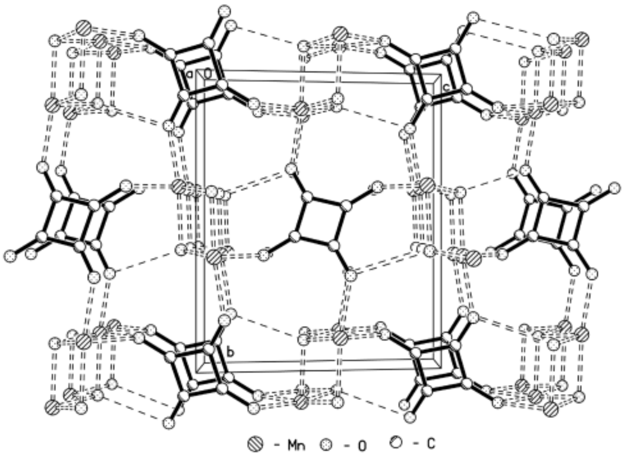

Fig. 3 Crystal packing of **1** (view along *a*). H-atoms omitted for clarity. Mn–O bonds are shown as double-dashed and H-bonds as single-dashed lines.

The only hydrogen bond in the structure links the hydroxy group with the O(2) carbonyl oxygen atom of the squarate anion. The result is a much closer crystal packing of **1** without substantial channels or cavities. This fact is probably the reason for the remarkable thermal behaviour of compound **1**: the crystal is virtually 'unshrinkable' from room temperature down to 10 K: in this range the unit cell volume changes from 295.5(1) to 292.9(1) Å^3—less than 1%.

At all temperatures studied the Mn–O, O–C and C–C distances are constant in the range 2–3σ. There is a slight tendency towards the contraction of the shortest Mn···Mn distance from 3.2055(6) Å at 120 K to 3.1974(6) Å at 10 K, and the Mn(1)–O3–Mn(1B) angle from 96.18(7)° to 95.72(2)°. These changes happen progressively across the whole range of temperatures studied and obviously are the result of thermal contraction rather than of a structural phase transition.

Since there is no apparent change in the symmetry of the crystallographic unit cell on passing through the magnetic phase transition, we can draw the conclusion that the source of the canting is an antisymmetric exchange interaction. Importantly this shows that **1** may be used as a model system in which the canting can unequivocally be ascribed to one type of anisotropy. Many of the types of magnetic behaviour which are the subject of considerable current interest, such as single molecule magnets, metamagnets and spin-flop phases, canted ferro- and antiferromagnets, are caused by different sources of anisotropy. Hence we hope that the title compound will provide an insight into antisymmetric exchange that can be used as a component in much-needed reliable magnetostructural correlations.

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Notes and references

‡ The static magnetic susceptibility measurements were made between 2 and 300 K in an applied field of 100 G on a Quantum Design MPMS SQUID magnetometer. Data have been deposited as electronic supplementary information (http://www.rsc.org/suppdata/cc/1999/1561).

§ *Crystal data* for **1**, $C_4H_2Mn_2O_6$, M = 255.94, $F(000)$ = 248, μ = 4.29 mm^{-1}, monoclinic, space group $P2_1/c$, Z = 2. At 10 K a = 3.3760(7), b = 10.268(2), c = 8.575(2) Å, β = 99.82(3)°, U = 292.9(1) Å^3, D_c = 2.902 g cm^{-1}. The crystal data at 20, 45, 120 and 293 K are available as electronic supplementary information (http://www.rsc.org/suppdata/cc/1999/1561) as well as the results of the refinements. All the data were collected from the same single crystal on a *Fddd* four circle diffractometer equipped with an APD-202 Displex cryogenic refrigerator and a Bruker AXS rotating anode generator with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 (SHELXL-93). For the 10 K data final $R(F^2)$ = 0.0234 for all 2588 reflections. CCDC 182/1328. See http://www.rsc.org/suppdata/cc/1999/1561 for crystallographic files in .cif format.

Microanalysis: found C 18.7%, H 0.7%; calculated for $C_4H_2O_6Mn_2$: C, 18.8%, H, 0.8%.

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