ChemComm
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First example of a tetra-carboxylate bridged dimanganese species†

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Received (in Cambridge, UK) 29th November 2002, Accepted 13th January 2003
First published as an Advance Article on the web 23rd January 2003

The compound [Mn(tda)(bipy)] (tda = $S(CH_2COO)_2^{2-}$) features the first structurally characterized tetra-carboxylate dimanganese antiferromagnetic system with 'copper acetate' core; the binuclear units, completed by bipyridine chelates, are doubly chained by the tda anions that adopt an unprecedented μ,μ'-$\eta^1,\eta^1,\eta^1,\eta^1$ coordination mode.

There are more than 1000 structurally characterized transition metal species having the most classic paddle-wheel 'copper-acetate' core (four carboxylate bridges).[1] Amongst the first row transition metals, only the Sc and Mn species are still missing, while there are a few more holes in the second and third rows (Zr, Hf, Nb, Ta, Ir, Pd). Concerning manganese, its carboxylate coordination chemistry is rich and, amongst the plethora of different products,[2] dimers with up to three carboxylate bridges are known.[3] Conversely, the $Mn_2(\mu\text{-}OOCR)_4$ skeleton has been only occasionally claimed and not confirmed by any structural characterization.[4] Since Mn paramagnetic ions get easily involved in through-bridge magnetic exchange interactions, potential enhancement of the latter could be favoured by four cooperating carboxylate bridges.

In the course of ongoing studies on metal complexes of the oxo- and thio-diacetate ligands $X(CH_2COO)_2^{2-}$ (oda or tda for X = O or S, respectively),[5] we came to explore the reactivity of the latter toward manganese dichloride.[6] Interesting results are obtained with tda that are in general less investigated.[7]

Treatment of an aerobic aqueous solution of $MnCl_2$ with a 1:1 mixture of Na_2CO_3 and thiodiacetic acid, $S(CH_2COOH)_2$, affords, after work up, colourless crystals of complex $Mn(tda)\cdot H_2O$ (**1**).† Further reaction of **1** with 2,2′-bipyridine (bipy) gives a polymeric species of formula [Mn(tda)(bipy)] (**2**), that may be isolated as a yellow crystalline solid.†

The X-ray structure of **2**‡ consists of parallel ribbons formed by binuclear Mn_2 units held together by double tda chains (Fig. 1). The polymeric arrangement is generated by inversion centres at the core of each Mn_2 dimeric unit and in between their connecting chains. Each dimer features the first certified example of a Mn_2 tetra-carboxylate bridged system. A bipy chelate completes approximate trigonal prismatic coordination at each Mn(II) ion. Two prisms are glued together through rectangular faces (the separation between the two O_4 groupings is 2.22 Å). Such a composition of polyhedra is almost unique for binuclear compounds as it is found only in two tetracarboxylate cadmium(II) dimers, with two terminal nitrate chelates.[8] In the plethora of 'copper-acetate' structures with or without axial monodentate ligands, the overall geometry results from either two square pyramids joined through the bases or two facing squares (occasionally also a mixture of the latter situations is observed). The presence of the bipy ligands, combined with the unprecedented μ,μ'-$\eta^1,\eta^1,\eta^1,\eta^1$ binding mode of tda, confers unique 3D features to **2**. Fig. 1 shows how two adjacent ribbons (parallel to the *a* axis) intercalate with each other. One bipy (all of them are distributed in parallel planes) inserts in between a pair of equivalent ligands belonging to the adjacent ribbon (gear-like arrangement). Such a weak but synergetic π stacking (adjacent head-to-tail bipy ligands are separated by *ca.* 4 Å, *i.e.* half of the *a* axis) gives compactness and, most likely, extra stability to the structure. The average Mn–O and Mn–N bond distances of 2.162(3) and 2.311(2) Å, respectively, are long and consistent with the partial population also of some metal–ligand antibonding MOs. The very long Mn–Mn distance of 3.502(1) Å excludes any direct bonding. By contrast, multiple M–M bonding is a persistent feature in known tetracarboxylate dimers of Re and Tc,[9] (invariably in the oxidation state III) or in a few d^5–d^5 systems formed by Ru(III) and Os(III) ions.[10]

The temperature dependence of the magnetic properties of **2** (χ_M and μ_{eff}) are plotted in Fig. 2. At 300 K, the effective magnetic moment per atom is 5.6 μ_B close to that expected for an uncorrelated Mn(II) ion. On decreasing temperature μ_{eff} steadily decreases indicating an antiferromagnetic interaction in the binuclear unit. In fact χ_M goes through a maximum at *ca.* 30 K and then declines rapidly and is practically zeroed at 1.8 K. The experimental data could be satisfactorily fit with a Bleaney–Bowers-like equation yielding a magnetic coupling constant $J = -8.2\ cm^{-1}$, that is one of the largest values found for the Mn(II) carboxylate dimers.[11]

A glimpse of the basic electronic structure of the molecular model $Mn_2(\mu\text{-}OOCH)_4(bipy)_2$ is caught through the qualitative EHMO diagram[12] of Scheme 1. In the local trigonal prismatic coordination (D_{3h}), the d metal orbitals split into a_1'+e'+e'' sets.[13] The non-bonding z^2 is followed by the orbitals *xy* and

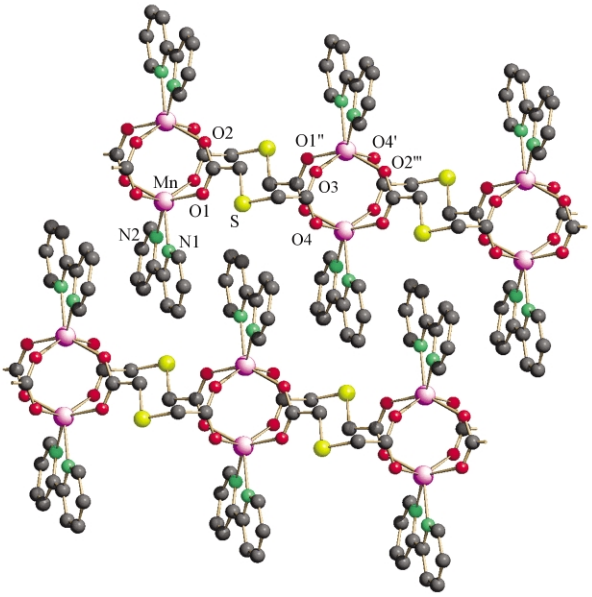

Fig. 1 Crystal structure of (**2**). Selected bond lengths [Å] and angles [°]: Mn–O1 2.153(2), Mn–O2′ 2.160(2), Mn–O3″ 2.164(2), Mn–O4‴ 2.172(2), Mn–N1 2.304(2), Mn–N2 2.318(2), Mn···Mn′ 3.502(1), O1–Mn–O2′ 144.61(9), O1–Mn–O3″ 82.98(9), O2′–Mn–O3″ 88.71(10), O1–Mn–O4‴ 85.04(10), O2′–Mn–O4‴ 82.36(9), O3″–Mn–O4‴ 145.04(8), N1–Mn–N2 69.41(8). The symbols ′, ″ and ‴ refer to the symmetry transformations −*x*+1 −*y*+1 −*z*, −*x* −*y*+1 −*z* and *x*+1 *y z*, respectively.

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† Electronic supplementary information (ESI) available: experimental section and computational details. See http://www.rsc.org/suppdata/cc/b2/b211886f/

DOI: 10.1039/b211886f

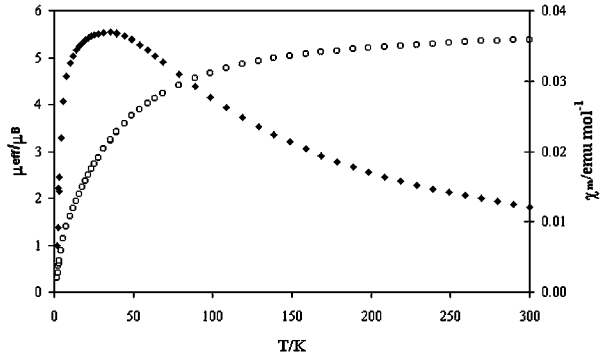
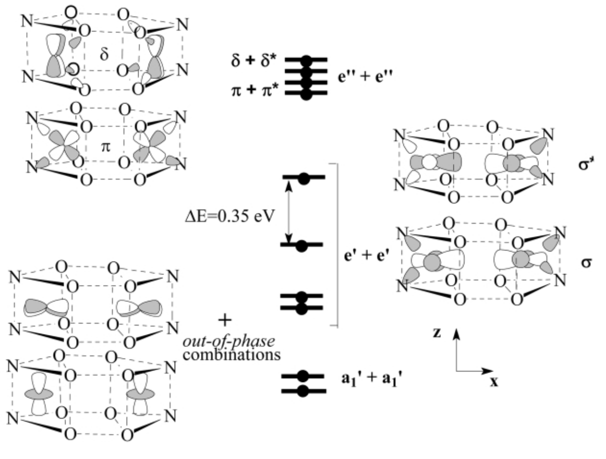


Fig. 2 Plot of μ_{eff} (○) and χ_M (◆) *versus* temperature for complex **2**.

x^2-y^2, that are somewhat affected by the N donors. The highest levels *xz* and *yz* have the most pronounced M–L antibonding character. In spite of the spread d band of *ca.* 1.8 eV the Mn(II) ion features five unpaired electrons that double in number when the prisms are joined with a long Mn–Mn separation. A single point UHF calculation (LANL2DZ)† for the dimeric model with $S = 11$ confirms the width of the band containing the unpaired electrons.

As long debated,[14] the triplet–singlet equilibrium in copper tetra-acetate dimers is attributable to through-bridge interactions that affect differently the highest δ and δ* combinations. In the present case, the antiferromagnetism is a much more complicated issue as the possible spin multiplicities are in the range 1–11. However the highest magnetic orbitals still have δ symmetry on account of their through-bridge destabilization. This is less effective for the close π and π* levels that are pushed up mainly by the terminal N donors. Interestingly, the MO picture also points out a through-space interaction that separates the σ and σ* levels by about 0.35 eV. This is due to the significant hybridisation of the x^2-y^2 lobes induced by the *trans* N donors. Lowering of the magnetic moment is initially attributable to the classic super-exchange mechanism within the e″ set. At low temperatures, the latter levels may be empty with possible contraction of the metal coordination spheres. If σ* also gets depopulated (for a shorter Mn–Mn distance), the paramagnetism may be quenched completely. Full EPR characterization of the system is in progress as well as *ab-initio* calculations to test the different spin multiplicities.

In conclusion, the compound combines several aspects of interest. Particularly beautiful is the crystal structure, where the 'copper acetate' core, new for dimanganese, associates to two different patterns of supramolecular disposition: string of beads (binuclear units) that extend in one dimension and chains that are intercalated in a gear-like arrangement. Also, the preliminary magnetic study prospects relevant features with potential implications for the study of biological systems based on carboxylate Mn_2 cores (catalases, arginase, ribonucleotide reductase, *etc.*[15]).



Scheme 1

Support of MURST, MCYT (BQU2001-3715) and Junta de Andalucía is acknowledged. Thanks are expressed to Professors A. Caneschi and D. Gatteschi for fruitful discussions.

Notes and references

‡ *Crystal data*: $C_{14}H_{12}MnN_2O_4S$, $M = 359.27$, triclinic, space group P_{-1}, $a = 8.018(3)$, $b = 9.104$ (3), $c = 10.484(4)$ Å, $\alpha = 73.86(2)$, $\beta = 72.86(3)$, $\gamma = 80.71(3)°$, $U = 699.8(5)$ Å^3, $Z = 2$, $D_c = 1.705$ g cm^{-3}, μ(Mo-Kα) = 1.112 mm^{-1}, $F(000) = 366$. A total of 2612 reflections were collected on a CAD4 automatic diffractometer with a Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K. The structure was solved by direct methods and refined by a full-matrix least-squares technique based on F^2. R_1 and wR_2 are 0.045 and 0.119, respectively, for 199 parameters and 2463 reflections [$I > 2\sigma(I)$]. CCDC 198988. See http://www.rsc.org/suppdata/cc/b2/b211886f/ for crystallographic data in CIF or other electronic format.

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