Synthesis, crystal structure and magnetic properties of a new mixed-valence $[Mn_4^{III}Mn^{II}]$ pentanuclear complex†

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Received (in Montpellier, France) 14th May 2007, Accepted 22nd June 2007
First published as an Advance Article on the web 4th July 2007
DOI: 10.1039/b707170a

Downloaded by University of Belgrade on 01 January 2013
Published on 04 July 2007 on http://pubs.rsc.org | doi:10.1039/B707170A

A novel pentanuclear mixed-valence manganese (II/III) complex $[Mn_5Na_2O_2(O_2CMe)_4(L')_4(DMF)_4(H_2O)] \cdot 3DMF$ (where H_2L' = 2-hydroxyphenyl-1,3,4-oxadiazole-2(3*H*)-thione) has been synthesized, structurally and magnetically characterized and presents a butterfly-type spin topology with competing antiferromagnetic interactions.

Polynuclear complexes of manganese have been much investigated over the past years for interest in biochemistry or in molecular magnetism. They are for instance involved in many metalloenzymes, such as catalases[1] or the oxygen evolving center of photosystem II.[2] In the molecular magnetism field, compared to those of other transition metals, complexes of manganese are often characterized by large spin ground states and this, in conjunction with the presence of Jahn–Teller distorted Mn^{3+} ions, makes manganese polynuclear complexes ideal candidates for Single Molecule Magnet behaviour, the archetype of SMMs being indeed the extensively studied $[Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4]$.[3]

Numerous recent works in manganese carboxylate chemistry describe interesting directions for the synthesis of new polynuclear Mn complex with various sorts of capping/bridging ligands (Schiff bases, oximes, amino-alcohol...) and interesting magnetic properties.[4–8] Following these results, we investigated many reaction conditions between acetate and/or acetylacetonate manganese sources with easily accessible salicyl derivative ligands bearing various different (in terms of Lewis base hardness or softness) coordination sites. Such ligands have proved to be very versatile, and they also present numerous possibilities for hydrogen bonds or van der Waals 'weak' contacts. These investigations led us to rapid and quantitative synthesis of new mono- and dinuclear manganese (II and III) complexes.[9–11] In a previous work we reported the synthesis and properties of a new di-(μ-methoxo)-bridged binuclear Mn(III) complex using the 2-salicyloyl-hydrazono-1,3-dithiolane ligand. The peculiar asymmetry of this dimer, which presents a very strong intramolecular ferromagnetic interaction, was attributed to the occurrence of two non-classical C–H···π hydrogen bonds imposed by the dithiolane ligand.[11] The potential control of the structures of the obtained complexes as well as of their magnetic properties may then be possible *via* minor modifications of the chelating ligand. We have thus started to explore the coordination chemistry of the deprotected dithiocarbamate derivative of the previously used dithiolane ligand.

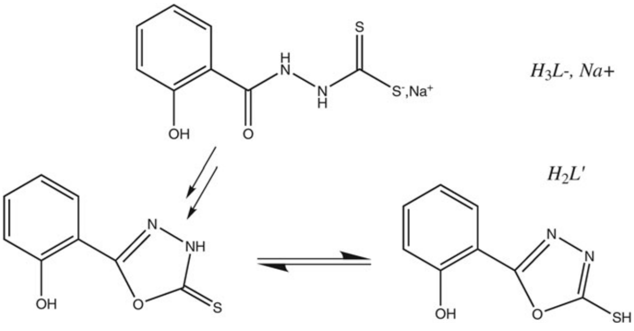
In this communication, we report the synthesis, crystal structure and magnetic properties of a new pentanuclear mixed-valence $[Mn_4^{III}Mn^{II}]$ complex obtained by reaction of Mn(II) acetate and 2-salicyloyl-hydrazinedithiocarboxylate ligand ($H_3L^-Na^+$).

The $[Mn_5Na_2O_2(O_2CMe)_4(L')_4(DMF)_4(H_2O)] \cdot 3DMF$ complex (thereafter named **Mn_5**) was prepared from the sodium salt of 2-(2-hydroxybenzoyl)-hydrazinedithiocarboxylic acid (H_3L^--Na^+) and Mn(II) acetate, and fully characterized at the crystalline solid state.

The H_2L' ligand (2-hydroxyphenyl-1,3,4-oxadiazole-2(3*H*)-thione, Scheme 1) probably comes from an internal reaction of the dithiocarbamate salt H_3L^- during the formation of the complex. This type of cyclization reaction (Scheme 1) was previously described by Young and Wood.[12]

Mn_5 crystallizes in the monoclinic space group $P2_1/c$. The crystal structure consists of a $[Mn_5O_2]^{10+}$ core held together by two μ_3-O^{2-}, three μ_3-$MeCO_2^-$, one μ_2-$MeCO_2^-$, two μ_3-L'^{2-} and two μ_4-L'^{2-} ions (see Fig. 1 and 2 as well as Fig. S1 and S2 for the full labelled ORTEP views in the ESI†).

The complex is of mixed valence type (4 Mn^{III}, 1 Mn^{II}) with the Mn^{II} ion in the molecule centre, bridged by two μ_3-O^{2-} ions to four peripheral Mn^{III}, two on each side, forming two almost perpendicular planes (88°) (see Fig. 1 and 2). From molecular polyhedra filling, it can be seen that this complex can be described by four deformed octahedra connected by their corners, as depicted in Fig. 2.



Scheme 1 Transformation of (H_3L^-, Na^+) into H_2L'.

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† Electronic supplementary information (ESI) available: Full ORTEP figures of the Mn_5 complex, crystal data and refinement details, list of hydrogen bonds, list of bond lengths. See DOI: 10.1039/b707170a

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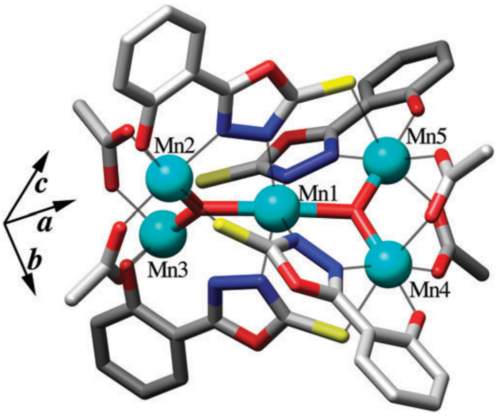


Fig. 1 Ball and stick representation of the pentanuclear $Mn_4^{III}Mn^{II}$ core. The hydrogen and sodium atoms and solvent molecules have been omitted for clarity.

All oxidation states were assigned using charge balance consideration and bond length analysis. Careful inspection of the metric parameters led to the identification of Mn^{III} Jahn–Teller (JT) elongation axes on all Mn atoms except Mn1. In the case of the Mn2, Mn3, Mn4 and Mn5 atoms, the Mn–N bonds are in the range 1.996–2.013 Å; Mn–O bonds are in the range 1.825–1.970 Å, but the fourth Mn^{III}–O bonds are longer (2.163–2.183 Å), presumably due to the Jahn–Teller effect; Mn–S bonds are in the range 2.831–2.858 Å, corresponding to an elongated Mn^{III}–S bond length, forming, with the elongated Mn–O bonds, the four Jahn–Teller axes (S–Mn–O). The Mn1–O and Mn1–N bonds are in the range 2.153–2.172 Å and 2.212–2.247 Å, respectively, corresponding to the lengths of classical X–Mn^{II} bonds. The $Mn^{II}\cdots Mn^{III}$ distances are between 3.426 and 3.487 Å, while the $Mn^{III}\cdots Mn^{III}$ distances are between 3.210 and 3.221 Å.

Two $(L')^{-2}$ ligands show the common μ_3:κ^2:κ^1:κ^1 coordination mode (**A**) (Scheme 2) bridging three manganese ions, while the other two bridge three manganese ions and one sodium ion, adopting the μ_4:(μ_2:κ^1:κ^2):κ^1:κ^1 mode (**B**) (Scheme 2).

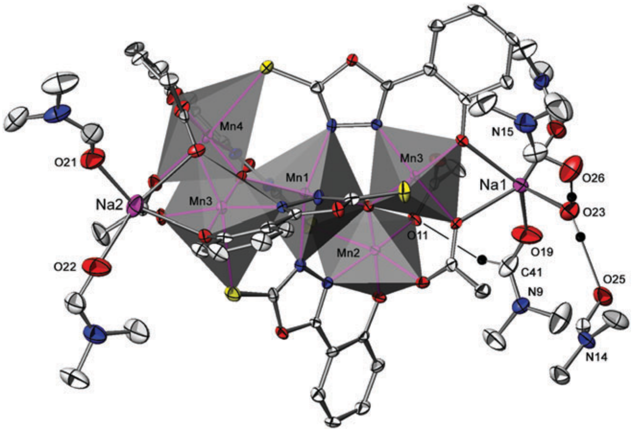
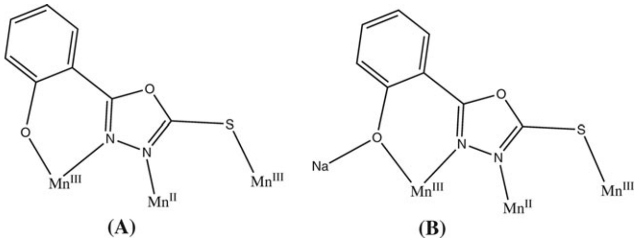


Fig. 2 Molecular polyhedra filling representation of the pentanuclear $Mn_4^{III}Mn^{II}$ complex. The hydrogen atoms (excepted H atoms involved in H bonds) and one DMF (solvent molecule) have been omitted for clarity. The ellipsoids enclose 50% of the electronic density. Small black lines indicate hydrogen bonds.



Scheme 2 Coordination modes of L'^{2-} ligand in the $\mathbf{Mn_5}$ complex.

Both Na^+ ions are five-coordinate and in addition to the bridge made by the $(L')^{2-}$ ligands, each Na^+ ion is connected to two Mn^{III} by bridging acetate groups. Na1 is linked to Mn2 and Mn3 by one acetate in the μ_3:(μ_2:κ^1:κ^1):κ^1 coordination mode whereas Na2 is linked to Mn4 and Mn5 by only one acetate in the same coordination mode. The coordination sphere is completed by two terminal DMF and one water molecule for Na1 and two terminal DMF for Na2.

From the supramolecular point of view, the crystal structure of the pentanuclear complex is stabilized by specific hydrogen bonds such as O–H···O and C–H···O, as determined by PLATON software (Table S2†).[13–15] Only one intramolecular hydrogen bond is detected between C(41) and O(11) (Fig. 2). The other hydrogen bonds concern for a large part the water molecule (O23) which coordinates the Na1 atom and the DMF solvent molecules (O26, O25) (Fig. 2 and Table S2†). Finally, in this molecular structure, 24 intermolecular C–H···π interactions are detected.[13] A packing diagram of the pentanuclear complex is given in the ESI (Fig. S3).†

The magnetic susceptibility χ of $\mathbf{Mn_5}$ was measured under a 0.5 T applied field in the temperature range 300–1.8 K (Fig. 3). The value of the χT product at room temperature (15 $cm^3\ mol^{-1}$ K) is a bit smaller than expected for one high-spin Mn(II) ion ($S = 5/2$) and four high-spin Mn(III) ions ($S = 2$) (16.375 $cm^3\ mol^{-1}$ K considering $g = 2$). Upon cooling, the χT product shows a continuous decrease ($\chi T = 1.77$ $cm^3\ mol^{-1}$ K at 1.8 K) which indicates the presence of antiferromagnetic interactions.

Although the complex is not perfectly symmetric, the two Mn^{III}–Mn^{III} interactions can be considered as equal (J_1) as well as the four interactions between the central Mn^{II} ion and the peripheral Mn^{III} (J_2). The interactions between Mn(III) ions

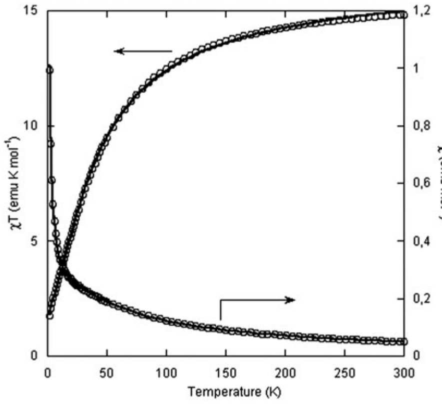


Fig. 3 $\chi(T)$ and $\chi T(T)$ curves for $\mathbf{Mn_5}$ (○: experimental, —: fit).

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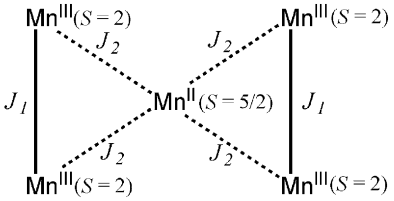

Scheme 3 Spin topology of the $\mathbf{Mn_5}$ complex.

via the L'^{2-} ligand may be reasonably neglected, thus leading us to consider a butterfly interaction topology (Scheme 3).

Considering the spin topology described in Scheme 3 and assuming each pairwise interaction is describable in terms of the Heisenberg Hamiltonian of the form $\hat{H} = -J_{ij}\,\hat{S}_i \cdot \hat{S}_j$, the complete spin Hamiltonian for $\mathbf{Mn_5}$ is given as:

$$\hat{H} = -J_1\,(\hat{S}_2 \cdot \hat{S}_3 + \hat{S}_4 \cdot \hat{S}_5) - J_2\,(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_1 \cdot \hat{S}_3 + \hat{S}_1 \cdot \hat{S}_4 + \hat{S}_1 \cdot \hat{S}_5)$$

where $\hat{S}_2$, $\hat{S}_3$, $\hat{S}_4$, $\hat{S}_5$ are the spin operators associated with the spin moments of the four peripheral Mn^{III} ions, respectively and $\hat{S}_1$ is the spin operator associated with the spin moment of the central Mn^{II} ion. For a system of four $S = 2$ and one $S = 5/2$ ions disposed in a butterfly-type arrangement, the overall degeneracy ($5^4 \times 6 = 3750$) is distributed over 433 spin states with S values ranging from $S = 1/2$ to $S = 21/2$. The fit was performed using an analytical procedure and full diagonalization of the interaction matrix using the SPIN programme implemented with the MINUIT minimization subroutine.[16]

The fit leads $J_1 = -6.8(1)$ cm^{-1}, $J_2 = 2.3(1)$ cm^{-1}, and $g = 2.00(5)$ (the g factor was considered as equal for Mn^{II} and Mn^{III}). For this fit, we neglected zero-field splitting as well as intermolecular interactions, which would have led to overparametrization without significantly improving the fit.

The peculiar butterfly topology for $\mathbf{Mn_5}$ and the occurrence of competing intramolecular antiferromagnetic interactions gives rise to spin frustration, preventing any direct determination of the spin ground state, as explained by Hendrickson and Christou in the case of a $[Mn_4O_2]^{8+}$ complex.[17]

In conclusion, we have reported the synthesis, structure and magnetic properties of a new mixed-valence pentanuclear $[Mn_4^{III}Mn^{II}]$ which illustrates the very rich coordination chemistry of the multidentate hydrazino salicyl derivative ligands bearing sulfur groups. This opens a very broad spectrum of new opportunities for further investigations, for instance the use of other metals or of other counter ions, or the potential exchange of the peripheral acetate ligands (just as for the Mn_{12} chemistry[18]) in order to functionalise the Mn_5 core or to build new coordination polymers.

Experimental

Methods and materials

All reactions and manipulations were carried out under an inert atmosphere of argon using standard Schlenk tube techniques. Dimethylformamide was dried over sodium hydride under nitrogen before use.

Elemental C, H, N, and S analyses were performed by the 'Service de Microanalyses' of the Institut Le Bel and of the Institut Charles Sadron (ULP, Strasbourg, France).

Infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrometer.

Magnetic measurements were carried out using a Quantum Design MPMS-XL SQUID magnetometer. The susceptibility measurement was performed in the 300–1.8 K temperature range with an applied field of 0.5 T. Data were corrected for the sample holder and diamagnetism was estimated from Pascal constants. *SPIN*, a computer programme for calculation and analysis of the magnetic properties was employed.[16]

Syntheses

2-(2-Hydroxybenzoyl)-hydrazinedithiocarboxylic acid ($\mathbf{H_3L^-Na^+}$). The salt of the dithiocarbamate ligand was prepared according to the reported method[19] with a few modifications (see ESI†).

$\mathbf{Mn_5Na_2O_2(O_2CMe)_4(L')_4(DMF)_4(H_2O) \cdot 3DMF}$. A solution of manganese (II) acetate tetrahydrate $Mn(O_2CMe)_2 \cdot 4H_2O$ (0.122 g, 0.5 mmol) in DMF (1.5 mL) was added to a solution of ($H_3L^-Na^+$) (0.100 g, 0.4 mmol) in DMF (1.5 mL) at room temperature. A dark brown solution was obtained. Single crystals suitable for X-ray analysis were obtained as dark rectangular platelets by slow diffusion of diethyl ether in the DMF solution at room temperature for two days. Yield: 34%. Found: C, 38.7; H, 4.4; N 11.1. Calc. for $C_{61}H_{79}N_{15}O_{26}S_4Mn_5Na_2$: C, 38.8; H, 4.2; N, 11.1%. IR (KBr, cm^{-1}): 3443, 1665, 1608, 1590, 1573, 1433, 1256, 859, 755, 668, 584, 553, 534.

X-Ray crystallography

A single crystal of $[Mn_5Na_2O_2(O_2CMe)_4(L')_4(DMF)_4(H_2O)] \cdot 3DMF$ was mounted on a Nonius Kappa-CCD area detector diffractometer at 173 K, using graphite-monochromated MoKα radiation (λ = 0.71073 Å). The cell parameters were determined from reflections taken from one set of 10 frames (1.0° steps in ϕ angle), each at 20 s exposure.[20] The structures were solved using direct methods and refined against F^2 using the SHELXL-97 software.[21] An absorption correction was not considered necessary. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were introduced as fixed contribution (SHELXL-97 procedure).

$C_{61}H_{79}N_{15}O_{26}S_4Mn_5Na_2$, M_w = 1887.31 g mol^{-1}, monoclinic space group $P2_1/c$, a = 26.349(5) Å, b = 12.877(5) Å, c = 25.364(5) Å, β = 111.33(5)°, V = 8016(3) Å^3, Z = 4, ρ_{calc} = 1.564 g cm^{-3}, λ(Mo-Kα) = 0.71073 Å, μ = 0.966 mm^{-1}, T = 173(2) K, $1.62° < \theta < 27.10°$, dataset [h, k, l]: −33/33, −16/16, −28/32, 19 861 reflections ($I > 2\sigma(I)$), 11 362 unique (R_{int} = 0.1032), 1063 parameters refined, R_1 = 0.0847, R_2 = 0.1530, wR_2 = 0.1569, GoF = 1.114. CCDC reference number 617037. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b707170a

Acknowledgements

We are grateful to the Université Louis Pasteur and to the CNRS for financial support. We thank Dr Pierre Rabu, IPCMS, Strasbourg, for his help with the use of the SPIN software.

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