Synthesis of Novel Trimeric μ-Oxo-bridged Manganese(IV) Complexes: $[L_3Mn_3^{IV}(\mu_2\text{-}O)_3(\mu_3\text{-}XO_4)]Br_3$ (X = P, As, or V^V; L = 1,4,7-Triazacyclononane)

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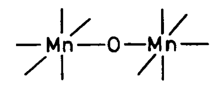
The reaction of $(L_2Mn^{III}_2(\mu\text{-}O)(\mu\text{-}MeCO_2)_2](ClO_4)_2$ with Na_2HPO_4, $(NH_4)_3VO_4$, or Na_2HAsO_4 in aqueous solution (pH *ca.* 9) in the presence of air yields, upon addition of NaBr, deep red crystals of $[L_3Mn^{IV}_3(\mu_2\text{-}O)_3(\mu_3\text{-}XO_4)]Br_3$ (X = P, As, or V^V; L = 1,4,7-triazacyclononane); characterization of the μ-phosphato complex by *X*-ray crystallography showed the presence of discrete trimeric cations $[L_3Mn^{IV}_3(\mu\text{-}O)_3(\mu\text{-}PO_4)]^{3+}$ where three Mn^{IV} centres are in a distorted octahedral *fac*-N_3O_3 donor set connected by three μ_2-oxo bridges and a μ_3-PO_4 bridge.

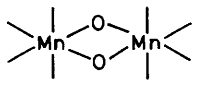
Octahedral complexes of manganese(IV) with an $N_{6-n}O_n$ donor set are difficult to prepare and not many species are well characterized.[1] This is due to the inherent thermodynamic stability of MnO_2 which is the common reaction product in alkaline solution. Only recently, a number of mononuclear[2] and binuclear[3] complexes and a tetranuclear[4] complex of this type have been structurally characterized. The search for such compounds has in recent years been considerably intensified because they serve as model compounds for the manganese cluster in the water-oxidizing enzyme photosystem II (PS II). EXAFS data of PS II in various oxidation levels have become available[5] and their interpretation depends critically on the availability of good low molecular weight model complexes with known structures and spectroscopic as well as magnetic properties. To date dinuclear compounds containing one, two, and three oxo bridges have been characterized where the $Mn^{IV}\cdots Mn^{IV}$ distances vary from 3.54 to 2.63 to 2.296 Å. In addition, a tetranuclear species containing the adamantane-like skeleton $[Mn_4O_6]^{4+}$ has been identified with an average $Mn\cdots Mn$ distance of 3.21 Å.[4]

We here report the synthesis and magnetic properties of a novel series of trinuclear manganese(IV) complexes of composition $[L_3Mn_3(\mu\text{-}O)_3(\mu_3\text{-}XO_4)]Br_3$ (X = P, As, or V; L = 1,4,7-triazacyclononane).

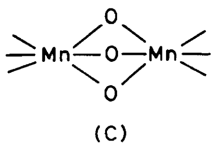
When an aqueous solution (40 cm^3) of $[L_2Mn^{III}_2(\mu\text{-}O)(\mu\text{-}MeCO_2)_2](ClO_4)_2$[3b,6] (0.5 g) was treated with Na_2HPO_4 (1 g) in the presence of air at room temperature and NaBr (2 g) was added, red needle-shaped crystals of $[L_3Mn^{IV}_3(\mu_2\text{-}O)_3(\mu_3\text{-}PO_4)]Br_3$ were precipitated (yield 0.4 g). Using $(NH_4)_3VO_4$ or Na_2HAsO_4 instead of Na_2HPO_4 and adjusting the pH of the resulting solutions to 8—9 under otherwise identical conditions gave red crystals of $[L_3Mn_3(\mu\text{-}O)_3(\mu\text{-}AsO_4)]Br_3\cdot 3H_2O$ or $[L_3Mn_3(\mu\text{-}O)_3(\mu\text{-}VO_4)]Br_3\cdot 3H_2O$. In some instances small amounts of MnO_2 were precipitated before the desired products. This was filtered off. Figure 1 shows the cation in $[L_3Mn_3(\mu\text{-}O)_3(\mu\text{-}PO_4)]Br_3$† which consists of three distorted octahedrally co-ordinated manganese(IV) centres (*fac*-MnN_3O_3) connected by three symmetrical μ_2-oxo bridges forming a puckered six-membered ring. A μ_3-phosphato group bridges to three Mn^{IV} ions capping the six-membered ring. The short Mn–O_{oxo} bond length of 1.785 Å is typical of the Mn^{IV}–O–Mn^{IV} unit.[3,4] The Mn distances for Mn *trans* to



(A)



(B)



(C)

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† *Crystal data*: $[(C_6H_{15}N_3)_3Mn_3(O)_3(PO_4)]Br_3$, trigonal, space group *R*3*m* (C^5_{3v}, No. 160) $a = 20.442(6)$, $c = 7.031(2)$ Å, $Z = 3$, $R = 0.048$ for 536 observed $[I \geqslant 2.5\sigma(I)]$ diffractometer-collected reflections (Mo-K_α radiation, 293 K) and 72 least-squares parameters. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

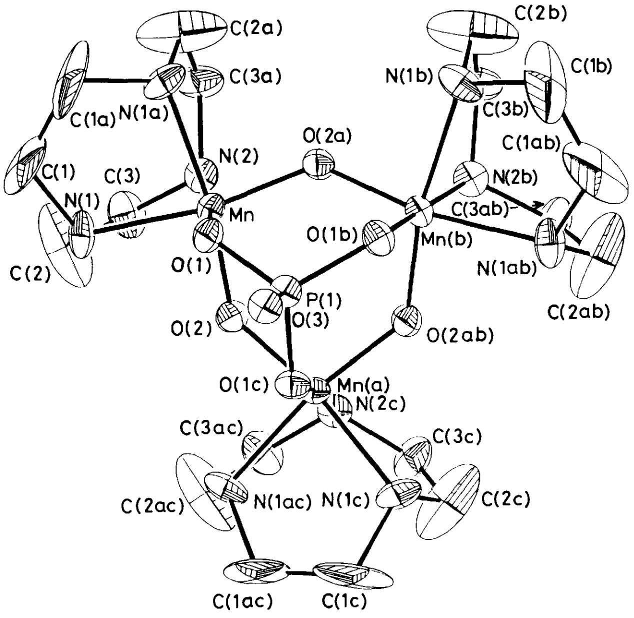

Figure 1. Perspective view of the cation in $[L_3Mn_3(\mu\text{-}O)_3(\mu\text{-}PO_4)]Br_3$. Selected bond distances (Å) and angles (°):

Mn-O(1)	1.883(9)	Mn-N(1)	2.054(3)	P(1)-O(1)	1.543(5)
Mn-O(2)	1.785(6)	Mn-N(2)	2.010(11)	P(1)-O(3)	1,480(15)
Mn···Mn	3.226(1)				
Mn-O(2)-Mn(a)	129.3(5)	O(2)-Mn-O(2a)	101.0(6)		
Mn-O(1)-P(1)	123.5(4)	O(1)-P(1)-O(3)	110.7(3)		
O(1)-P(1)-O(1a)	108.2(4)	N(1)-Mn-N(2)	83.0(3)		
O(1)-Mn-N(1)	91.8(2)	O(2)-Mn-N(1)	88.1(3)		
N(1)-Mn-N(1a)	82.1(5)				

the Mn–O_{oxo} bond are longer by 0.044 Å than for that in the *cis*-position, indicating a structural *trans*-influence of the oxo bridges. The three bridging P–O bonds are longer by 0.063 Å than the single P=O bond where the oxygen is not coordinated to Mn. The structure of the $[Mn_3(\mu\text{-}O)_3(\mu\text{-}PO_4)]^{3+}$ moiety resembles the adamantane skeleton in the $[Mn_4O_6]^{4+}$ core[4] if in the latter a manganese(IV) centre is formally replaced by a P=O group. The structures of $[L_3Mn_3(\mu\text{-}O)_3(\mu\text{-}AsO_4)]Br_3\cdot 3H_2O$ and $[L_3Mn_3(\mu\text{-}O)_3(\mu\text{-}VO_4)]Br_3\cdot 3H_2O$ are assumed to be analogous.

In the i.r. spectrum (KBr disc) of the μ-PO_4 complex bands at 1140m, 1070m, and 920s cm^{-1} are assigned to the $\nu(PO_4)$ stretching frequencies in C_{3v} symmetry. Analoguously, the bands at 880 and 800 cm^{-1} are assigned to the $\nu(AsO_4)$ frequencies in the μ-AsO_4 complex‡ and at 930 and 780 cm^{-1} in the μ-VO_4 complex. A strong, broad band at 730 cm^{-1} is due to the Mn_3O_6 skeleton. In the visible spectrum absorption maxima are at 950sh nm (ε 120 $dm^3\,mol^{-1}\,cm^{-1}$), 786 (257), 745sh (296), and 526 (1.9×10^3).

The magnetic moment per Mn^{IV} centre (d^3) of $[L_3Mn_3(\mu\text{-}O)_3(\mu\text{-}PO_4)]Br_3$ as a function of the temperature decreases from 3.6 μ_B at 280 K (indicating nearly spin-only behaviour) to 0.85 μ_B at 4.2 K, which corresponds to a magnetic moment of 1.65 μ_B per trimer. Thus intramolecular antiferromagnetic spin exchange coupling is observed and $S = \frac{1}{2}$ is the ground state of the trimer. For comparison, in complexes of types (A) and (B) strong antiferromagnetic coupling and in the tri-μ-oxo bridged species very strong antiferromagnetic coupling has been reported ($S = 0$ ground states). In contrast, in $[L_4Mn_4O_6]Br_4\cdot 5.5H_2O$ weak ferromagnetic coupling has been observed. A more detailed analysis of these spin coupling phenomena will be discussed in the full report of this work.

This work was supported by the Fonds der Chemischen Industrie.

Received, 22nd April 1988; Com. 8/01595C

References

1 'Comprehensive Coordination Chemistry,' eds. G. Wilkinson, R. D. Gillard, and J. A. McCleverty, Pergamon, Oxford, vol. 4, 1987.

2 P. S. Pavacik, J. C. Huffman, and G. Christou, *J. Chem. Soc., Chem. Commun.*, 1986, 43.

3 (a) M. Stebler, A. Ludi, and H. B. Bürgi, *Inorg. Chem.*, 1986, **25**, 4743; (b) K. Wieghardt, U. Bossek, B. Nuber, J. Weiss, J. Bouvoisin, M. Corbella, S. E. Vitols, and J. J. Girerd, *J. Am. Chem. Soc.*, in the press; (c) B. C. Schardt, F. J. Hollander, and C. L. Hill, *J. Chem. Soc., Chem. Commun.*, 1981, 765; (d) B. C. Schardt, F. J. Hollander, and C. L. Hill, *J. Am. Chem. Soc.*, 1982, 104, 3964.

4 K. Wieghardt, U. Bossek, and W. Gebert, *Angew. Chem.*, 1983, **95**, 320; *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 328.

5 (a) J. A. Kirby, A. S. Robertson, J. P. Smith, A. C. Thompson, S. R. Cooper, and M. P. Klein, *J. Am. Chem. Soc.*, 1981, **103**, 5529; (b) J. A. Kirby, D. B. Goodin, T. Wydrzynski, A. S. Robertson, and M. P. Klein, *ibid.*, p. 5537; (c) D. B. Goodin, V. K. Yachandra, R. D. Britt, K. Sauer, and M. P. Klein, *Biochim. Biophys. Acta*, 1984, **767**, 209.

6 K. Wieghardt, U. Bossek, D. Ventur, and J. Weiss, *J. Chem. Soc., Chem. Commun*, 1985, 347.

7 F. A. Cotton and S. J. Lippard, *J. Am. Chem. Soc.*, 1966, **88**, 1882.

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‡ Similar bands have been observed for $Re_3Br_3(\mu_3\text{-}AsO_4)_2(Me_2SO)_3$.[7]