Polyhedron Vol. 11, No. 2, pp. 251–255, 1992
Printed in Great Britain

0277–5387/92 \$5.00+.00

SYNTHESIS AND STRUCTURE OF $[Mn_6O_2(O_2CPh)_{10}(EtOH)_4(H_2O)]\cdot EtOH$, A MANGANESE AGGREGATE CONTAINING THREE TYPES OF BENZOATE LIGATION. ISOMERISM IN $[Mn_6O_2(O_2CPh)_{10}]$ COMPLEXES

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(*Received* 5 *May* 1991; *accepted* 21 *August* 1991)

Abstract—The reaction of $Mn(O_2CPh)_2\cdot 4H_2O$ with $KMnO_4$ in warm ethanol in the presence of benzoic acid has been found to give, in addition to the previously reported "manganic benzoate", the new hexanuclear mixed-valence manganese cluster $[Mn_6O_2(O_2CPh)_{10}(EtOH)_4(H_2O)]\cdot EtOH$ (**1**) in 40% yield. X-ray crystal structure determination at -172°C shows that the complex contains a distorted $[Mn^{II}_4Mn^{III}_2O_2]^{10+}$ core and, in addition to terminal EtOH and H_2O groups, three different types of benzoate ligation viz. μ_3-bridging, μ_2-bridging and monodentate terminal forms.

The chemistry of higher oxidation state manganese clusters is currently a subject of intense research due to the importance of manganese to such biological systems as the water oxidation centre of Photosystem II.[1–4] As metal ligation in these systems appears to be primarily oxygen-based, we have been concerned with preparing manganese clusters containing such biologically-relevant oxygen-donors as carboxylates and phenoxides, and we have now reported a number of such species.[5] We herein describe the synthesis and structure of $[Mn_6O_2(O_2CPh)_{10}(EtOH)_4(H_2O)]\cdot EtOH$ (**1**), a new mixed-valence hexanuclear cluster having completely oxygen-based ligation and containing three different types of benzoate coordination.

EXPERIMENTAL

All preparations were carried out under aerobic conditions. All chemicals were used as received. IR spectra (KBr disks) were recorded on a Nicolet 510P Fourier Transform instrument. Microanalyses were performed at the Microanalytical Laboratory, Department of Chemistry, University of Manchester, U.K.

Synthesis

$[Mn_6O_2(O_2CPh)_{10}(EtOH)_4(H_2O)]\cdot EtOH$. To a stirred solution of benzoic acid (10 g, 81.9 mmol) and $Mn(O_2CPh)_2\cdot 4H_2O$ (15.0 g, 40.6 mmol) in warm EtOH (100 cm^3) was added powdered $KMnO_4$ (1.6 g, 10.1 mmol) in small portions. The resulting deep brown/orange solution was stirred for 1 h and then filtered to remove a precipitate (see Discussion). The filtrate was stored in the freezer for 1 week to give a low yield (1.2 g) of "manganic benzoate" that was removed by filtration. Storage of this filtrate in the freezer for 3 weeks gave a good yield (*ca* 6 g, ~40%) of $[Mn_6O_2(O_2CPh)_{10}(EtOH)_4(H_2O)]\cdot EtOH$ (**1**) as a brown powder. X-ray quality crystals of (**1**) were obtained by a modification to the above method. To a stirred solution of benzoic acid (0.98 g, 8.0 mmol) and $Mn(O_2CPh)_2\cdot 4H_2O$ (1.48 g, 4.00 mmol) in warm EtOH (40 cm^3) was added powdered $KMnO_4$ (0.13 g, 0.82 mmol). Stirring was continued for 20 min whereupon the deep brown/orange solution was filtered. Slow evaporation of the filtrate gave black crystals of **1**. Found: C, 52.6; H, 4.5; Mn, 17.4. Calc. for $[Mn_6O_2(O_2CPh)_{10}(EtOH)_4(H_2O)]\cdot EtOH$: C, 52.8; H, 4.5; Mn, 18.1%. IR data (KBr disks): 1592 (s), 1550 (s), 1485 (m), 1440 (m), 1395 (vs), 1172 (w), 1064 (w), 1018 (w), 710 (s), 678 (m), 668 (m), 600 (m).

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X-ray crystallography and structure solution

Data were collected on a Picker four-circle diffractometer at −172°C; details of the diffractometry, low-temperature facilities and computational facilities employed by the Molecular Structure Center are available elsewhere.[6] Data collection parameters are summarized in Table 1. A search of a limited hemisphere of reciprocal space revealed a set of diffraction maxima with symmetry and systematic absences corresponding to the unique monoclinic space group $P2_1/c$. Data were collected, and the structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. The six manganese atoms were located in the E-map and the remaining non-hydrogen atoms were located in successive difference Fourier iterations. Peaks (2.0–2.5 e Å^{-3}) in the difference Fourier map near O(34) were found to be due to a disordered ethanol ligand. This was modelled by two pairs of carbon atoms, each with 50% occupancy, that were kept in fixed positions. All of the hydrogen atoms were included in fixed, idealized positions during the final cycles of full-matrix least-squares refinement. Non-hydrogen atoms (excluding the atoms of the solvent molecule and disordered ethanol ligand) were refined anisotropically. Final discrepancy indices are included in Table 1.

RESULTS AND DISCUSSION

We are currently involved in the preparation and study of multinuclear ($\geqslant 2$) higher-oxidation state ($\geqslant$ II) manganese clusters as models for metallobiomolecules such as the water oxidation center of Photosystem II[2, 1–5] and as potential precursors to molecular ferromagnets.[7] Entry into Mn^{III}- and Mn^{IV}-containing aggregates has been achieved by two methods: (a) comproportionation of Mn^{II} and Mn^{VII}; and (b) reaction of preformed Mn^{III} aggregates with a variety of ligands. The latter approach has proven particularly useful for the preparation of tetranuclear manganese complexes; the triangular Mn^{III} species $[Mn_3O(OAc)_6(py)_3](ClO_4)$ (**2**) and $[Mn_3O(O_2CPh)_6(py)_3](ClO_4)$ (**3**) react with 2,2′-bipyridine (bpy) to give the acetate and benzoate "butterfly" complexes $[Mn_4O_2(O_2CR)_7(bpy)_2](ClO_4)$ [$R = CH_3$, (**4**); $R = Ph$, (**5**)], respectively.[5–8] As **2** is essentially the pyridine adduct of the well-known organic oxidant "manganic acetate" ($[Mn_3O(OAc)_6]OAc \cdot HOAc$, (**6**)), we had wondered whether the latter compound would behave in a similar fashion in its reaction with bpy. However, the poor solubility of **6** in such solvents as MeCN and CH_2Cl_2 led us to attempt preparation of its benzoate analogue by the method of Weinland and Fischer.[9] This involves the comproportionation of $Mn(O_2CPh)_2 \cdot 4H_2O$ with a stoichiometric amount of $KMnO_4$ in warm EtOH in the presence of benzoic acid; this gives a deep brown solution that deposits a precipitate of "manganese dioxide, co-crystallized benzoic acid and a crystalline precipitate"[9] on cooling. Following removal of solids by filtration, the "manganic benzoate" product crystallized from the filtrate in poor (< 20%) yield. In our hands, the precipitate described by Weinland and Fischer was invariably found to contain unreacted $KMnO_4$, thus accounting for the poor yield of the product and suggesting the possible presence of a mixed-valence product in the filtrate. Indeed, after collection of "manganic benzoate" and storage of the filtrate in the freezer for 3 weeks, a light brown powder of complex **1** was isolated in moderate yield (~ 40%). Crystals of this sparingly-soluble material could not be obtained by recrystallization but it was found that the same material could be prepared as black X-ray quality crystals by using a slight excess of $Mn(O_2CPh)_2 \cdot 4H_2O$ in the above procedure. As a result, the product was shown by X-ray crystallography to be $[Mn_6O_2(O_2CPh)_{10}(EtOH)_4(H_2O)] \cdot EtOH$ (**1**), an ORTEP representation of which is shown in Fig. 1. The structure consists of an $[Mn_6O_2]^{10+}$ core containing two μ_4-O^{2-} ions that is well described as two edge-sharing Mn_4 tetrahedra. The manganese atoms are further bridged by both μ_2- and μ_3-benzoate groups, and ligation about each manganese atom is completed by a combination of terminal EtOH, H_2O or benzoate groups. Charge considerations necessitate the molecule to contain four Mn^{2+} and two Mn^{3+}

Table 1. Crystallographic data for $[Mn_6O_2(O_2CPh)_{10}(EtOH)_4(H_2O)] \cdot EtOH$

M_r	1821.18
Space group	$P2_1/c$
a (Å)	13.736(2)
b (Å)	33.972(5)
c (Å)	18.599(3)
β (°)	110.73(1)
Z	4
V (Å^3)	8117.56
ρ_{calcd} (g cm^{-3})	1.486
μ (cm^{-1})	9.458
T (°C)	−172
λ (Å)	0.71073
Range	$6° \leqslant 2\theta \leqslant 45°$
Observed data; $F > 3\sigma(F)$	6837
R	7.43%
R_w	6.78%

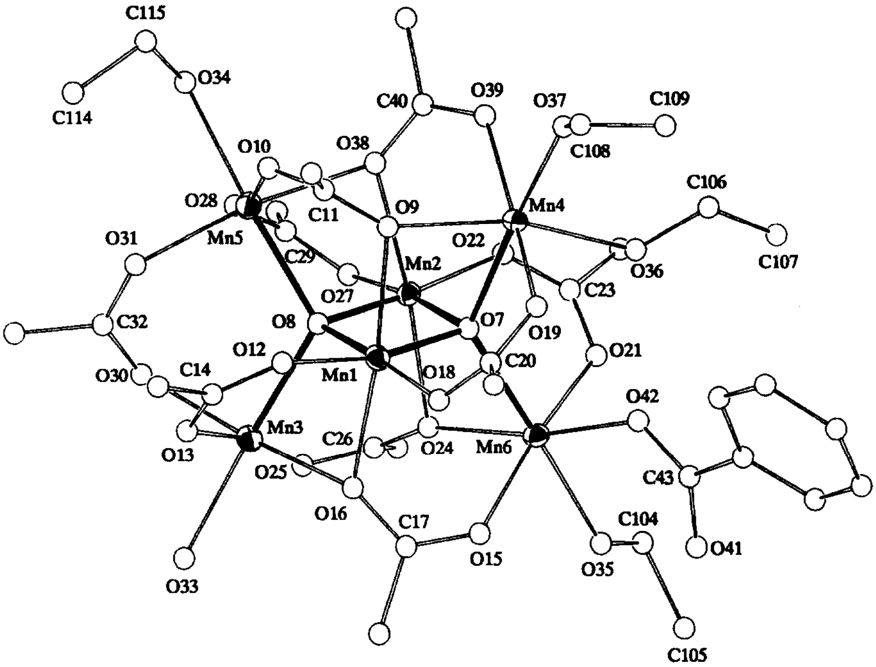

Fig. 1. ORTEP representation at the 50% level of $[Mn_6O_2(O_2CPh)_{10}(EtOH)_4(H_2O)]\cdot EtOH$. The ethanol ligand bound to Mn(5) is disordered over two sites, only one of which is shown.

ions. The latter are assigned as Mn(1) and Mn(2) on the basis of their possessing relatively short Mn—O bond distances (< 2 Å) and the observation of a Jahn–Teller (high-spin d^4) elongation of the Mn(1)—O(9), Mn(1)—O(16), Mn(2)—O(24) and Mn(2)—O(38) bonds (Table 2). Overall, the structure is similar to those of $[Mn_6O_2(O_2CPh)_{10}(py)_2(MeCN)_2]\cdot 2MeCN$ (**7**) and $[Mn_6O_2(O_2CPh)_{10}(py)_4]\cdot Et_2O$ (**8**), both of which have been reported recently.[10] However, in this case, the differing terminal ligation and the presence of a unique monodentate benzoate appreciably distorts the $[Mn_6O_2]^{10+}$ core. In complexes **7** and **8**, μ_2-benzoates bridge both Mn(5)—Mn(3) and Mn(4)—Mn(6). As may be seen for **1** in Fig. 1, however, *two* EtOH ligands complete ligation around Mn(4), thus preventing the terminal benzoate ligand bound to Mn(6) from bridging to Mn(4). This allows the Mn(6)—O(7)—Mn(4) angle [128.7(3)°] to open up appreciably relative to both the Mn(5)—O(8)—Mn(3) angle [117.0(3)°] in this structure, and the corresponding angles in compounds **7** and **8** (~119°). This is also reflected in the Mn(4)···Mn(6) distance (4.021 Å), which is considerably longer than the Mn(3)···Mn(5) distance (3.744 Å). Two other examples of the $[Mn_6O_2]^{10+}$ core have been briefly communicated[11,12] but structural comparisons with these compounds are not possible owing to the limited structural data available.

It is interesting to note the three types of benzoate ligation within complex **1**. There are five μ_2-bridging benzoates, each having both carboxylate oxygen atoms terminally bound to a manganese atom. The four μ_3-bridging benzoates have on oxygen atom [O(10), O(15), O(25) and O(39)] bound terminally to an Mn^{II} atom and the other oxygen [O(9), O(16), O(24) and O(38)] bound in a μ_2-bridging manner to both an Mn^{II} and Mn^{III} atom. This is a very rare mode of carboxylate ligation in manganese chemistry and only a few other examples are known.[10–12] The third ligation type in complex **1** is the monodentate benzoate group bound to Mn(6) via oxygen atom O(42). This is again a relatively rare mode of carboxylate coordination in manganese chemistry, with these ligands almost invariably preferring to bridge adjacent manganese atoms, or, less commonly, to chelate to a single metal atom. Monodentate ligation of a carboxylic acid moiety to the $[Mn_6O_2]^{10+}$ core has previously been observed in the complex $[Mn_6O_2(Me_3CCO_2H)_4(Me_3CCOO)_{10}]$[12] but in the present case, the monodentate, deprotonated *carboxylate* appears to derive stability by formation of a hydrogen bond between the unligated benzoate oxygen O(41) and the nearby ethanol oxygen O(35), with an O···O distance of 2.658 Å.

The observation that the major difference between complex **1** and the previous $[Mn_6O_2]^{10+}$ complexes is the presence in the former of two ter-

Table 2. Selected bond distances (Å) and angles (°) for $[Mn_6O_2(O_2CPh)_{10}(EtOH)_4(H_2O)]\cdot EtOH$

Bond distances			
Mn(1)···Mn(2)	2.802(2)	Mn(3)—O(8)	2.199(6)
Mn(1)···Mn(3)	3.130(2)	Mn(3)—O(13)	2.173(6)
Mn(1)···Mn(4)	3.165(2)	Mn(3)—O(16)	2.249(6)
Mn(1)···Mn(5)	3.555(2)	Mn(3)—O(25)	2.185(6)
Mn(1)···Mn(6)	3.461(2)	Mn(3)—O(30)	2.183(7)
Mn(2)···Mn(3)	3.575(2)	Mn(3)—O(33)	2.203(7)
Mn(2)···Mn(4)	3.470(3)	Mn(4)—O(7)	2.245(6)
Mn(2)···Mn(5)	3.155(2)	Mn(4)—O(9)	2.217(6)
Mn(2)···Mn(6)	3.153(2)	Mn(4)—O(19)	2.131(6)
Mn(3)···Mn(5)	3.744(2)	Mn(4)—O(36)	2.180(7)
Mn(3)···Mn(6)	4.737(2)	Mn(4)—O(37)	2.171(6)
Mn(4)···Mn(5)	4.724(2)	Mn(4)—O(39)	2.122(6)
Mn(4)···Mn(6)	4.021(3)	Mn(5)—O(8)	2.191(6)
Mn(1)—O(7)	1.890(6)	Mn(5)—O(10)	2.142(7)
Mn(1)—O(8)	1.893(6)	Mn(5)—O(28)	2.181(6)
Mn(1)—O(9)	2.271(6)	Mn(5)—O(31)	2.114(7)
Mn(1)—O(12)	1.958(6)	Mn(5)—O(34)	2.222(7)
Mn(1)—O(16)	2.228(6)	Mn(5)—O(38)	2.265(7)
Mn(1)—O(18)	1.950(7)	Mn(6)—O(7)	2.215(7)
Mn(2)—O(7)	1.890(6)	Mn(6)—O(15)	2.110(6)
Mn(2)—O(8)	1.885(6)	Mn(6)—O(21)	2.136(7)
Mn(2)—O(22)	1.952(7)	Mn(6)—O(24)	2.302(7)
Mn(2)—O(24)	2.287(6)	Mn(6)—O(35)	2.231(6)
Mn(2)—O(17)	1.960(7)	Mn(6)—O(42)	2.171(6)
Mn(2)—O(38)	2.205(6)		
Bond angles			
O(7)—Mn(1)—O(8)	84.20(26)	Mn(2)—O(7)—Mn(4)	113.8(3)
O(7)—Mn(2)—O(8)	84.42(27)	Mn(2)—O(7)—Mn(6)	100.02(27)
Mn(1)—O(7)—Mn(2)	95.6(3)	Mn(2)—O(8)—Mn(3)	122.0(3)
Mn(1)—O(7)—Mn(4)	99.53(27)	Mn(2)—O(8)—Mn(5)	101.2(3)
Mn(1)—O(8)—Mn(2)	95.73(28)	Mn(2)—O(24)—Mn(6)	86.79(23)
Mn(1)—O(8)—Mn(3)	99.52(28)	Mn(2)—O(38)—Mn(5)	89.75(23)
Mn(1)—O(8)—Mn(5)	120.8(3)	Mn(3)—O(8)—Mn(5)	117.03(28)
Mn(1)—O(9)—Mn(4)	89.68(22)	Mn(4)—O(7)—Mn(6)	128.7(3)
Mn(1)—O(16)—Mn(3)	88.71(22)		

minal ligands ($PhCO_2^-$/EtOH) in place of the single bridging ligand ($PhCO_2^-$) in the latter provides some interesting food for thought. Given the large number of metallobiomolecules known or suspected to involve carboxylate-bridged multinuclear metal sites, one wonders whether the conversion of a bridging RCO_2^- to a terminal mode by cleavage of one of the M—O bonds might be a convenient means to open up a substrate-binding site. In this sense, the RCO_2^- group could function as a gatekeeper controlling access to the metal. One could readily propose such a possibility for the water oxidation centre, for example.

$$Mn(\mu\text{-}O_2CR)Mn \longrightarrow (RCO_2)Mn\cdots Mn(H_2O)$$

Supplementary material available: Complete listing of atomic coordinates, isotropic and anisotropic thermal parameters, bond lengths and angles, and lists of observed and calculated structure factors. Ordering information is given on any current masthead page. A complete MSC structure report (No. 90259) is available on request from the Indiana University Chemistry Library.

Acknowledgements—This work was supported by NIH Grant GM 39083. G.C. is a Camille and Henry Dreyfus Teacher-Scholar (1987–92).

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