

Bromide Incorporation into a High-oxidation-state Manganese Aggregate, and Reversible Redox Processes for the $[\text{Mn}_4\text{O}_3\text{X}(\text{OAc})_3(\text{dbm})_3]$ ($\text{X} = \text{Cl}, \text{Br}$) Complexes

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Treatment of $[\text{Mn}_4\text{O}_2(\text{OAc})_6(\text{py})_2(\text{dbm})_2]$ (dbmH = dibenzoylmethane) with either NBu_4Br in hot MeCN or Me_3SiBr in CH_2Br_2 leads to the $3\text{Mn}^{\text{III}}, \text{Mn}^{\text{IV}}$ cubane complex $[\text{Mn}_4\text{O}_3\text{Br}(\text{OAc})_3(\text{dbm})_3]$ **3**, the initial example of Br^- bridging high-oxidation-state ($\geq \text{III}$) Mn ions; in addition, **3** and its Cl^- analogue display similar and reversible redox processes and similar magnetic exchange interactions, observations of significant biological relevance to the photosynthetic water-oxidation enzyme.

Our interest in the detailed study of Mn carboxylate chemistry¹ is stimulated in part by the occurrence of a tetranuclear Mn aggregate at the photosynthetic water-oxidation centre (WOC) and the adoption by the latter of various oxidation levels (termed S_n states; in order of increasing oxidation level, $n = -1$ to 4).² One intriguing property of the WOC from an inorganic viewpoint is its Cl^- requirement for activity.³ It has been suggested that Cl^- may be ligated to the Mn, or that it may be bound to nearby Ca^{2+} , involved in charge neutralization, or some other function not involving Mn-binding. However, some crucial recent evidence does indicate Mn-halide linkages.⁴ In the absence of Cl^- , an abnormal S_2 state of the WOC is formed and advancement to S_3 is blocked.⁵ Also intriguing is the observation that Br^- can be substituted for Cl^- in Cl^- -depleted systems with major retention of activity;⁶ thus, whatever the function of Cl^- may be, it appears that it can also be carried out by Br^- . However, isostructural polynuclear Mn complexes containing Cl^-/Br^- have unfortunately not been available to date to probe this important dual-halide question.

Recently, we reported the pivotal role of Cl^- in triggering the conversion of $[\text{Mn}_4\text{O}_2(\text{OAc})_6(\text{py})_2(\text{dbm})_2]$ **1** into $[\text{Mn}_4\text{O}_3\text{Cl}(\text{OAc})_3(\text{dbm})_3]$ **2** (dbmH = dibenzoylmethane, py = pyridine).⁷ The latter ($3\text{Mn}^{\text{III}}, \text{Mn}^{\text{IV}}$) is a potential model for the WOC S_2 state^{1,2} and possesses a $[\text{Mn}_4\text{O}_3\text{Cl}]^{6+}$

cubane-like core with a $\mu_3\text{-Cl}^-$ atom. The need for Cl^- in generating and stabilizing this unique type of unit at the $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$ level has potential biological significance and immediately begged the question of whether the Br^- analogue could be prepared, and if so, what might be the resulting change, if any, in structural and physicochemical properties. Since higher oxidation state ($\geq \text{III}$) Mn chemistry with Br^- is extremely rare owing to redox instability,⁸ we did not anticipate this objective to be a trivial one. However, we herein report the successful preparation of $[\text{Mn}_4\text{O}_3\text{Br}(\text{OAc})_3(\text{dbm})_3]$ **3**. In addition, we report that both **2** and **3** can support reversible redox processes at essentially identical potentials and that they have near-identical magnetochemical properties; these observations are considered to be of significant biological relevance.

After a number of unsuccessful attempts, the following procedures were developed. To a filtered, brown solution of **1** in hot MeCN was added solid NBu_4Br . The stirred, red-brown solution began to deposit red-brown microcrystals within minutes. The solution was cooled to room temperature and the product $[\text{Mn}_4\text{O}_3\text{Br}(\text{OAc})_3(\text{dbm})_3]$ **3** was collected by filtration; the yield was 24% based on dbmH. A higher yield may be obtained in CH_2Br_2 solution employing Me_3SiBr as the Br^- source; treatment of a CH_2Br_2 solution of complex **1** with *ca.* 1.5 equiv. of Me_3SiBr gave a red-brown solution

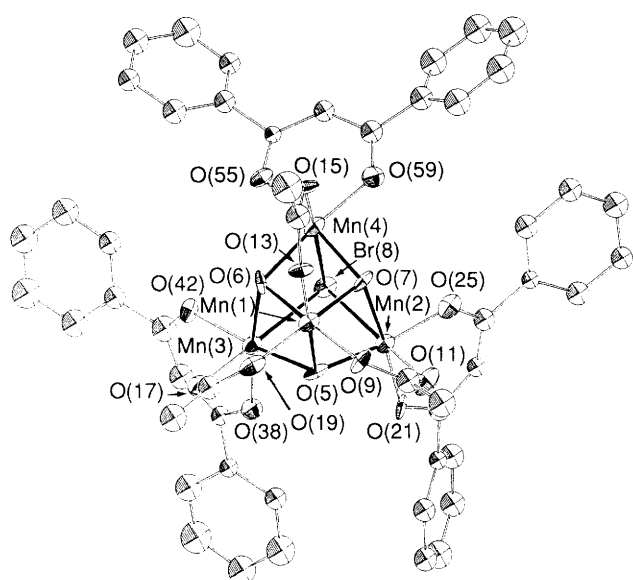


Fig. 1 ORTEP representation of complex **3** at the 50% probability level. Selected bond distances (Å) and angles (°): Mn(1)···Mn(2), 2.804(4); Mn(1)···Mn(3), 2.786(3); Mn(1)···Mn(4), 2.793(4); Mn(2)···Mn(3), 3.274(4); Mn(3)···Mn(4), 3.285(4); Mn(2)···Mn(4), 3.286(4); Mn(2)–Br(8), 2.802(3); Mn(3)–Br(8), 2.807(3); Mn(4)–Br(8), 2.799(3); O(5)–Mn(1,2,3), 1.856(11), 1.918(13), 1.915(12), respectively; O(6)–Mn(1,3,4), 1.871(12), 1.947(12), 1.937(12), respectively; O(7)–Mn(1,2,4), 1.857(12), 1.950(12), 1.915(11), respectively; Mn(2)–O(11), 2.168(13); Mn(3)–O(17), 2.174(12); Mn(4)–O(15), 2.148(12); Mn(2)–Br(8)–Mn(3), 71.43(9); Mn(2)–Br(8)–Mn(4), 71.83(9); Mn(3)–Br(8)–Mn(4), 71.74(10); Mn(1)–O(5)–Mn(2), 96.0(6); Mn(1)–O(5)–Mn(3), 95.3(5); Mn(2)–O(5)–Mn(3), 117.4(6); Mn(1)–O(6)–Mn(3), 93.7(6); Mn(1)–O(6)–Mn(4), 94.3(5); Mn(3)–O(6)–Mn(4), 115.5(6); Mn(1)–O(7)–Mn(2), 94.9(5); Mn(1)–O(7)–Mn(4), 95.5(5); Mn(2)–O(7)–Mn(4), 116.4(5).

which, after filtration, was layered with Et₂O. After several days, black crystals of **3** were collected in 55% yield.† The structure‡ of **3** (Fig. 1) comprises an Mn₄ pyramid with Mn^{IV} atom Mn(1) at the apex and three Mn^{III} atoms at the base; these assignments are based on structural parameters and the observation of Jahn–Teller elongations at Mn(2)–Mn(4). Each vertical face is bridged by the μ₃-O²⁻ atom [O(5), O(6) and O(7)] and the basal plane is bridged by the μ₃-Br⁻ atom Br(8). Peripheral ligation is provided by three bridging AcO⁻ and three chelating dbm⁻ groups. Complex **3** is thus very similar to **27** and the two structures are essentially superimposable, except for the Mn^{III}–Br bonds (av 2.803 Å) being longer than the Mn^{III}–Cl bonds (av 2.650 Å). Complex **3** is the first example of Br⁻ in a complex containing a Mn^{IV} ion and the first example of Br⁻ bridging Mn^{III} centres; it thus provides important and hitherto-lacking precedence for the possibility that Cl⁻ and Br⁻ in the WOC may be directly attached to

† Among the many problems encountered before a method for obtaining pure **3** was developed was the serious contamination of **3** with **2** if CH₂Cl₂ was employed as the reaction solvent.

‡ The X-ray structure was performed on a solvent-free crystal from the NBu₄Br/MeCN method. The Me₃SiBr/CH₂Br₂ method gives samples containing lattice CH₂Br₂ and Et₂O molecules that are slowly lost from filtered crystals. *Crystal data*: C₅₁H₄₂O₁₅BrMn₄, monoclinic, *P*2₁/*n*, *T* = –155 °C, *a* = 13.644(2), *b* = 22.190(4), *c* = 16.548(3) Å, β = 106.64(1)°, *V* = 4800.31 Å³, *Z* = 4, 6° ≤ 2θ ≤ 45°, 6295 unique, 2809 observed reflections, *I* > 2.33σ(*I*). Only Mn, Br and O atoms were refined anisotropically; other non-hydrogen atoms were refined isotropically. Hydrogen atoms were included as fixed contributors in calculated positions; final *R*(*R*_w) = 7.37 (6.89)%. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

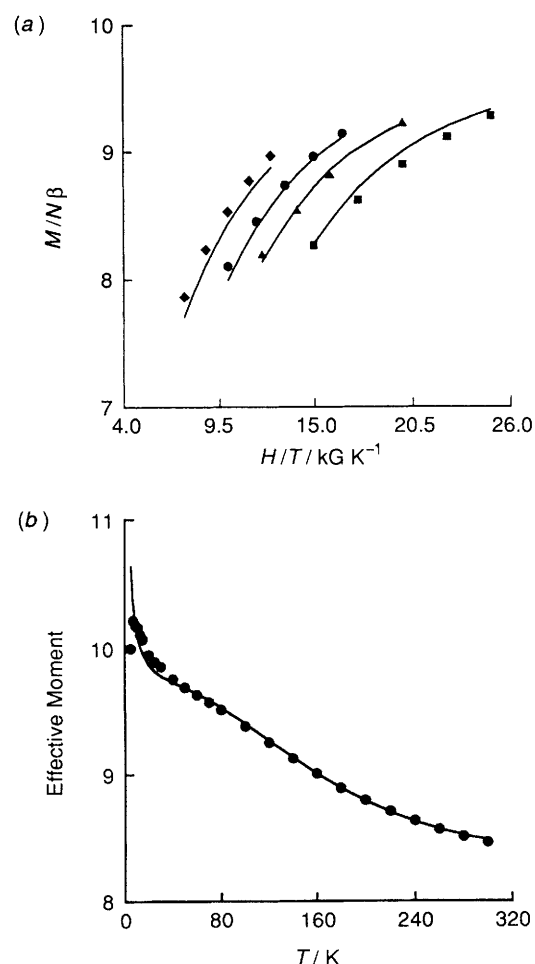


Fig. 2 Plot of μ_{eff} per molecule vs. temperature (b) for a polycrystalline sample of **3** maintained at 10.0 kG. The solid line represents a least-squares fit of the data to the previous⁹ model. In (a) are shown plots of reduced magnetization ($M/N\beta$) vs. H/T for a Vaseline-mull of polycrystalline complex **3**. Four isothermal data sets are shown (■, 2.0 K; ▲, 2.5 K; ●, 3.0 K; ◆, 4.0 K); for each, the field is in the range 30.0–50.0 kG. All data were fit, to give the solid lines, for a $S = 9/2$ ground state. (1 G = 10⁻⁴ T).

high-oxidation-level Mn aggregates at S₂ and without the Br⁻ causing any structural perturbation *vis-à-vis* the Cl⁻ structure.

Variable-temperature solid-state magnetic-susceptibility studies on **3** show that the effective magnetic moment, μ_{eff} , per Mn₄ molecule steadily rises from 8.47 μ_B at 300 K to 10.2 μ_B at 7.01 K (Fig. 2). Fitting of the data to the theoretical susceptibility equation derived previously⁹ gave J_1 (Mn^{III}–Mn^{IV}) = –28.8 cm⁻¹ and J_2 (Mn^{III}–Mn^{III}) = +6.80 cm⁻¹; these values are similar to those for **2** ($J_1 = -33.4$ cm⁻¹, $J_2 = +5.1$ cm⁻¹) and similarly yield an $S = 9/2$ ground state. The $S = 9/2$ ground state for **3** was further substantiated by collecting variable-field (30–50 kG) magnetization data at 2.0, 2.5, 3.0 and 4.0 K. These data were least-squares fit by a full-matrix diagonalization approach to a $S = 9/2$ ground state with $g = 2.1$ and $D = -0.45$ cm⁻¹. It is thus clear that substitution of Cl⁻ with Br⁻ has a minimal effect on the electronic structure. This is consistent with our detailed analysis⁹ of magnetic interactions within the [Mn₄O₃Cl]⁶⁺ core where it is concluded that spin-frustration effects are operative and that the antiferromagnetic J_1 interaction dominates J_2 leading to parallel alignment of the Mn^{III} spins and a consequent $S = 9/2$ ground state. The Cl⁻-to-Br⁻ substitution does not affect the dominant J_1 exchange pathway and thus has an insignificant effect on the observed magnetic properties.

Particularly surprising, but very welcome, was the observation that complexes **2** and **3** both support reversible redox processes, in stark contrast to other known [Mn₄O₃Cl]⁶⁺

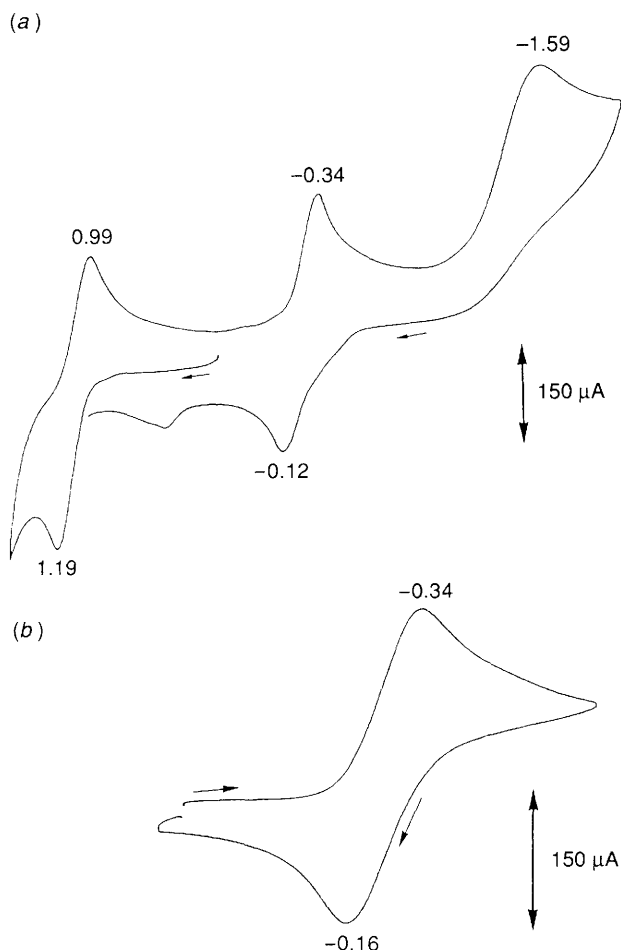
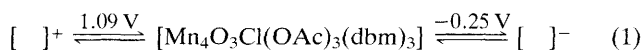


Fig. 3 (a) The CV of complex **2** in CH_2Cl_2 with NBu_4PF_6 as the supporting electrolyte. The scan rate was 100 mV s^{-1} . (b) First reduction process. The CV of complex **3** is extremely similar.

complexes.⁹ The cyclic voltammograms (CV) and differential pulse voltammograms (DPV) of **2** and **3** are extremely similar;§ both complexes show a reversible oxidation at potentials of (in the format **2/3**) $1.09/1.06 \text{ V}$ and a reversible reduction at $-0.25/-0.23 \text{ V}$ (Fig. 3). Both complexes also show an irreversible reduction at $E_p = -1.5$ to -1.6 V . The reversible features define the three-membered redox series of eqn. (1).



The mono-cation (2Mn^{III} , 2Mn^{IV}) may correspond to the WOC S_3 state, and Mn_4 complexes at this average oxidation are thus important to access; they are currently limited to $[\text{Mn}_4\text{O}_4(\text{tphpn})_2]^{4+}$ and $[\text{Mn}_4\text{O}_4(\text{tmdp})_2(\text{H}_2\text{O})_2]^{4+}$ which have a 'dimer of dimers' structure.¹⁰ Similarly, the mono-anion (4Mn^{III}) may correspond to the S_1 state and thus will be important to study; several Mn_4 species at this level are known,^{11–15} with the most characterized to-date being species possessing an $[\text{Mn}_4(\mu_3\text{-O})_2]$ core with a planar or 'butterfly' Mn_4 disposition. The anion of **3** would have structural parameters and a 'short' (ca. 2.8 \AA): 'long' (ca. 3.3 \AA) ratio (1:1) of $\text{Mn}\cdots\text{Mn}$ separations more consistent with the most recent EXAFS data than currently known Mn^{III}_4 complexes.^{4,16} For all the above reasons, the generation and crystallization of 3^+ and 3^- are currently being sought.

In summary, two important developments are being reported: (i) the first example of Br^- bridging Mn^{III} centres,

with the resulting establishment of a precedence for Cl^- and Br^- being able to support similar higher oxidation state Mn chemistry; and (ii) substitution of Br^- for Cl^- can occur with insignificant changes to the structural parameters, the electronic structure or the redox potentials. A prototype pair of isostructural complexes is thus now available to rationalize the retention of water oxidation activity by the WOC when Cl^- is replaced by Br^- .

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§ Electrochemical measurements were performed with a glassy carbon working electrode, a Pt wire auxiliary, and a SCE (saturated calomel electrode) reference electrode; potentials are referenced to the ferrocene-ferrocenium couple under the same conditions.