**NBu₄[Mn₄O₂(H₂O)(O₂CPh)₉]**, a Butterfly Complex with Bound H₂O, and Its Use to Prepare Octanuclear and Undecanuclear Metal Complexes

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Manganese chemistry at the higher metal oxidation states (≥ 5) is currently an area of great activity. One reason for this is the occurrence of Mn in biological systems, particularly the Mn₄ aggregate in the photosynthetic water oxidation center (WOC). To model the WOC, we have prepared complexes of formulation [Mn₄(O₂CMe)(L-L)₂Y] (x = 6 or 7; L-L = a chelate ligand; x = −1, 0, +1) possessing the [Mn₄(μ₁-O₂)₂]³⁺ core with a butterfly disposition of Mn atoms. Higher nuclearity Mnₙ aggregates (y ≥ 6) have also been attracting increasing interest, not least for their aesthetic qualities. Only a limited number of higher nuclearity Mn aggregates are currently known, including various structural types and oxidation levels. We have pointed out elsewhere the potential utility of discrete Mn aggregates with large spin ground states as precursors to molecular ferromagnets. We herein describe results of relevance to both the above areas: namely, the preparation of an Mn₄O₂ complex with a bound H₂O ligand, and its employment as a stepping-stone to new Mn₉ and Na₂Mn₉ aggregates.

The comproportionation between [Mn(O₂CPh)₂]·2H₂O and NBu₄MnO₄ (Bu = nBu) in an approximate 2.5:1 ratio in EtOH/MeCN yields dark red crystals of (NBu₄)[Mn₄O₂(H₂O)(O₂CPh)₉] (I) in 90–95% yield after recrystallization. The structure of the anion of I (Fig. 1) shows a butterfly [Mn₄O₆]³⁺ core similar to that in, for example, [Mn₄O₂(O₂CMe)(bpy)₃]⁺ and [Mn₄O₂(O₂CMe)(pic)]⁺. However, the absence of chelating bpy or pic has interesting consequences; Mn₄ possesses instead an additional benzoate group in a rare asymmetrical chelating mode, where Mn₄-O₂⁺ (2.373(11) Å) is much longer than Mn₄-O₂⁻ (1.947(11) Å). There is also an additional benzoate group at Mn₃ but this is ligated in a monodentate fashion; the remaining site is occupied by a terminal aqua ligand (O18), which is hydrogen-bonded to the unligated benzoate atom O25 (O18...O25, 2.634(24) Å).

Complex 1 represents important progress for our WOC modeling work since it possesses a water-binding site. The ligation of H₂O and its hydrogen bonding to a carboxylate group may be providing a glimpse into how the WOC binds its substrate H₂O and activates it to deprotonation, a necessary step in water oxidation. We are, therefore, studying the reactivity of 1. Initial efforts have unearthed unusual products from the reactions with benzoyl peroxide and Me₃SiCl. Attempted oxidation of 1 with equimolar amounts of (PhCO)₂O in MeCN causes a darkening of color and crystallization of [Na₂Mn₉O₇(O₂CPh)₅(MeCN)_3] · 3 MeCN (2) in 31% yield after addition of NaClO₄. The structure of 2 (Fig. 2) comprises a mixed-metal undecanuclear [Na₂Mn₉O₇]¹⁻ core peripherally ligated by benzoate and MeCN groups; the two Na⁺ ions are linked to the Mn atoms by both core oxide and benzoate bridges. Thus we...
prefer a mixed-metal aggregate description to an ion-pairing description. The Mn atoms are all in the +III oxidation state as evidenced by interatomic distances and Jahn-Teller elongations; the MnS portion of 2 is similar to that observed in \([\text{Mn}_4\text{O}_8\text{Cl}_8]\) [66]. It consists of two \([\text{Mn}_4\text{O}_8\text{Cl}_8]^2+\) units (Mn(1,2,4,7) and Mn(2,3,5,6)) which share the square-pyramidal Mn2 atom and are capped by MnS and Mn9 through O14, O15, and O16. The complex has idealized C2v symmetry. There were no changes in the metal's oxidation state in the conversion of 1 into 2, so the precise function of the (PhCO)2O2 is unclear; however, the yield of 2 is only 31% and the presence of other products in the reaction filtrate is under investigation. The influence of experimental conditions on the reaction of 1 with (PhCO)2O2 is also being studied.

Carboxylate abstraction from complex 1 with 4 equiv of Me3SiCl in CH2Cl2, followed by addition of Et2O to the red-brown solution, produces a dark red precipitate. Recrystallization from CH2Cl2/Et2O yields dark red crystals of the octanuclear MnIII complex \((\text{NBu}_4)[\text{Mn}_8\text{O}_6\text{Cl}_6(\text{O}_2\text{CPh})_2](\text{H}_2\text{O})_2 \times \text{CH}_2\text{Cl}_2\) (3, Bu = nBu, 45–60% yield) [13]. The structure of the anion of 3 (Fig. 3) consists of a \([\text{Mn}_8\text{O}_6\text{Cl}_6]\) core coordinated on its periphery to bridging PhCO2−, terminal Cl−, and terminal H2O ligands. As in 2, the \([\text{Mn}_8\text{O}_6\text{Cl}_6]\) core may again be conveniently considered to be constructed from the fusion of two \([\text{Mn}_4\text{O}_8\text{Cl}_8]\) butterfly units (Mn(1,2,4,7) and Mn(2,3,5,6)) sharing Mn2; this time there is only one capping Mn atom (Mn8) connected through O13 and O14. Moreover, the core now contains bridging Cl− atoms. The core would possess C2 symmetry and a C2 axis passing through Mn2, the midpoint of the O13⋯O14 vector, and Mn8, except that the Mn8 lies off the C2 axis to form a bond to Cl15. This converts Cl15 into an unusual example of a μ4-Cl atom, bridging a nearly planar
Mn₃ unit. Another unusual structural feature is to be found at Mn2. The core structure as described above designates Mn2 as five-coordinate with square-pyramidal geometry as seen for Mn2 in complex 2. It is clear, however, that Mn2 has two additional bonds to O13 and O14; these are long (average 2.656 Å) but they are real because Mn2 lies approximately in the plane containing O9–O12 [5] and not below it, as expected for sp geometry and seen in 2, and because O13 and O14 are approximately trigonal planar, whereas the other bridging oxides are pyramidal. Indeed, O13 and O14 lie slightly out of their Mn₃ planes towards Mn2. [5] Thus, Mn2 is best described as seven-coordinate, and O13 and O14 as four-coordinate trigonal pyramidal.

Very unusually for higher nuclearity Mn aggregates, complex 3 supports reversible redox processes. Shown in Figure 4 is the cyclic voltammogram in CH₂Cl₂. Both a reduction and an oxidation process are observed at potentials of 0.12 and 0.91 V vs. ferrocene, respectively. Complex 3 is thus the central member of the electron transfer series shown in Equation (a). While the oxidation is at a quite high potential, the reduction is much more facile. Attempts to generate and isolate both the neutral and dianionic forms are currently in progress; it will be interesting to determine the site of oxidation/reduction and any resulting structural perturbations.

In summary, the preparation of complex 1 is both important for continuing WOC modeling efforts and provides a new, easily prepared, and convenient starting point for the preparation of the next higher nuclearity Mn aggregates 2 and 3.

Received: July 23, 1991 [Z 4818 IE]

German version: Angew. Chem. 103 (1991) 1661


[9] Correct elemental analysis for C₆H₅NO₂Mn⁺: electronic spectrum in CH₂Cl₂; λ₀0 (μmol⁻¹ cm⁻¹), 476 (11,560).

[10] Crystal data: C₆H₅NO₂Mn⁺, monoclinic, P2₁/c, T = −129°C, a = 17.394(3), b = 19.040(3), c = 25.660(5) Å, β = 103.51(1°), V = 8262.73 Å³, Z = 4.6° ≤ 2θ ≤ 45°, 10788 unique. 4590 observed reflections, F > 2σ(F). All non-hydrogen atoms were readily located. Due to the large number of independent atoms, only the Mn and O atoms were refined anisotropically. Hydrogen atoms, except those of the water molecule, were included in calculated positions as fixed contributors. Final R = 0.0931, R₁ = 0.0926.

[11] The crystals lose MeCN on drying and appear to be hypsochromic. Correct elemental analysis for C₁₉H₁₄N₂O₄Cl₆Mn⁺: electronic spectrum in CH₂Cl₂; λ₀₀ (μmol⁻¹ cm⁻¹), 442 (4200), 488 (3310).

[12] Crystal data: C₁₀H₁₄N₂O₄Mn⁺, triclinic, P₁, T = −170°C, a = 15.116(2), b = 27.903(4), c = 15.067(2) Å, α = 102.40(1), β = 112.36(1), γ = 84.17(1), V = 3715.26 Å³, Z = 2.6° ≤ 2θ ≤ 45°. All non-hydrogen atoms were refined with anisotropic thermal parameters except those of the lattice solvent molecules; the latter were refined isotropically, as were the hydrogen atoms, which were included in calculated positions. R = 0.0514, R₁ = 0.0522.

[13] The crystals lose CH₂Cl₂ on drying and the analysis shows no solvent of crystallization. Correct elemental analysis for C₁₀H₁₄N₂O₄Cl₆Mn⁺: electronic spectrum in CH₂Cl₂; λ₀₀ (μmol⁻¹ cm⁻¹), 442 (4200), 488 (3310).

[14] Crystal data: C₁₀H₁₄N₂O₄Cl₆Mn⁺·xCH₂Cl₂, triclinic, P₁, T = −169°C, a = 16.104(4), b = 21.501(6), c = 14.843(4) Å, α = 94.24(1), β = 105.96(1), γ = 89.07(1), V = 4927.79 Å³, Z = 2, 6° ≤ 2θ ≤ 45°, 11794 unique. 10108 observed reflections, F > 3σ(F); one butyl group and one phenyl group showed disordered C atoms; H atoms were included as fixed contributors, three CH₂Cl₂ groups were clearly observed but with approximately half occupancy; two additional peaks with low occupancy were also found that were lower occupancy CH₂Cl₂ groups or possibly H₂O groups. Final R = 0.0912, R₁ = 0.0944. Further details of the crystal structure investigations are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, CB2 1EW (UK), on quoting the complete journal citation.

[15] a) Mn2 lies only 0.084 Å below the least-squares plane containing atoms O9–O12. b) O13 and O14 lie 0.104 and 0.129 Å, respectively, out of their Mn₃ planes towards Mn2.