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 $(NBu_4)[Mn_4O_2(H_2O)(O_2CPh)_9]$, a Butterfly Complex with Bound H_2O , and Its Use to Prepare Octanuclear and Undecanuclear Metal Complexes **

By Sheyi Wang, John C. Huffman, Kirsten Folting, William E. Streib, Emil B. Lobkovsky, and George Christou*

Manganese chemistry at the higher metal oxidation states $(\geq II)$ is currently an area of great activity. One reason for this is the occurrence of Mn in biological systems,^[1] particularly the Mn₄ aggregate in the photosynthetic water oxidation center (WOC).^[2] To model the WOC, we have prepared complexes of formulation $[Mn_4^{III}O_2(O_2CR)_x(L-L)_2]^z$ (x = 6 or 7; L-L = a chelate ligand; z = -1, 0, +1) possessing the $[Mn_4(\mu_3-O)_2]^{8+}$ core with a butterfly disposition of Mn atoms.^[3] Higher nuclearity Mn_y aggregates ($y \geq 6$) have also been attracting increasing interest, not least for their aesthetic qualities.^[4-8] More importantly, however, these aggregates have displayed a propensity for large spin ground states.^[4c, 8b, d] Only a limited number of higher nuclearity Mn aggregates are currently known, including various struc-

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tural types and oxidation levels; $^{[4-8]}$ we have pointed out elsewhere the potential utility of discrete Mn aggregates with large spin ground states as precursors to molecular ferromagnets. $^{[8b]}$ We herein describe results of relevance to both the above areas: namely, the preparation of an Mn_4O_2 complex with a bound H_2O ligand, and its employment as a stepping-stone to new Mn_8 and Na_2Mn_9 aggregates.

The comproportionation between $[Mn(O_2CPh)_2] \cdot 2H_2O$ and NBu₄MnO₄ (Bu = nBu) in an approximate 2.5:1 ratio in EtOH/MeCN yields dark red crystals of (NBu₄)[Mn₄O₂(H₂O)(O₂CPh)₉] (1) in 90-95 % yield after recrystallization.^[9] The structure^[10] of the anion of 1 (Fig. 1) shows a butterfly [Mn^{III}₄O₂]⁸⁺ core similar to that in, for example, [Mn₄O₂(O₂CMe)₇(bpy)₂]⁺ and $[Mn_4O_2(O_2CMe)_7(pic)_2]^-$ (bpy = 2,2'-bipyridine; pic⁻ = 2picolinate).^[3] 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-O24 (2.373(11) Å) is much longer than Mn4-O22 (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).



Fig. 1. ORTEP representation of the anion of complex 2. For clarity, only one benzoate phenyl carbon atom is shown. Selected bond distances [Å]: Mn1…Mn2, 2.816(4), Mn1…Mn3, 3.367(4), Mn1…Mn4, 3.296(4), Mn2…Mn3, 3.302(4), Mn2…Mn4, 3.365(4), O5-Mn1, 1.900(11), O5-Mn2, 1.913(10), O5-Mn3, 1.823(11), O6-Mn1, 1.909(10), O6-Mn2, 1.905(11), O6-Mn4, 1.825(10), Mn1-O7, 1.946(11), Mn1-O8, 1.940(12), Mn1-O9, 2.206(12), Mn2-O11, 2.202(12), Mn2-O12, 1.923(11), Mn2-O13, 1.973(11), Mn2-O14, 2.136(11), Mn3-O15, 2.136(12), Mn3-O16, 1.902(12), Mn3-O16, 1.982(11), Mn3-O17, 2.111(12), Mn3-O18, 2.102(13), Mn3-O19, 1.903(13), Mn4-O20, 2.038(12), Mn4-O21, 2.037(12), Mn4-O22, 1.974(11), Mn4-O23, 2.016(12), Mn4-O24, 2.373(11), O18…O25, 2.634(24).

Complex 1 represents important progress for our WOC modeling work since it possesses a water-binding site. The ligation of H_2O and its hydrogen bonding to a carboxylate group may be providing a glimpse into how the WOC binds its substrate H_2O 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 (Ph-CO)₂O₂ in MeCN causes a darkening of color and crystallization of $[Na_2Mn_9O_7(O_2CPh)_{15}(MeCN)_2] \cdot 3 MeCN (2 \cdot 3 MeCN)$ in 31 % yield after addition of $NaClO_4$.^[11] The structure^[12] of 2 (Fig. 2) comprises a mixed-metal undecanuclear $[Na_2Mn_9O_7]^{15+}$ 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

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Fig. 2. OK 1EP representation and stereoriew of complex 2. Only one pnenty carbon of the benzoate ligand is shown. Selected bond distances [Å]: Mn1 … Mn2, 2.886(3), Mn2 … Mn3, 2.871(3), Mn1 … Mn4, 3.359(3), Mn1 … Mn7, 3.318(3), Mn2 … Mn4, 3.311(3), Mn2 … Mn5, 3.241(3), Mn2 … Mn6, 3.318(3), Mn2 … Mn7, 3.261(3), Mn3 … Mn5, 3.315(3), Mn3 … Mn6, 3.358(3), Mn2 … Mn8, 3.388(3), Mn2 … Mn9, 3.393(3), Mn8 … Mn9, 3.281(3), O10-Mn1, 1.893(4), O10-Mn2 1.934(4), O10-Mn4 1.888(4), O10-Na153, 2.537(5), O11-Mn2 1.906(4), O11-Mn3 1.884(4), O11-Mn5 1.858(4), O11-Na153, 2.824(5), O12-Mn2 1.927(4), O12-Mn3 1.895(4), O12-Mn6 1.891(4), O12-Na152, 2.610(5), O13-Mn1 1.892(4), O13-Mn7 1.890(4), O13-Mn2 1.911(4), O13-Mn7 1.890(4), O13-Nn52, 2.596(5), O14-Mn2 2.111(4), O14-Mn8 1.851(4), O14-Mn9 1.859(4), O15-Mn6 1.845(4), O16-Mn7 1.872(4), O15-Mn8 1.884(4), O16-Mn4 1.849(4), O16-Mn5 1.886(4), O16-Mn9 1.889(4).

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 elon-gations; the Mn₉ portion of **2** is similar to that observed in $[Mn_9O_7(O_2CPh)_{13}(py)_2]$.^[6b] It consists of two $[Mn_4O_2]^{8+}$ units (Mn(1,2,4,7) and Mn(2,3,5,6)) which share the square-pyramidal Mn2 atom and are capped by Mn8 and Mn9 through μ_3 -oxides O14, O15, and O16. The complex has idealized C₂ 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 Me_3SiCl in CH_2Cl_2 , followed by addition of Et_2O to the

red-brown solution, produces a dark red precipitate. Recrystallization from CH2Cl2/Et2O yields dark red crystals of the octanuclear Mn^{III} complex (NBu₄)[Mn₈O₆Cl₆(O₂CPh)₇- $(H_2O)_2$ · x CH₂Cl₂ (3, Bu = nBu, 45-60 % yield).^[13] The structure^[14] of the anion of 3 (Fig. 3) consists of an [Mn₈O₆Cl₄]⁸⁺ core coordinated on its periphery to bridging PhCO₂, terminal Cl⁻, and terminal H₂O ligands. As in 2, the [Mn₈O₆Cl₄]⁸⁺ core may again be conveniently considered to be constructed from the fusion of two [Mn₄O₂]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 C_{2v} 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 μ_4 -Cl atom, bridging a nearly planar



Fig. 3. Labeled ORTEP representation and stereoview of the anion of complex 3. For clarity, only one phenyl carbon of each benzoate group is shown. Selected bond distances [Å]: Mn1...Mn2, 2.828(3), Mn1...Mn4, 3.145(2), Mn1...Mn7, 3.137(3), Mn2...Mn3, 2.791(3), Mn2 ···· Mn4, 3.191(2), Mn2...Mn5, 3.218(2), Mn2...Mn6, 3.197(3), Mn2...Mn7, 3.180(3), Mn2 ··· Mn8, 3.625(2), Mn3 ··· Mn5, 3.141(2), Mn3 ··· Mn6, 3.131(3), Mn4...Mn5, 3.171(3), Mn4...Mn8, 3.150(3), Mn5...Mn8, 3.493(3). Mn6 ··· Mn7, 3.176(3), Mn6 ··· Mn8, 3.508(3), Mn7 ··· Mn8, 3.158(2), O9-Mn1 1.887 (8), O9-Mn2 1.900 (7), O9-Mn4 1.881 (8), O10-Mn1 1.872 (7), O10-Mn2 1.928(8), O10-Mn7 1.878(7), O11-Mn2 1.912(8), O11-Mn3 1.881(7), O11-Mn51.867(8), O12-Mn21.901(7), O12-Mn31.888(8), O12-Mn61.883(7), O13-Mn2 2.676 (7), O13-Mn4 1.878 (7), O13-Mn5 1.929 (8), O13-Mn8 1.885 (7), O14-Mn2 2.636 (7), O14-Mn6 1.932 (7), O14-Mn7 1.892 (8), O14-Mn8 1.891 (7), Cl15-Mn1 2.692(4), Cl15-Mn4 2.787(3), Cl15-Mn7 2.776(3), Cl15-Mn8 2.709(4), Cl16-Mn3 2.602(4), Cl16-Mn5 2.703(4), Cl16-Mn6 2.685(4), Cl17-Mn4 2.461 (4), Cl17-Mn5 2.571 (3), Cl18-Mn6 2.616 (4), Cl18-Mn7 2.466 (3), Mn5-Cl19, 2.263(4), Mn6-Cl20, 2.246(4), Mn1-O84, 2.191(9), Mn8-O85, 2.184(9)

 Mn_4 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^[15a] 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.^[15b] 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 CH_2Cl_2 . Both a reduction



Fig. 4. Cyclic voltammogram at 50 mVs^{-1} for complex 3 in CH₂Cl₂. The quoted potentials are referred to the ferrocene/ferricinium couple under the same conditions.

and an oxidation process are observed at potentials of 0.12and 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,

$$\begin{bmatrix}] & \underbrace{0.91 \, V}_{7 \, \text{Mn}^{\text{III}},\text{Mn}^{\text{IV}}} & \begin{bmatrix} \text{Mn}_8 \text{O}_6 \text{Cl}_6 (\text{O}_2 \text{CPh})_7 (\text{H}_2 \text{O})_2 \end{bmatrix}^{-} & \underbrace{0.12 \, V}_{8 \, \text{Mn}^{\text{III}}} & \begin{bmatrix}]^{2^-} \\ \text{Mn}^{\text{II}}, 7 \, \text{Mn}^{\text{III}} & \end{bmatrix}$$
(a)

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 new higher nuclearity Mn aggregates 2 and 3.

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- [3] a) J. B. Vincent, C. Christmas, H.-R. Chang, Q. Li, P. D. W. Boyd, J. C. Huffman, D. N. Hendrickson, G. Christou, J. Am. Chem. Soc. 111 (1989) 2086; b) G. Christou, Acc. Chem. Res. 22 (1989) 328; c) E. Libby, J. K. McCusker, E. A. Schmitt, K. Folting, J. C. Huffman, D. N. Hendrickson, G. Christou, Inorg. Chem. 30 (1991) 3486.
- [4] Mn₆ complexes: a) A. R. E. Baikie, A. J. Howes, M. B. Hursthouse, A. B. Quick, P. Thornton, J. Chem. Soc. Chem. Commun. 1986, 1587; b) N. V. Gerbeleu, A. S. Batsanov, G. A. Timko, Y. T. Struchkov, K. M. Indirchan, G. A. Popovich, Dokl. Akad. Nauk SSSR 294 (1987) 256; c) A. Caneschi, D. Gatteschi, J. Laugier, P. Rey, R. Sessoli, C. Zanchini, J. Am. Chem. Soc. 110 (1988) 2795; d) A. R. Schake, J. B. Vincent, Q. Li, P. D. W. Boyd, K. Folting, J. C. Huffman, D. N. Hendrickson, G. Christou, Inorg.

Chem. 28 (1989) 1915; e) R. Bhula, S. Collier, W. T. Robinson, D. C. Weatherburn, Inorg. Chem. 29 (1990) 4027.

- [5] Mn₈ complexes: E. Libby, K. Folting, J. C. Huffman, G. Christou, J. Am. Chem. Soc. 112 (1990) 5354.
- [6] Mn₉ complexes: a) C. Christmas, J. B. Vincent, H.-R. Chang, J. C. Huffman, G. Christou, D. N. Hendrickson, J. Am. Chem. Soc. 110 (1988) 823;
 b) D. W. Low, D. M. Eichhorn, A. Draganescu, W. H. Armstrong, Inorg. Chem. 30 (1991) 877.
- [7] Mn₁₀ complexes: K. S. Hagen, W. H. Armstrong, M. M. Olmstead, J. Am. Chem. Soc. 111 (1989) 774.
- [8] Mn₁₂ complexes: a) T. Lis, Acta Crystallogr. Sect. B 36 (1980) 2042; b) P. D. W. Boyd, Q. Li, J. B. Vincent, K. Folting, H.-R. Chang, W. E. Streib, J. C. Huffman, G. Christou, D. N. Hendrickson, J. Am. Chem. Soc. 110 (1988) 8537; c) D. Luneau, J.-M. Savariault, J.-P. Tuchagues, Inorg. Chem. 27 (1988) 3912; d) A. Caneschi, D. Gatteschi, R. Sessol, A. L. Barra, L. C. Brunel, M. Guillet, J. Am. Chem. Soc. 113 (1991) 5873.
- [9] Correct elemental analysis for $C_{79}H_{a_3}NO_{21}Mn_4$; electronic spectrum in CH_2Cl_2 : λ_{max} [nm](ϵ_m [Lmol⁻¹ cm⁻¹]), 476 (11,560).
- [10] Crystal data: C₇₉H₈₃NO₂₁Mn₄, monoclinic, $P2_1/c$, T = -129 °C, a = 17.394 (3), b = 19.040 (3), c = 25.660 (5) Å, $\beta = 103.51$ (1)°, V = 8262.73 Å³, $Z = 4.6^{\circ} \le 2\theta \le 45^{\circ}$, 10788 unique, 4590 observed reflections, $F > 2.33\sigma(F)$. 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 = 0.0911, $R_* = 0.0926$.
- [11] The crystals lose MeCN on drying and appear to be hygroscopic. Correct elemental analysis for $C_{109}H_{84}N_2O_{38.5}Na_2Mn_9$ (2 ·1.5 H_2O).
- [12] Crystal data: $C_{109}H_{84}N_2O_{38.5}Na_2Mn_9$, triclinic, $P\overline{1}$, T = -170 °C, a = 15.116(2), b = 27.903(4), c = 15.007(2)Å, $\alpha = 102.40(1)$, $\beta = 112.36(1)$, $\gamma = 84.17(1)^\circ$, V = 5715.26Å³, $Z = 2.6^\circ \le 2\theta \le 45^\circ$. All nonhydrogen 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, $R_w = 0.0525$.
- [13] The crystals lose CH₂Cl₂ on drying and the analysis shows no solvent of crystallization. Correct elemental analysis for C₆₅N₇₅NO₂₂Cl₆Mn₈; electronic spectrum in CH₂Cl₂: λ_{max} [nm] (ε_M [L mol⁻¹ cm⁻¹]), 442 (4200), 488 (3510).
- [14] Crystal data: C₆₅H₇₅NO₂₂Cl₆Mn₈·xCH₂Cl₂, triclinic, P₁^T, 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° ≤ 20 ≤ 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, R_w = 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, GB-Cambridge, 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.

A. L. KLANDE, A. ..., L. RETERLIK LANDER (2011) A. ..., M. L. ..., M. L. ..., M. ..., M.

a) K. Wieghardt, Angew. Chem. 101 (1989) 1179; Angew. Chem. Int. Ed. Engl. 28 (1989) 1153; b) J. B. Vincent, G. Christou, Adv. Inorg. Chem. 33 (1989) 197.

 ^[2] a) E. Renger, Angew. Chem. 99 (1987) 660; Angew. Chem. Int. Ed. Engl. 26 (1987) 643; b) G. T. Babcock in J. Amesz (Ed.): New Comprehensive Biochemistry, Vol 15, Elsevier, Dordrecht 1987, p. 125-158; c) G. W. Brudvig, R. H. Crabtree, Prog. Inorg. Chem. 37 (1989) 99; d) D. Ghanotakis, C. F. Yocum, Annu. Rev. Plant Physiol. Plant Mol. Biol. 41 (1990) 255.