High-nuclearity Manganese Carbonyl Complexes: Structures of [{Mn(μ_3-OH)(CO)$_3$}$_4$] and [Mn$_7$(μ_3-OH)$_8$(CO)$_{18}$]

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One-pot high-yield synthesis of the cubane-like complexes [{Mn(μ_3-OH)(CO)$_3$}$_4$] **1**, and mixed-valence [Mn$_7$(μ_3-OH)$_8$(CO)$_{18}$] **2**, is reported: **1** and **2** have been characterized *via* X-ray crystallography, **2** being the largest Mn carbonyl complex yet structurally characterized.

Interest in the neutral tetrameric cubane-like series of complexes [M(μ_3-X)(CO)$_3$]$_4$ (M = Mn^I, Re^I; X = OH, OR, SR) peaked in the 1970's and an extensive range of compounds was characterized.[1-3] A recent literature review[4] surprisingly reveals that even today only one manganese carbonyl compound of higher nuclearity, the unrelated hexanuclear complex [Mn$_6$(CO)$_9${μ-OP(OEt)$_3$}$_9$],[5] has been crystallographically characterized. Our interest in [(arene)Mn(CO)$_3$]$^+$ chemistry[6] caused us to seek new routes to arene manganese complexes and we chose to investigate the reaction of Mn$_2$(CO)$_{10}$ with Me$_3$N–O, a well known reagent in the context of substitution of transition metal carbonyl complexes.[7] In this communication we report the unexpected results of this study, facile one-pot synthesis of [{Mn(μ_3-OH)(CO)$_3$}$_4$] **1**, and [Mn$_7$(μ_3-OH)$_8$(CO)$_{18}$] **2**, a novel mixed-valence heptanuclear Mn carbonyl complex.

Synthesis of **1** was accomplished by stirring Mn$_2$(CO)$_{10}$ (2.00 g, 5.13 mmol) in tetrahydrofuran (thf) in the presence of Me$_3$N-O·2H$_2$O (3.42g, 30.8 mmol) under ambient conditions for 18 h. Solvent removal and recrystallization from hot toluene afforded 2.07 g (2.56 mmol, 100%) of **1**·2toluene [IR (KBr) ν/cm^{-1}: $\nu_{\text{Mn–CO}}$ 2027m, 1932s, 1891s; ν_{OH} 3566m]. The X-ray structure of **1**·2toluene confirms† the expected[2,3,8] tetrameric structure that is based upon a distorted cubane (Fig. 1). Synthesis of **2** was conducted as for **1** but in the presence of 0.80 g (4.39 mmol) of benzophenone. Recrystallization of the crude reaction product from CHCl$_3$ layered with hexanes afforded 1.88 g (1.04 mmol, 71%) of **2**·3Ph$_2$CO·2CHCl$_3$ [IR (KBr) ν/cm^{-1}: $\nu_{\text{Mn–CO}}$ 2024m, 1915s; ν_{OH} 3628m]. The X-ray structure† reveals (Fig. 2) a symmetrical C_{3v} heptanuclear molecule that may be regarded as the result of oxidation of **1** followed by fusion with another molecule of **1**. As **2** is only isolated in the presence of benzophenone it would seem reasonable to attribute the oxidation to electron transfer from **1** to benzophenone; however no reduced benzophenone was detected. There are two Mn environments in **2**. The outer six Mn atoms are statistically identical to those in **1** but the core Mn atom, Mn(1), which has to be assigned an oxidation state of two in order to balance the charge of the complex, is quite different. The Mn(1)–O distances average 2.169(2) Å *versus* the 2.055(9) Å average to the outer six Mn atoms. The former value is typical of Mn^{II}–O distances.[9] The geometry around Mn(1) is quite unusual as it is intermediate between an octahedron and a trigonal prism, presumably a manifestation of steric repulsion between the OH moieties. The benzophenone molecules act as hydrogen bond acceptors to μ_3-OH moieties with O · · · H separations of 1.79–1.93 Å. Complex **1** also shows a strong tendency to act as a hydrogen bond donor

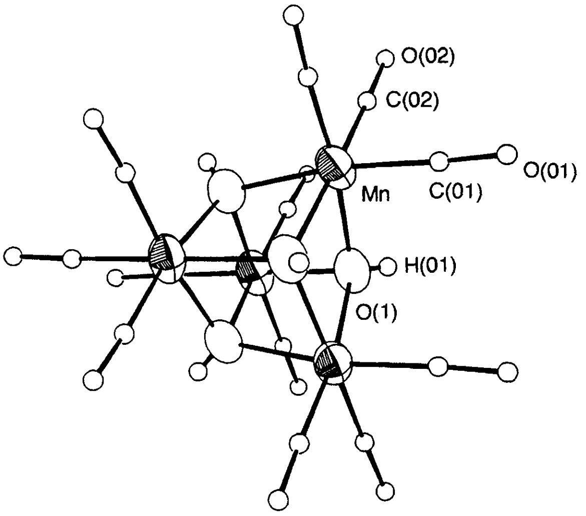

Fig. 1 ORTEP perspective view of **1**; average bond distances (Å): Mn–C 1.807(2), Mn–O 2.051(3), C–O 1.136

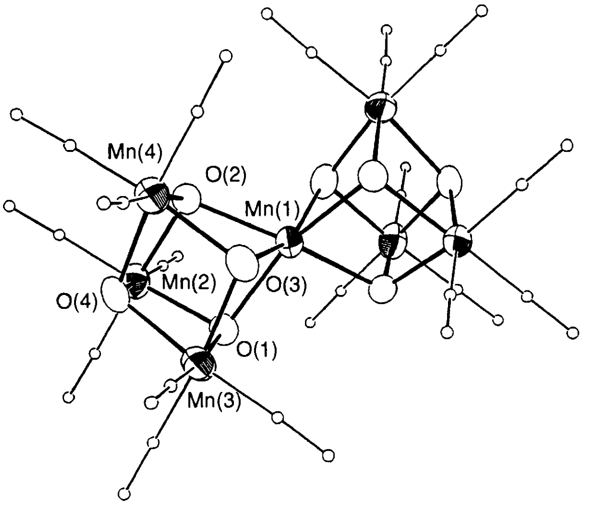

Fig. 2 ORTEP perspective view of **2**; average bond distances (Å): Mn–C 1.774(5), Mn^I–O 2.055(9), Mn^{II}–O 2.169(2), C–O 1.158(4)

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† *Crystal data*: [{Mn(μ_3-OH)(CO)$_3$}]·2 toluene, **1**·2toluene, crystallizes in the tetragonal space group $P4_2/nnm$ (Z = 2) with a = 11.1206(8), c = 12.6696(15) Å, V = 1566.8(2) Å^3, D_c = 1.71 g cm^{-3}, μ = 15.8 cm^{-1}. The structure was solved by direct methods and gave R = 0.029, R_w = 0.032 for 514 unique, absorption-corrected, observed reflections with $F_o \geqslant 3\sigma(F_o)$ collected on an Enraf-Nonius CAD-4 diffractometer. The complex lies around a $\bar{4}2m$ position and the toluene solvate methyl substituents are disordered.

[Mn$_7$(μ_3-OH)(CO)$_{18}$]·3benzophenone·2CHCl$_3$, **2**·3benzophenone·2CHCl$_3$, crystallizes in the monoclinic space group $I2/a$ (Z = 4) with a = 22.0088(16), b = 14.3630(9), c = 25.0403(15) Å, β = 113.156(6)°, V = 7277.9(8) Å^3, D_c = 1.62 g cm^{-3}, μ = 14.3 cm^{-1}. The structure was solved by direct methods and gave R = 0.033 and R_w = 0.034 for 2832 unique, absorption-corrected, observed reflections with $F_o \geqslant 2.5\sigma(F_o)$ collected on an Enraf-Nonius CAD-4 diffractometer. The central atom of the complex, Mn(1), resides on a crystallographic 2-fold axis.

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.

and we have isolated **1** hydrogen bonded to diacetone alcohol (**1**·diacetone alcohol) and water (**1**·4H_2O).

Complex **2** is of more than aesthetic interest since it has recently been realized that mixed-valence tetrameric Mn_4O_4 aggregates probably represent the donor site of water oxidation in the photosynthetic enzyme PS II.[9,10] Furthermore, higher nuclearity synthetic analogues have been shown to contain an Mn_4O_4[11] cubane core. The present study is not directly relevant in the context of PS II as the carbonyl ligands manifest themselves by stabilizing lower-valent Mn atoms than those in PS II and model compounds. However, evaluation of the redox chemistry of **2** and its derivatives represents an obvious and immediate goal as does extension of the synthetic methodology (including the use of other mild oxidising agents) to other transition metal binary carbonyl compounds.

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