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Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

Supramolecular properties of $[Mn(CO)_3(\mu_3\text{-}OH)]_4$, a neutral organometallic molecule that is capable of binding a variety of small and large guest molecules

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To cite this Article Clerk, Michael D. , Copp, Steven B. , Subramanian, S. and Zaworotko, Michael J.(1992) 'Supramolecular properties of $[Mn(CO)_3(\mu_3\text{-}OH)]_4$, a neutral organometallic molecule that is capable of binding a variety of small and large guest molecules', Supramolecular Chemistry, 1: 1, 7 — 9

To link to this Article: DOI: 10.1080/10610279208027434

URL: http://dx.doi.org/10.1080/10610279208027434

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SUPRAMOLECULAR CHEMISTRY, Vol. 1, pp. 7–9
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COMMUNICATION

Supramolecular properties of $[Mn(CO)_3(\mu_3\text{-}OH)]_4$, a neutral organometallic molecule that is capable of binding a variety of small and large guest molecules

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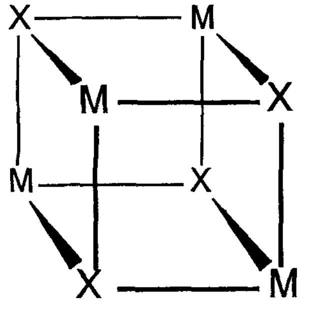
$[Mn(CO)_3(\mu_3\text{-}OH)]_4$, 1, is able to form stable adducts with a variety of guests as a result of O-H....X hydrogen bonding between its μ_3-OH groups and hydrogen bond acceptor moieties of the guest molecules. Two such structures are detailed: $1.4H_2O$ and $1.4PPh_3O$.

The existence of M_4X_4 cubane-like structures, I, is a feature of the chemistry of many metals over a wide range of oxidation states and metal types. The diversity and ubiquity of such moieties is illustrated by a few recent examples based upon the following M, X combinations: Ga^{III}, S^{2-}[1]; Ru^{III}, S^{2-}[2]; Ni^{IV}, Se^{2-}[3], and Cr^{III}, O^{2-}[4]. When one considers that such cubes are also known to be biochemically relevant[5] it is surprising that little exploration of their supramolecular chemistry has yet been conducted. Clusters based upon M = Mn^I and a variety of univalent X moieties were first reported in the 1970's[6]. We recently reported a high yield, one-step route to the low valent analogue $[Mn(CO)_3(\mu_3\text{-}OH)]_4$[7], 1, which is based upon a $Mn^I_4(OH)_4$ distorted cube. 1 is apparently indefinitely stable under ambient conditions and is soluble in a wide range of solvents including water. Our unexpected observation that 1 forms stable adducts with toluene[7] (1:2, **1a**) or diacetone alcohol[8] (1:1, **1b**; 1:2, **1c**) prompted us to further explore the ability of 1 to act as a host molecule. In this communication we report the details of the X-ray crystal structures of two new 1:4 adducts, $1.4H_2O$, **1d**, and $1.4PPh_3O$, **1e**. We discuss their relevance in the context of our earlier work and a series of model compound studies related to the Mn based water oxidation enzyme, photosystem II (PS-II),[9,10] for which an Mn_4O_3Cl cube has been considered as a model of one of the five oxidation levels of the active site.[9c,d]



I

Pale yellow crystals of **1d** suitable for study by X-ray crystallography were grown from a saturated solution of **1a** in $CHCl_3$ that was exposed to atmospheric moisture. The structure of **1d**[11] is illustrated with an ORTEP[13] perspective view in Fig. 1. The Figure reveals how each μ_3-OH ligand is hydrogen-bonded to the oxygen atom of a water molecule. The H-bonding interactions (dO....O = 2.911(7) Å) are relatively weak and crystallographically imposed symmetry means that all four water molecules are equivalent. The O-H....O angles approach linearity (164(7)°). A similar interaction was recently reported in the μ-OH Cu^{II} dimer $[Cu_2(\mu\text{-}OH)(\mu\text{-}Cl)(\mu\text{-}OAc)(bpy)_2]^+$[14] (O-H....O distance of 2.02(7) Å and O-H....O angle of 171.0(6)°).

Yellow/orange crystals of **1e** were obtained in ca. 80% yield via reacting **1a** with triphenylphosphine in CBr_4, extracting the insolubles with hot acetonitrile,

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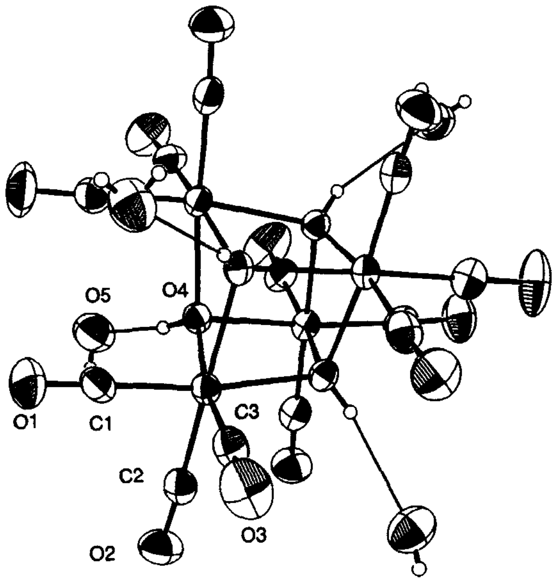

Figure 1 Perspective view of 1d. $d_{O....O}$ distances of 2.911(7) Å are observed for all four μ_3-OH....OH_2 interactions.

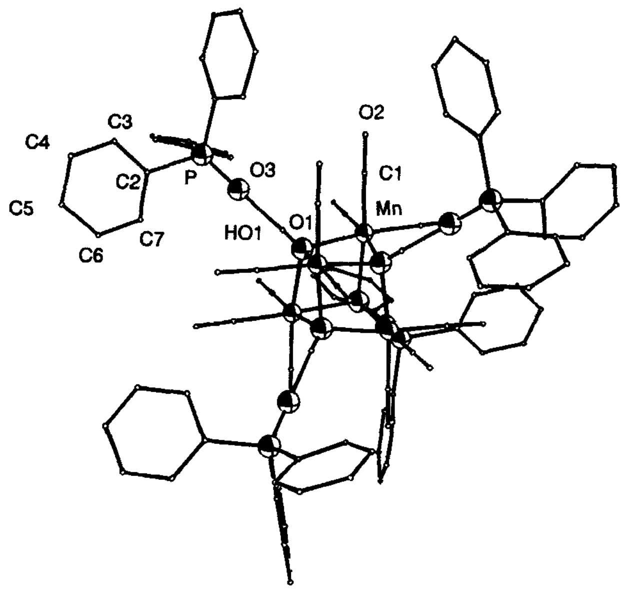

Figure 2 Perspective view of 1e. $d_{O....O}$ distances of 2.563(8) Å are observed for all four μ_3-OH....$OPPh_3$ interactions.

and slow cooling of the acetonitrile solution. They may also be obtained via direct reaction of **1e** with PPh_3O. The structure of **1e**[15] is illustrated in Fig. 2 and reveals how each μ_3-OH moiety forms a strong hydrogen bond (dO....O = 2.563(8) Å to a molecule of triphenylphosphine oxide. The crystallographically imposed symmetry means that each hydrogen bond is identical and precisely linear.

The manganese atoms in **1d,e** are formally in the +1 oxidation state and have 18-electron counts. Mn-Mn bonding would therefore not be expected and the Mn-Mn intramolecular distances, which range from 3.15 to 3.23 Å, support this assertion. All other bond distances and angles within the cubane hosts are within expected ranges[16] and are statistically identical with each other and **1a–c**.

This study therefore confirms that **1** is capable of bonding to as wide a group of molecules as water, triphenylphosphine oxide and possibly even toluene.[17] The salient feature of this observation is extrapolation of the phenomenon to other Mn(μ-OH) complexes which are of more direct relevance to PS-II. **1** cannot, of course, be regarded as a direct analogue of the active Mn species in PS-II (as a result of the low valence of the manganese atoms stabilized by the carbonyl ligands). However, the ability of μ-OH ligands to hydrogen bond to water and other substrates is very relevant to PS-II, which is likely to contain such groups in one or more of its oxidation levels, and such a mode of interaction offers an alternative to direct ligation of water. Intramolecular H-bonding of water to a PS-II model compound has been reported recently[18], but the interaction is much stronger (<2.6 Å), is from a μ-oxo to a hydrogen atom of a coordinated water molecule (rather than a μ-hydroxo to the oxygen of a water molecule), and the Mn_4 cluster is not a cubane. Furthermore, **1** contains potential redox active sites and could therefore still be expected to offer analogous chemistry, but based upon Mn^{I}-Mn^{II} redox cycles rather than the Mn^{II}-Mn^{III} and Mn^{III}-Mn^{IV} processes proposed for PS-II.[9,10] Finally, **1** also inherently possesses numerous pathways for derivatization via the carbonyl ligands and recent work shows that the cubane core is even stable as $[Mn_4^{IV}O_4]^{8+}$.[19] Derivatization of **1** could be effected with a view to inducing a much greater degree to the selectivity of **1** for a variety of molecules and modifying its redox activity. Both aspects are currently under investigation.

ACKNOWLEDGEMENT

We thank the N.S.E.R.C. (Canada) for financial support of this work (operating grant to M.J.Z. and postgraduate fellowship to M.D.C.) and Saint Mary's University for provision of the X-ray diffractometer.

(Received February 24, 1992)

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11. ν_{OH} 3613s, 3400b; ν_{CO} 2035s, 1941s cm^{-1}. Crystal data for **1d**: $C_{12}H_{12}Mn_4O_{20}$, FW = 696.0, tetragonal, I$\bar{4}$, Z = 2, a = 11.4400(7), c = 9.0301(8) Å, V = 1181.80(13) Å^3, ρ_{calc} = 1.96 g/cm^3. Intensity data were collected to $2\Theta = 50°$ on an Enraf-Nonius CAD-4 diffractometer at 17 °C using graphite monochromated Mo radiation ($\lambda(K\alpha)$ = 0.70930 Å). Measurement of 612 intensities (606 unique) afforded 561 observed ($I > 2.5\sigma(I)$) corrections. The data were corrected for Lorentz, polarization and absorption effects. The structure was solved via direct methods and following location and refinement of all hydrogen atoms full-matrix least squares refinement of 94 variables gave R = 0.023 and Rw = 0.027. The cube lies around a crystallographic $\bar{4}$ position. All crystallographic calculations were conducted with the PC version of the NRCVAX[12] program system on 486 based IBM compatible computers.
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15. ν_{OH} 3150b; ν_{CO} 2013s, 1913s cm^{-1}. Crystal data for **1e**: $C_{84}H_{64}Mn_4O_{20}P_4$, FW = 1737.1, cubic, P$\bar{4}$3n, Z = 2, a = 16.233(2) Å, V = 4277.6(5) Å^3, ρ_{calc} = 1.35 g/cm^3. Other details as for **1a** except: 330 observed ($I > 3\sigma(I)$) reflections out of 708 unique, phenyl C-H hydrogen atoms were placed in calculated positions, R = 0.029, Rw = 0.028 and the molecule lies around a 23 position with Mn, OH, and P = 0 moieties lying on 3-fold axes.
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