The *X*-Ray Crystal Structure of μ_4-Oxo-hexa-μ-iodotetrakis[tripropylphosphinemanganese(II)], a Manganese(II) Cluster derived from the Interaction of Di-iodotripropylphosphinemanganese(II) with Dioxygen

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Exposure of an n-pentane solution of $MnI_2(PPr^n{}_3)$ to a trace amount of anhydrous dioxygen at room temperature leads to the isolation of $MnI_2(PPr^n{}_3)_2$ and $Mn_4OI_6(PPr^n{}_3)_4$; the latter consists of a tetrahedron of manganese atoms held together by one μ_4-bridging oxygen and six μ-bridging iodine atoms, the five co-ordination about the manganese atoms being completed by capping tri-n-propylphosphine ligands.

We have previously reported the ability of some manganese(II) phosphine complexes, MnX_2 (phosphine), to reversibly co-ordinate molecular oxygen[1] and have observed trends in the P_{50} values[2—4] which can be related to the nature of the phosphine and the halogen. Thus, in solution below 0 °C the ability to bind dioxygen is generally in the order $Cl > Br > I$ and $PR_3 > PPhR_2 > PPh_2R \gg PPh_3$ (no ability); even under high pressures $MnX_2(PPh_3)$ do not bind dioxygen. The trialkylphosphine complexes represent the other extreme, where binding of dioxygen is strongest and not always reversible. Within this group the trimethylphosphine complexes are extraordinary because they react irreversibly with dioxygen to produce manganese(III) species and other products. For example, the reaction of $MnI_2(PMe_3)$ with dioxygen leads to the formation of the trigonal bipyramidal bisphosphine manganese(III) complex, *trans*-$MnI_3(PMe_3)_2$; no phosphine oxidation is observed.[5]

Because of these differences in reactivity towards dioxygen we are investigating other trialkylphosphine complexes, $MnX_2(PR_3)$, and report here a novel μ_4-oxo-system derived from the reaction of $MnI_2(PPr^n{}_3)$ with trace amounts of dioxygen at room temperature. To a dilute solution of $MnI_2(PPr^n{}_3)$† in n-pentane was introduced a trace (1% O_2/99% Ar) of rigorously anhydrous dioxygen. Immediately the colourless solution became green, indicative of the formation of a dioxygen complex. On standing in the refrigerator two types of crystal were observed to have

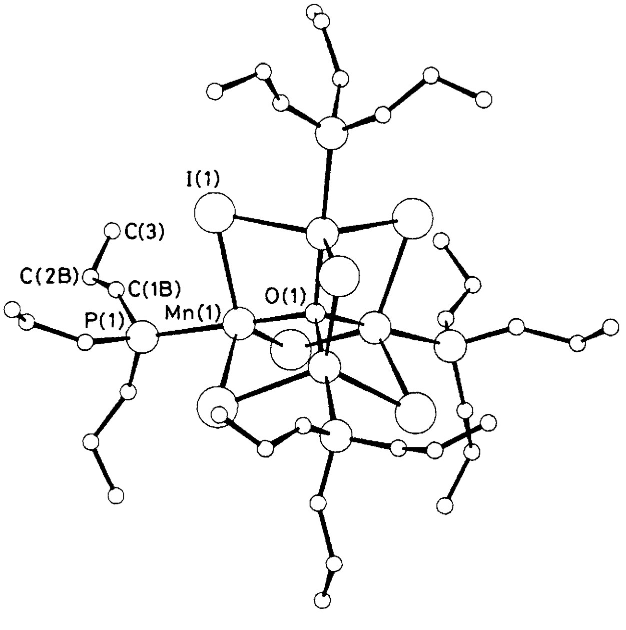

Figure 1. The molecular structure of $Mn_4I_6O[P(CH_2CH_2CH_3)_3]_4$ showing the atomic numbering scheme. Selected bond lengths (Å): Mn(1)–I(1) 2.835(1), Mn(1)–P(1) 2.02(9), Mn(1)–O(1) 2.063(4), Mn(1)–Mn(1) 3.369(6). Selected bond angles (°): I(1)–Mn(1)–P(1) 91.2(1), I(1)–Mn(1)–O(1) 88.8(1), Mn(1)–I(1)–Mn(1) 72.9(1), P(1)–Mn(1)–O(1) 180, Mn(1)–O(1)–Mn(1) 109.5.

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† Satisfactory elemental analyses were obtained for $MnI_2(PPr^n{}_3)$.

formed. A sample of the pink crystals was found by *X*-ray analysis to be pseudotetrahedral monomeric $MnI_2(PPr^n{}_3)_2$. Although interesting in its own right, $MnI_2(PPr^n{}_3)_2$ is not novel; we,[6] and others[7] have previously crystallographically characterised a similar bisphosphine complex, $MnI_2(PEt_3)_2$. However, the second type of crystal (pale green in colour) proved to have a most unexpected structure, $[Mn_4OI_6(PPr^n{}_3)_4]$;‡ this complex is certainly novel and of great interest.

The molecular structure is shown in Figure 1. The molecule consists of a tetrahedron of manganese atoms held together by one central μ_4-bridging oxygen atom and six μ-bridging iodine atoms. In addition each manganese is capped by a tripropylphosphine ligand. Each n-propyl substituent is disordered with the methylene carbons distributed over two sites.

There is a good deal of current interest in bi- and tetra-manganese systems as models for O_2 evolution on photosystem II. One such model, $[Mn_4O_3Cl_4(OAc)_3(py)_3]$ (py = pyridyl), contained a μ_3-oxygen,[9] presumably formed from a water molecule. However, there are only a few molecular compounds in which oxygen is four co-ordinate, *e.g.* $[Mg_4OBr_6(C_4H_{10}O)_4]$,[10] $[Be_4O(C_2H_3O_2)_6]$,[11] and $[Mn_6O_2(Me_3CCO_2H)_4(Me_3CCO_2)_{10}]$,[12] and there are examples of the type $Cu_4OCl_6L_4$.[13–17] In most cases the source of oxygen in the cluster has not been identified. It could originate in either a dioxygen or a water molecule, since often neither species was excluded, or in some other oxygenated species. However, in our preparation water was rigorously excluded and we thus conclude that the reaction of $MnI_2(PPr^n{}_3)$ with dioxygen in n-pentane leads to O–O bond cleavage and the formation of $[Mn_4OI_6(PPr^n{}_3)_4]$ and $MnI_2(PPr^n{}_3)_2$ as the main products. We have previously observed phosphine oxidation[1] when, *e.g.*, the $MnI_2(PBu^n{}_3)$ complex reacts with O_2 at temperatures >0 °C and our observations here demonstrate the activation of dioxygen by $MnI_2(PPr^n{}_3)$ to yield the unusual $Mn_4OI_6(PPr^n{}_3)_4$.

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References

1 C. A. McAuliffe, H. F. Al-Khateeb, D. S. Barratt, J. C. Briggs, A. Challita, A. Hosseiny, M. G. Little, A. G. Mackie, and K. L. Minten, *J. Chem. Soc., Dalton Trans.*, 1983, 2147.
2 K. L. Minten, Ph.D. Thesis, University of Manchester, 1983.
3 M. G. Little, C. A. McAuliffe, and J. B. Raynor, *J. Chem. Soc., Chem. Commun.*, 1982, 68.
4 C. A. McAuliffe, *J. Organomet. Chem.*, 1982, **228**, 255.
5 B. Beagley, C. A. McAuliffe, K. Minten, and R. G. Pritchard, *J. Chem. Soc., Chem. Commun.*, 1984, 658.
6 B. Beagley, J. C. Briggs, A. Challita, J. Fawcett, C. A. McAuliffe, R. G. Pritchard, and D. Russell, unpublished work.
7 N. Hebendanz, F. H. Kohler, and G. Muller, *Inorg. Chem.*, 1984, **23**, 3044.
8 G. M. Sheldrick, Nicolet SHELXTL Users Manual, Nicolet XRD Corporation, Madison, WI, U.S.A., 1988.
9 Q. Li, J. B. Vincent, E. Libby, H.-R. Chang, J. C. Huffman, P. D. W. Boyd, G. Christou, and D. N. Hendrickson, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1731.
10 G. Stucky and R. E. Rundle, *J. Am. Chem. Soc.*, 1964, **86**, 4821.
11 W. H. Bragg and G. T. Morgan, *Proc. R. Soc. London, Ser. A*, 1923, **104**, 437.
12 A. R. E. Baikie, A. J. Howes, M. B. Hursthouse, A. B. Quick, and P. Thornton, *J. Chem. Soc., Chem. Commun.*, 1986, 1587.
13 R. C. Dickinson, F. T. Helm, W. A. Baker, Jr., T. D. Black, and W. H. Watson, Jr., *Inorg. Chem.*, 1977, **16**, 1530.
14 N. S. Gill and M. Sterns, *Inorg. Chem.*, 1970, **9**, 1619.
15 M. R. Churchill, B. G. DeBoer, and S. J. Mendak, *Inorg. Chem.*, 1975, **14**, 2496.
16 D. D. Swank, D. O. Nielson, and R. D. Willett, *Inorg. Chim. Acta*, 1973, **7**, 91.
17 J. A. Bertrand, *Inorg. Chem.*, 1967, **6**, 495.

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‡ *Crystal data* for $[Mn_4OI_6(PPr^n{}_3)_4]$, $C_{36}H_{84}P_4Mn_4I_6O$: $M = 1638.1$, cubic, space group $I23$, $a = 14.471(5)$ Å, $U = 3030(1)$ Å^3, $D_c = 1.795(2)$ Mg m^{-3}, $Z = 2$. Graphite monochromatized Mo-K_α radiation, $\lambda = 0.71069$ Å, $\mu = 3.94$ mm^{-1}. The pale green crystal, 0.3 × 0.3 × 0.2 mm^3, was sealed in a Lindeman tube under dry argon and the diffraction data was collected on a Nicolet R3m/V diffractomer at 223 K. 1364 Reflections were measured with 393 considered as observed $[F_o > 5\sigma(F_o)]$. The structure was solved by standard heavy atom methods followed by full-matrix least-squares refinement to a final $R = 0.049$ (merging $R_w = 0.024$ after absorption correction by azimuthal scan technique). Appropriate positional and vibrational constraints were applied during refinement to atoms occupying special sites, namely O(2a), Mn and P(8c) and I(12d), with I, Mn, and P being treated anisotropically, C and O isotropically, and H atoms ignored. Calculations were performed on a micro-Vax computer using the SHELX TL suite of programs.[8] Neutral atom scattering factors were used throughout. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.