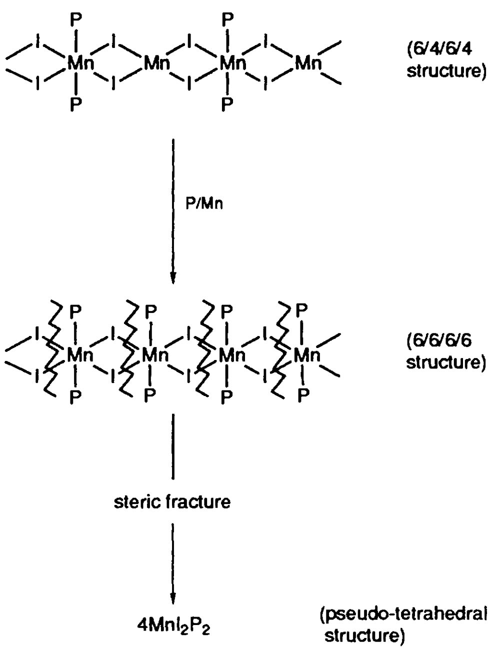
Crystal Structures of Trinuclear [{$MnI_2(PPhMe_2)_{1.33}$}$_3$] and Tetranuclear [$Mn_4(\mu_4\text{-}O)I_6(PPhMe_2)_4$] formed by O=O Bond Cleavage by the Former†

Brian Beagley, Anthony G. Mackie, Philomena P. Matear, Charles A. McAuliffe,* Peter T. Ndifon and Robin G. Pritchard
Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD, UK

The unique trinuclear complex [{$MnI_2(PPhMe_2)_{1.33}$}$_3$] has been prepared and its crystal structure determined. It consists of a pseudo-octahedral MnI_4P_2 unit sandwiched by two pseudo-tetrahedral MnI_3P units held together by bridging iodines. Under controlled conditions this complex cleaves dioxygen to produce the tetranuclear complex [$Mn_4(\mu_4\text{-}O)I_6(PPhMe_2)_4$], the structure of which has also been determined.

There is a good deal of interest in the bonding of tertiary phosphines to manganese(II) and we,[1,2] Wilkinson and co-workers[3–5] and Hebendanz *et al.*[6] have reported the crystal structures of some manganese(II)–tertiary phosphine species. Our interest in these simple complexes stems from the fact that they are able reversibly or irreversibly to bind dioxygen and other small molecules[7–11] either in the solid state or in solution. We have prepared and characterised a series of these compounds having a 1:1 Mn:P stoichiometry and they appear to be polymeric. The X-ray crystal structure of $MnI_2(PPhMe_2)$[1] reveals an iodide-bridged polymer chain consisting of alternate pseudo-octahedral *trans*-MnI_4P_2 units and tetrahedral MnI_4 units (*i.e.* the 6/4/6/4 structure). We[2] and Hebendanz *et al.*[6] have reported the crystal structures of a series of bis(tertiary phosphine)manganese(II) diiodide complexes, [$MnI_2(phosphine)_2$], which are all mononuclear with a pseudo-tetrahedral arrangement of ligands about the manganese centre. It is very likely that these complexes are formed by the addition of tertiary phosphine ligands to the unsaturated manganese centres of the 6/4/6/4 polymeric chain structure and, because of steric factors, the resulting 6/6/6/6 polymeric chain breaks to give the mononuclear bis(tertiary phosphine) as outlined in Scheme 1.

We now report a unique type of manganese(II) phosphine complex, the trinuclear [{$MnI_2(PPhMe_2)_{1.33}$}$_3$], and propose a scheme for its formation from the known polymeric [{$MnI_2(PPhMe_2)$}$_n$]. Moreover, by the isolation of this oligomer these studies shed light on the formation of the monomeric bis(phosphine) complexes, [$MnX_2(phosphine)_2$], from the polymeric $MnX_2(phosphine)_n$ complexes. Also of importance is the cleavage of dioxygen under ambient conditions by the trinuclear complex to form the μ_4-oxo species [$Mn_4(\mu_4\text{-}O)I_6(PPhMe_2)_4$]. Although a μ_4-oxygen system is rare, there are some examples in the literature, *viz.* [$Mg_4OBr_6(C_4H_{10}O)_4$],[12] [$Be_4O(C_2H_3O_2)_6$],[13] [$Mn_6O_2(Me_3CCO_2H)_4(Me_3CCO_2)_{10}$],[14] [$Ba_4O${$OC_6H_2(CH_2NMe_2)_3$-2,4,6}$_6$][15] and various copper(II) systems of type $Cu_4OL_4Cl_6$.[16–20]



Scheme 1 Mechanism for the formation of manganese(II) bis(phosphine) complexes

Results and Discussion

Studies on some manganese(II)–tertiary phosphine complexes have shown that it is possible to obtain these compounds in a variety of Mn:P stoichiometries with the P:Mn ratio ranging from 0.25 to 2:1.[21] We report here the X-ray crystal structure of [{$MnI_2(PPhMe_2)_{1.33}$}$_3$] **1**, having a P:Mn ratio of 1.33:1, obtained by refluxing MnI_2 with 1.4 mol equivalents of $PPhMe_2$ in pentane resulting, eventually, in the formation of pink-red crystals (see Experimental section).

The molecular structure (together with the atomic labelling) of [{$MnI_2(PPhMe_2)_{1.33}$}$_3$] is shown in Fig. 1. It consists of a trio of manganese atoms held together by bridging iodine atoms and comprising a centrosymmetric MnI_4P_2 unit sandwiched by two pseudo-tetrahedral units. While each of the two pseudo-tetrahedral manganese atoms is co-ordinated by a phosphine ligand and a terminal iodide, the central pseudo-octahedral manganese atom possesses four equatorial iodide ligands and two axial phosphine ligands, giving a P–Mn–P angle of 180° and a P–Mn–I angle of nearly 90°. The bond lengths and angles (together with the approximate standard deviations) are shown in the legend to Fig. 1.

The bond parameters for the [{$MnI_2(PPhMe_2)_{1.33}$}$_3$] complex are similar to those reported for the polymeric complex

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

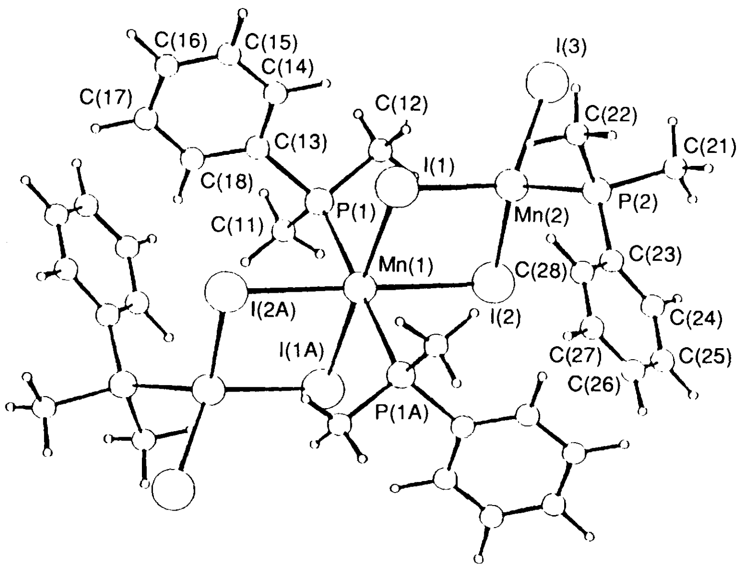


Fig. 1 X-Ray crystal structure of $[\{MnI_2(PPhMe_2)_{1.33}\}_3]$. Some of the disordered atoms of the phenyl ring, C(13)–C(18), have been omitted for clarity. Selected bond lengths/Å: Mn(1)–I(1) 2.983(1), Mn(1)–I(1A) 2.983(1), Mn(2)–I(1) 2.710(1), Mn(1)–I(2) 2.996(1), Mn(2)–I(2) 2.736(1), Mn(2)–I(3) 2.638(1), Mn(1)–P(1) 2.670(2), Mn(2)–P(2) 2.548(2), P(1)–C(11) 1.821(7) and Mn(1)···Mn(2) 3.921(1). Selected bond angles/°: I(1)–Mn(1)–I(2) 87.5(1), I(2)–Mn(2)–I(3) 119.1(1), I(1)–Mn(1)–P(1) 91.8(1), I(2)–Mn(1)–P(1) 87.3(1), I(2)–Mn(2)–I(1) 98.8(1), Mn(2)–I(1)–I(2) 40.8(0), Mn(1)–I(2)–I(1) 46.1(0), P(1)–Mn(1)–I(1A) 88.2(1), I(1)–Mn(2)–P(2) 119.6(1), I(2)–Mn(2)–P(2) 104.8(1), Mn(1)–P(1)–C(11) 114.2(3), P(1)–C(13)–C(14) 120.5(5), I(3)–Mn(2)–I(1) 116.0(1), I(3)–Mn(2)–P(2) 99.1(1), Mn(1)–I(1)–Mn(2) 86.9(0) and Mn(1)–I(2)–Mn(2) 86.2(1).

Table 1 Fractional atomic coordinates for non-hydrogen atoms of $[Mn_3I_6(PPhMe_2)_4]$

Atom	x	y	z
Mn(1)	0.000 00	0.000 00	0.500 00
Mn(2)	−0.204 8(1)	0.183 24(9)	0.212 29(8)
I(1)	0.088 87(5)	0.027 72(4)	0.251 83(3)
I(2)	−0.322 17(5)	0.154 01(4)	0.434 74(3)
I(3)	−0.244 13(8)	0.419 89(5)	0.068 60(5)
P(1)	0.032 7(2)	0.225 3(2)	0.476 2(1)
P(2)	−0.370 2(2)	0.116 9(2)	0.123 5(1)
C(11)	0.219 8(8)	0.208 8(8)	0.509 3(7)
C(12)	0.015 9(9)	0.341 7(7)	0.331 4(6)
C(13)	−0.100 0(7)	0.322 5(5)	0.564 0(5)
C(14)	−0.243 8(8)	0.411 0(7)	0.525 1(7)
C(15)	−0.345 2(10)	0.481 7(8)	0.593 5(9)
C(16)	−0.308 2(13)	0.467 2(9)	0.696 4(9)
C(17)	−0.167 1(13)	0.379 8(9)	0.739 6(8)
C(18)	−0.064 9(10)	0.309 3(7)	0.671 1(6)
C(21)	−0.354 5(11)	0.172 7(7)	−0.032 4(6)
C(22)	−0.570 0(8)	0.200 0(7)	0.160 5(7)
C(23)	−0.352 9(7)	−0.051 1(6)	0.160 2(5)
C(24)	−0.446 9(9)	−0.105 4(7)	0.246 6(6)
C(25)	−0.430 4(11)	−0.236 8(7)	0.277 4(7)
C(26)	−0.321 9(11)	−0.313 7(8)	0.220 1(7)
C(27)	−0.224 0(11)	−0.263 0(8)	0.134 3(8)
C(28)	−0.241 6(9)	−0.134 8(7)	0.104 4(6)

$[\{MnI_2(PPhMe_2)\}_n]$,[1] Fig. 1 and Table 1. The Mn–I (bridging) bond lengths in the pseudo-tetrahedral units of the trimer [2.710(1)–2.736(1) Å] compare with those in the polymer (2.694–2.720 Å), as do the Mn–I bond lengths in the pseudo-octahedral units [2.983(1)–2.996(1) Å for the trimer, 2.973–3.004 Å for the polymer].

Like the Mn–I bond lengths, the Mn–P bond lengths for the pseudo-tetrahedral units [2.548(2) Å] are also shorter than those in the pseudo-octahedral units [2.670(2) Å]. This suggests an electronic influence on the bond parameters as the two phosphine ligands at the octahedral manganese centre cause a greater electron density than does the single phosphine at the tetrahedral manganese.

The Mn(2)–I(3) bond [2.638(1) Å] is much shorter than the other two Mn–I bonds around the tetrahedrally co-ordinated manganese since it involves terminally co-ordinated rather than bridging iodine.

We propose that $[\{MnI_2(PPhMe_2)_{1.33}\}_3]$ is formed by the co-ordination of a phosphine ligand at the tetrahedral manganese centres of $[\{MnI_2(PPhMe_2)\}_n]$[1] (6/4/6/4 polymeric structure), followed by bond rupture, probably due to steric factors, to give the trinuclear moiety, as Scheme 2 suggests.

Complex **1** reacts with anhydrous dioxygen in pentane solution to form a deep green μ$_4$-oxo complex, $[Mn_4(\mu_4\text{-}O)I_6(PPhMe_2)_4]$ **2**. Thus, when a dilute rigorously anhydrous solution of **1** in pentane is exposed to a 99:1 Ar:O_2 mixture a deep green colour develops, from which crystals of hexa-μ-iodo-μ$_4$-oxo-tetrakis[(dimethylphenylphosphine)manganese(II)] **2** form, with pentane as solvent of crystallisation, Fig. 2 and Table 2. 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 dimethylphenylphosphine ligand.

It has been our general observation that these manganese(II) phosphine complexes can bind dioxygen reversibly at temperatures < 20 °C,[7] but that at ambient temperature exposure to relatively concentrated dioxygen [*ca.* 1 atm (*ca.* 10^5 Pa)] causes oxidation of the co-ordinated phosphine to phosphine oxide to yield, for example, $[MnI_2(PPh_2Me)(OPPh_2Me)]$[22] and $[MnI_2(OPPh_2Me)_2]$.[21]

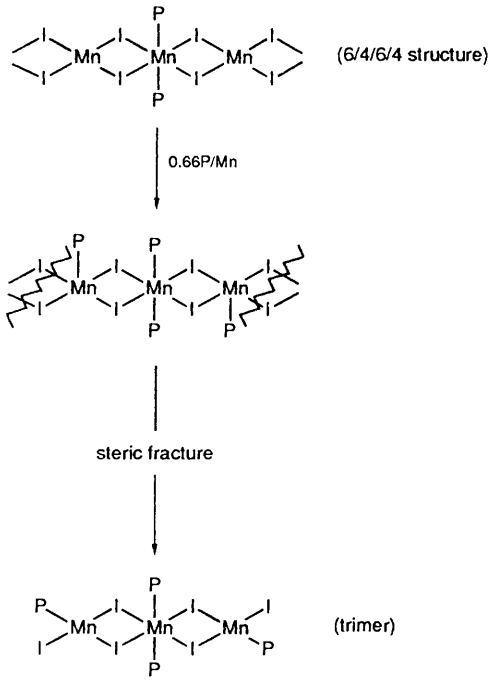
This clearly involves dioxygen bond rupture and in this study, by employing low concentrations of dioxygen, we have been able to isolate one of the products of such cleavage, namely $[Mn_4(\mu_4\text{-}O)I_6(PPhMe_2)_4]$. It is interesting that a reaction of dioxygen with $[MnI_2(PPr^n{}_3)]$ produces an identical product, $[Mn_4(\mu_4\text{-}O)I_6(PPr^n{}_3)_4]$.[22,23] The μ$_4$-oxo tetramer is clearly an important intermediate in the dioxygen bond-cleavage reaction and appears to be somewhat independent of the nature of the initial manganese phosphine complex.

Experimental

The complex $[\{MnI_2(PPhMe_2)_{1.33}\}_3]$ was prepared by mixing anhydrous manganese(II) iodide (0.309 g, 1.0 mmol) with

Table 2 Fractional atomic coordinates for non-hydrogen atoms of $[Mn_4(\mu_4\text{-}O)I_6(PPhMe_2)_4]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mn(1)	0.546 4(1)	0.322 0(1)	0 320 21(7)	C(22)	0.390 6(8)	−0.076 8(10)	0.174 5(6)
Mn(2)	0.478 8(1)	0.192 8(1)	0.197 43(7)	C(23)	0.422 7(9)	−0.020 4(10)	0.078 7(6)
Mn(3)	0.397 4(1)	0.423 9(1)	0.213 02(8)	C(24)	0.413 7(12)	−0.120 0(14)	0.053 4(8)
Mn(4)	0.576 9(1)	0.423 4(1)	0.210 31(7)	C(25)	0.383 2(13)	−0.127 2(20)	−0.007 9(10)
I(12)	0.529 55(6)	0.094 13(7)	0.306 63(4)	C(26)	0.367 4(18)	−0.038 4(18)	−0.037 9(9)
I(13)	0.411 61(6)	0.414 93(9)	0.326 61(4)	C(27)	0.375 8(22)	0.043 3(20)	−0.015 3(10)
I(14)	0.685 24(5)	0.426 23(8)	0.322 38(4)	C(28)	0.396 8(15)	0.055 1(17)	0.044 0(8)
I(23)	0.319 95(6)	0.246 10(8)	0.146 66(5)	C(31)	0.280 8(10)	0.670 0(11)	0.216 6(7)
I(24)	0.592 30(6)	0.236 30(7)	0.151 52(4)	C(32)	0.202 3(8)	0.471 5(13)	0.213 4(7)
I(34)	0.465 09(5)	0.594 26(7)	0.172 20(4)	C(33)	0.213 8(10)	0.550 1(13)	0.112 8(7)
P(1)	0.611 8(3)	0.296 3(3)	0.427 7(2)	C(34)	0.242 7(12)	0.547 6(22)	0.073 5(11)
P(2)	0.455 8(2)	−0.000 3(3)	0.153 5(1)	C(35)	0.203 2(18)	0.570 4(30)	0.016 2(10)
P(3)	0.269 2(2)	0.533 7(3)	0.186 3(2)	C(36)	0.132 7(15)	0.580 9(19)	−0.003 2(11)
P(4)	0.667 0(2)	0.537 7(3)	0.177 1(1)	C(37)	0.094 4(17)	0.572 4(24)	0.028 0(14)
O	0.499 8(4)	0.341 3(5)	0.234 6(3)	C(38)	0.139 0(15)	0.553 9(21)	0.090 2(10)
C(11)	0.557 7(12)	0.206 5(13)	0.456 1(7)	C(41)	0.762 8(8)	0.474 3(12)	0.197 6(7)
C(12)	0.703 8(9)	0.226 1(12)	0.449 3(6)	C(42)	0.688 4(8)	0.669 0(10)	0.209 0(6)
C(13)	0.627 7(10)	0.417 2(13)	0.472 2(6)	C(43)	0.633 8(8)	0.564 2(12)	0.100 7(6)
C(14A)	0.661 8(16)	0.399 0(22)	0.530 7(13)	C(44)	0.595 6(10)	0.654 0(15)	0.076 4(7)
C(15A)	0.679 0(19)	0.481 5(30)	0.568 3(14)	C(45)	0.565 8(13)	0.672 6(20)	0.019 9(10)
C(16)	0.653 3(13)	0.595 2(18)	0.541 8(8)	C(46)	0.576 9(12)	0.594 4(22)	−0.013 3(10)
C(17A)	0.628 0(17)	0.605 4(22)	0.486 2(13)	C(47)	0.615 5(12)	0.502 2(19)	0.007 1(8)
C(18A)	0.609 0(17)	0.507 7(25)	0.448 6(12)	C(48)	0.643 2(10)	0.483 3(15)	0.066 5(7)
C(14B)	0.697 9(35)	0.477 4(46)	0.489 3(22)	C(1E)	−0.174 6(17)	0.238 1(18)	0.126 2(11)
C(15B)	0.705 0(27)	0.582 3(35)	0.520 0(18)	C(2E)	−0.090 7(17)	0.249 3(23)	0.160 3(11)
C(17B)	0.579 0(35)	0.548 5(48)	0.516 1(23)	C(3E)	−0.056 1(10)	0.258 1(14)	0.126 7(6)
C(18B)	0.565 4(26)	0.451 1(36)	0.485 3(17)	C(4E)	0.018 9(16)	0.253 2(16)	0.154 6(10)
C(21)	0.543 2(8)	−0.081 1(9)	0.178 7(6)	C(5E)	0.059 5(12)	0.246 5(16)	0.116 7(8)



Scheme 2 Proposed mechanism for the formation of $[\{MnI_2(PPhMe_2)_{1.33}\}_3]$

$PPhMe_2$ (0.193 g, 1.4 mmol) in freshly distilled pentane (100 cm^3) under dry argon in a flame-dried three-necked flask (250 cm^3) and magnetically stirred. After stirring for 3 d at room temperature a clear solution had formed which, after 7 d in a refrigerator, produced copious (83% yield) pink-red crystals. These were filtered off using Schlenk techniques under dry argon [Found (Calc.): C, 18.1 (18.0); H, 3.5 (3.1); I, 57.0 (57.1)%].

A pink-red crystal (dimensions 0.25 × 0.2 × 0.2 mm) was sealed in a Lindemann tube and X-ray data collected on a Nicolet R3m/V diffractometer at room temperature (293 K). 3656 Unique reflections were considered as observed, $F_o > 3\sigma(F_o)$. The structure was solved by standard heavy-atom methods followed by least-squares refinement to give final $R = 0.038$ ($R' = 0.041$), with $w = 2.1040/[\sigma^2(F_o) + 0.00005\ F_o^2]$. Non-hydrogen atoms were subjected to anisotropic refinement, and hydrogen atoms constrained to chemically reasonable positions. Three standard reflections measured repeatedly at intervals of 150 reflections showed no systematic drift. Lorentz polarisation and absorption (azimuthal scan techniques, maximum and minimum transmissions 0.849 and 0.380 respectively) corrections were applied. Calculations were performed on a micro-VAX computer using the SHELXTL suite of programs.[24] Neutral atom scattering factors were used throughout.

Crystal data. $C_{32}H_{44}I_6Mn_3P_4$, $M = 1478.1$, triclinic, space group $P\bar{1}$, $a = 9.471(6)$, $b = 11.673(8)$, $c = 12.489(8)$ Å, $\alpha = 69.27(5)$, $\beta = 78.76(5)$, $\gamma = 67.70(5)°$, $U = 1191.8$ Å^3, $Z = 1$, $F(000) = 689$, $D_c = 2.06$ g cm^{-3}. Graphite monochromatised Mo-Kα radiation ($\lambda = 0.710\ 73$ Å), μ(Mo-Kα) = 4.53 mm^{-1}.

$[Mn_4(\mu_4\text{-}O)I_6(PPhMe_2)_4]$.—A solution of $[\{MnI_2(PPhMe_2)_{1.33}\}_3]$ (0.1 g) was made in anhydrous pentane (250 cm^3) by stirring under dry argon for *ca.* 3 h in a flame-dried three-necked flask (500 cm^3). The flask was then evacuated and exposed to a preformed strictly anhydrous mixture of argon and dioxygen (99:1 v/v). The previously pale pink solution immediately became deep green. It was allowed to stand in a refrigerator for *ca.* 11 d, whence the deep green crystals (49% yield) obtained were filtered off under dry argon using Schlenk techniques [Found (Calc.): C, 17.0 (17.1); H, 3.3 (3.1); I, 54.4 (54.2)%].

Crystal data. $C_{32}H_{44}I_6Mn_4OP_4 \cdot C_5H_{12}$, $M = 1621.9$, monoclinic, space group $P2_1/n$, $a = 18.797(8)$, $b = 12.400(4)$, $c = 25.610(9)$ Å, $\beta = 112.32(4)°$, $U = 5521.7$ Å^3, $Z = 4$, $F(000) = 2888$, $D_c = 1.95$ g cm^{-3}, crystal dimensions 0.2 × 0.2 × 0.15 mm. Graphite monochromatised Mo-Kα radiation, μ(Mo-Kα) = 4.12 mm^{-1}.

Data collection and processing was done in the same manner

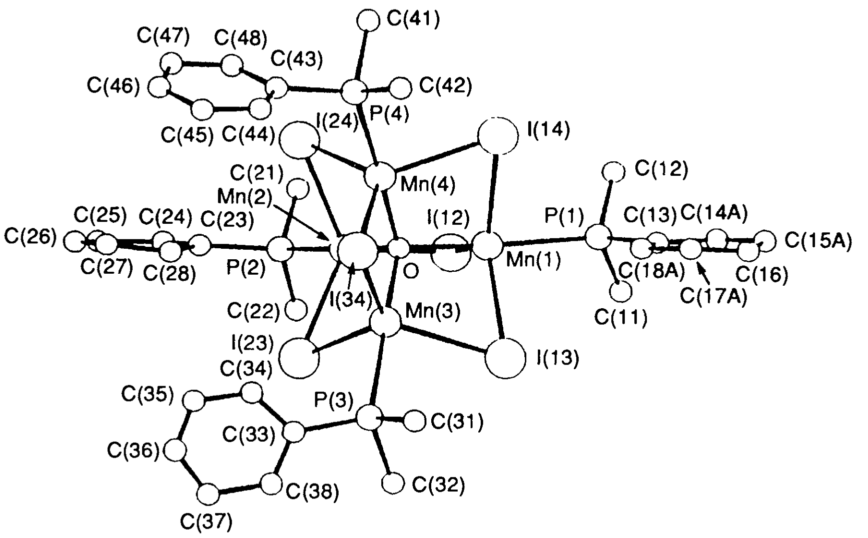


Fig. 2 X-Ray crystal structure of $[Mn_4(\mu_4\text{-}O)I_6(PPhMe_2)_4]\cdot C_5H_{12}$ (H atoms omitted for clarity). Selected bond lengths/Å: Mn(1)–I(12) 2.850(2), Mn(1)–I(13) 2.844(3), Mn(1)–I(14) 2.898(2), Mn(1)–P(1) 2.573(4), Mn(1)–O 2.042(7), Mn(2)–I(12) 2.864(2), Mn(2)–I(23) 2.845(2), Mn(2)–I(24) 2.852(3), Mn(2)–P(2) 2.610(4), Mn(2)–O 2.041(7), Mn(3)–I(13) 2.821(2), Mn(3)–I(23) 2.826(2), Mn(3)–P(3) 2.622(4), Mn(3)–O 2.062(7), Mn(4)–I(14) 2.819(2), Mn(4)–I(24) 2.840(2), Mn(4)–I(34) 2.880(2), Mn(4)–P(4) 2.587(5) and Mn(4)–O 2.052(8). Selected bond angles/°: I(12)–Mn(1)–I(13) 110.4(1), I(12)–Mn(1)–I(14) 120.2(1), I(14)–Mn(1)–I(13) 129.4(1), P(1)–Mn(1)–I(12) 89.6(1), P(1)–Mn(1)–I(13) 93.6(1), P(1)–Mn(1)–I(14) 88.5(1), O–Mn(1)–I(12) 90.1(2), O–Mn(1)–I(13) 89.2(2), O–Mn(1)–I(14) 89.1(2), O–Mn(1)–P(1) 177.0(3), I(23)–Mn(2)–I(12) 116.6(1), P(2)–Mn(2)–I(12) 88.2(1), O–Mn(4)–P(4) 176.0(2), Mn(2)–I(12)–Mn(1) 71.1(1), Mn(3)–I(13)–Mn(1) 72.2(1), C(11)–P(1)–Mn(1) 112.8(5), C(12)–P(1)–C(11) 101.1(8), C(13)– P(1)–Mn(1) 117.5(5), Mn(2)–O–Mn(1) 108.9(3), Mn(3)–O–Mn(1) 108.8(4), Mn(3)–O–Mn(2) 109.1(3) and Mn(4)–O–Mn(1) 108.6(3)

as described for $[\{MnI_2(PPhMe_2)_{1.33}\}_3]$. 9228 Unique reflections were measured of which 5014 were considered observed $[F_o > 5\sigma(F_o)]$, merging $R = 0.029$. The structure was solved by standard heavy-atom methods followed by least-squares refinement to give final $R = 0.029$ ($R' = 0.057$), with $w = 1.5989/[\sigma^2(F_o) + 0.0003\ F_o^2]$. Non-hydrogen atoms were subjected to anisotropic refinement, and hydrogen atoms constrained to chemically reasonable positions. Three standard reflections measured repeatedly at intervals of 150 reflections showed a 4% decline. Lorentz polarization, decomposition and absorption (azimuthal scan method, maximum and minimum transmissions 0.595 and 0.388 respectively) corrections were applied.

Additional material for both structures available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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