Rare Examples of Five-co-ordinate Manganese(II) Complexes containing Monodentate Ligands. Crystal Structures of [$MnBr_2(PEt_3)$] and [$MnI_2(PMeEt_2)$], and Their Reaction with Dioxygen†

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The five-co-ordinate trigonal-bipyramidal complexes [$MnBr_2(PEt_3)$] and [$MnI_2(PMeEt_2)$] have been prepared and their crystal structures determined. Both complexes contain polymeric $(MnX_2)_n$ chains with a single phosphine co-ordinated at each trigonal-bipyramidal centre. The complexes absorb one mole of O_2 per mole of complex in diethyl ether solution at −30 °C.

Although numerous tertiary phosphine complexes are known with divalent transition metals to the right of the first row of the Periodic Table, they are fairly rare for such elements in the middle of the first row.[1-3] The first manganese(II) phosphine complexes reported were by Warren and Bennett,[4] [MnX_2L_2] [L = *o*-phenylenebis(dimethylphosphine); X = Cl or Br], which are monomeric octahedral species. Subsequently, Wilkinson and co-workers[5] showed [$\{Mn(PMe_3)(CH_2SiMe_3)_2\}_2$] to be a tetrahedral dimer. A third type of complex, [$MnI_2(PEt_3)_2$], is a tetrahedral monomer.[6]

Our own work has been predominantly with complexes of stoichiometry $MnX_2(PR_3)$ (R = alkyl or aryl; X = Cl, Br, I or NCS).[7-11] One of these, [$MnI_2(PPhMe_2)$], has been shown to exist in two geometric isomeric forms. When prepared from the reaction of manganese(II) iodide with $PPhMe_2$, X-ray crystallography reveals the structure to consist of a polymeric chain of MnI_2 with alternating tetrahedral (MnI_4) and octahedral (*trans*-MnP_2I_4) units (the 4,6,4,6 structure).[9] However, when prepared by the reaction of manganese metal powder with $PhMe_2PI_2$ the structure of [$MnI_2(PPhMe_2)$] is a five-co-ordinate polymer in which each manganese has a single monodentate phosphine ligand co-ordinated syndiotactically to produce a trigonal-bipyramidal structure.[10] This novel isomer is the only reported example of a five-co-ordinate manganese(II) complex containing a monodentate phosphine ligand.

Since high-spin manganese(II) offers no crystal-field stabilisation energy for any geometry, it might be expected that five-co-ordination would be as common as any other configuration, but such complexes are rare and none were known until 1980 when Hugel and co-workers[12] reported the structure of dibromotris(*N*,*N*′-dimethylurea)manganese(II). Subsequently, reports concerning five-co-ordinate manganese(II) complexes, other than that of [$MnI_2(thf)_3$] (thf = tetrahydrofuran),[13] have essentially been limited to complexes containing porphyrins or chelating ligands;[14,15] of the latter the tripodal ligand $N(CH_2CH_2PPh_2)_3$ is designed to help impose trigonal-bipyramidal geometry because of its own steric requirements.[16]

Results and Discussion

We were intrigued by our observations that geometric isomers of [$MnI_2(PPhMe_2)$] were obtainable by different synthetic routes and we have investigated this further, only to find that by using the conventional synthesis of reaction of the manganese(II) salt with a tertiary phosphine ligand, five-co-ordinate 5,5,5,5 structures are obtained for [$MnBr_2(PEt_3)$] and [$MnI_2(PMeEt_2)$].

The complexes [$MnBr_2(PEt_3)$] and [$MnI_2(PMeEt_2)$] were prepared by mixing stoichiometric quantities of the anhydrous manganese(II) salt and the phosphine in dry diethyl ether under argon. Recrystallisation of the complexes from hot diethyl ether yielded crystals suitable for study by X-ray diffraction.

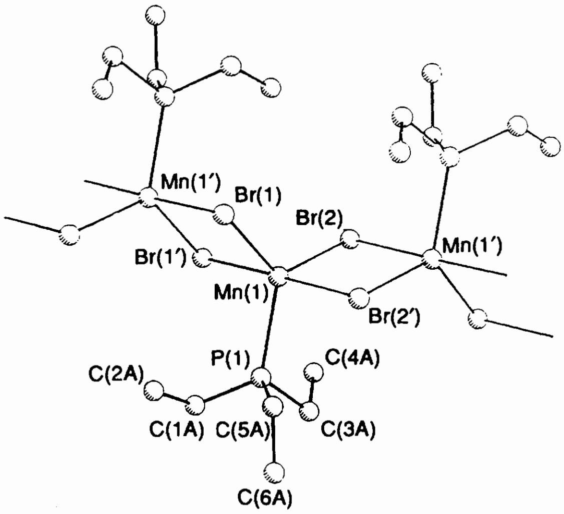

Fig. 1 Crystal structure of the polymeric five-co-ordinate complex [$MnBr_2(PEt_3)$]

The structure of [$MnBr_2(PEt_3)$] is illustrated in Fig. 1 and selected bond lengths and angles are given in Table 1. The asymmetric unit consists of a single $MnBr_2(PEt_3)$ moiety which, under the appropriate symmetry operators, yields a polymeric $(MnBr_2)_n$ chain with a single phosphine co-ordinated at each manganese(II) centre. The metal geometry is essentially trigonal bipyramidal with two axial and two equatorial bridging anions and a single phosphine ligand in the third equatorial position. This structure has only one precedent, that of the recently reported [$MnI_2(PPhMe_2)$],[10] and is a further example of rare five-co-ordination for manganese(II). It is also the first

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Selected bond lengths (Å) and angles (°) for $[MnBr_2(PEt_3)]$

Mn(1)–Br(1)	2.529(9)	P(1)–C(5B)	1.85(2)
Mn(1)–Br(2)	2.535(6)	Mn(1′)–Br(2′)	2.535(6)
Mn(1)–P(1)	2.57(2)	Mn(1′)–Br(1)	2.72(1)
Mn(1)–Br(1′)	2.72(1)	Mn(1′)–Br(2)	2.74(1)
P(1)–C(1B)	1.85(2)	Mn(1)–Br(2′)	2.74(1)
P(1)–C(3B)	1.85(2)		
Mn(1′)–Br(1)–Mn(1)	92.6(3)	Br(2′)–Mn(1)–Br(1)	93.7(3)
Br(2)–Mn(1)–Br(1)	119.9(3)	Br(2′)–Mn(1)–P(1)	90.0(6)
P(1)–Mn(1)–Br(2)	115.6(5)	Br(2′)–Mn(1)–Br(1′)	178.7(4)
Mn(1′)–Mn(1)–Br(2)	111.6(4)	C(1B)–P(1)–Mn(1)	104(2)
Br(1′)–Mn(1)–Br(1)	87.4(3)	C(3A)–P(1)–Mn(1)	116(2)
Br(1′)–Mn(1)–P(1)	88.9(5)		

Table 2 Selected bond lengths (Å) and angles (°) for $[MnI_2(PMeEt_2)]$

Mn(1)–I(1)	2.744(1)	P(1)–C(2)	1.91(2)
Mn(1)–I(1)	2.989(1)	P(1)–C(2)	1.76(2)
Mn(1)–P(1)	2.577(4)	C(2)–C(3)	1.47(3)
P(1)–C(1)	1.87(2)	C(4)–C(5)	1.53(3)
Mn(1)–I(1)–Mn(1^{II})	91.51(3)	I(1^{I})–Mn(1)–I(1^{IV})	179.92(9)
I(1)–Mn(1)–I(1^{III})	123.07(8)	I(1)–Mn(1)–P(1)	118.47(4)
I(1)–Mn(1)–I(1^{I})	88.49(3)	I(1)–Mn(1)–P(1)	89.96(5)
I(1^{I})–Mn(1)–I(1^{III})	91.55(3)		

Symmetry operation: I $+x, -y, \frac{1}{2} + z$; II $x, -y, z - \frac{1}{2}$; III $-x, y, \frac{1}{2} - z$; IV $-x, -y, \frac{1}{2} - z$.

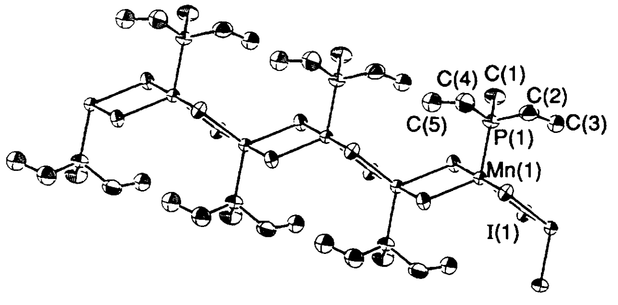

Fig. 2 Crystal structure of the polymeric five-co-ordinate complex $[MnI_2(PMeEt_2)]$

manganese(II) phosphine complex of this stoichiometry with bromide ligands to be crystallographically characterised.[17]

The complex $[MnI_2(PMeEt_2)]$ is isostructural with $[MnBr_2(PEt_3)]$, Fig. 2. Selected bond lengths and angles are given in Table 2. However, whilst they are isostructural, the phosphine ligand in $[MnI_2(PMeEt_2)]$ exists in two conformations related by C_2 symmetry about the Mn–P bond. The increased symmetry produces a mirror plane through the Mn–P bond and results in an asymmetric unit containing half an $MnI_2(PMeEt_2)$ moiety. The structure is, therefore, solved in a different space group, $C2_2/c$, but essentially yields the same overall geometry. It is notable that the $PMeEt_2$ ligand conformations must be disordered at room temperature, since cooling to −60 °C favours a single ligand geometry. As a result, the C_2 symmetry of the ligand is lost and the structure can be solved at low temperature in the same space group, $P2_1/c$, as $[MnBr_2(PEt_3)]$.

These results are interesting for several reasons. First, despite the paucity of previous reports of trigonal-bipyramidal manganese(II) complexes, it appears that this may now be a common geometry for complexes with monodentate phosphine ligands. The reasons for this are unclear, but are notable because of the fact that this geometry is virtually unknown for any other combination of donor ligands. Secondly, the occurrence of the 6,4,6,4 or the 5,5,5,5 structures for the $[MnX_2(PR_3)]$ complexes appear to be dependent on the synthetic route used, but not in any rationalisable way. The structures shown below have been established. We conclude that, although the reasons for obtaining the two isomeric forms upon changing the preparative route or PR_3 or X are not clear, both forms are obtainable from both synthetic routes.

Standard route, $MnX_2 + PR_3$:
$[MnI_2(PPhMe_2)]$ (6,4,6,4)[9]
$[MnBr_2(PEt_3)]$ (5,5,5,5) (this work)
$[MnI_2(PMeEt_2)]$ (5,5,5,5) (this work)

Novel route, $Mn + R_3PX_2$:
$[MnI_2(PPhMe_2)]$ (5,5,5,5)[10]
$[MnI_2(PMe_3)]$ (6,4,6,4)[11,18]

Activity Towards Dioxygen.—The reversible co-ordination of dioxygen by $[MnX_2(PR_3)]$ complexes has been extensively studied.[7,8] However, the slow decomposition of the $[MnX_2(PR_3)(O_2)]$ adducts to phosphine oxide complexes has prevented their crystallographic characterisation. In an attempt to counteract this problem, crystalline samples of the two compounds discussed here were therefore exposed to dioxygen at −30 °C. Intensely coloured compounds (X = I, green; X = Br, blue) commensurate with dioxygen co-ordination were observed. However, low-temperature X-ray diffraction studies revealed that both complexes yielded X-ray amorphous dioxygen adducts. Clearly, dioxygen co-ordination causes sufficient structural changes to prevent characterisation by this technique.

We have also studied the absorption of dioxygen by diethyl ether solutions of the two complexes at −30 °C. Gas-burette measurements indicate a quantitative 1 : 1 complex : O_2 reaction and the formation of an intense colour. Warming these solutions to 0 °C whilst applying a vacuum caused all of the colour to disappear; after subsequent cooling to −30 °C a further 1 : 1 complex : O_2 uptake was observed. This procedure was repeated a further two times indicating that, under these conditions the dioxygenation reaction is reversible. We also monitored the visible spectra of the dioxygenated complexes in order to obtain some impression of the relative stabilities of these adducts. At room temperature in diethyl ether the complex $[MnI_2(PMeEt_2)(O_2)]$ exhibited absorption maxima at 616 and 475 nm. However, decomposition was occurring quite rapidly and no meaningful absorption coefficient data could be obtained. It has previously been noted that of the $[MnX_2(PR_3)(O_2)]$ adducts, the iodo species are the most unstable and the co-ordinated phosphine is oxidised to the phosphine oxide.[7] However, the dioxygen adduct of $[MnBr_2(PEt_3)]$ proved to be much more stable, and its visible spectrum is shown in Fig. 3. Two bands are observed, a sharp 'spike' at 415 nm and a broader peak at 564 nm ($\varepsilon = 2.20 \times 10^4$ dm^3 mol^{-1} cm^{-1}). Both the band positions and the high absorption coefficients are similar to those reported for similar $[MnBr_2(PR_3)(O_2)]$ adducts.[7] However, the instability of both solid $[MnI_2(PMeEt_2)(O_2)]$ and $[MnBr_2(PEt_3)(O_2)]$ in the solid state at room temperature prevented meaningful elemental analyses being obtained.

Experimental

All complexes of stoichiometry $[MnX_2(PR_3)]$ are very air- and moisture-sensitive, especially those containing low molecular weight tertiary phosphine ligands. Consequently strictly anaerobic and anhydrous conditions were adhered to during the synthesis of the complexes, this being essential for their successful synthesis. Anhydrous $MnBr_2$ and MnI_2 were prepared by the thermal dehydration of $MnBr_2{\cdot}4H_2O$ (BDH) and $MnI_2{\cdot}4H_2O$ (Ross Chemicals). The salts were progressively heated to 180 and 120 °C, respectively, *in vacuo* over a period of

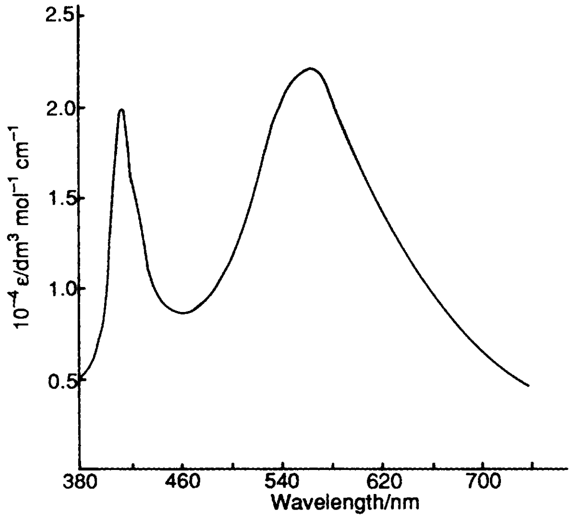

Fig. 3 Visible spectrum of $[MnBr_2(PEt_3)(O_2)]$ in diethyl ether

ca. 7 d. After Karl–Fischer water analysis indicated < 0.03% H_2O, the samples were stored under nitrogen. Triethylphosphine (Strem) was used as received. Diethylmethylphosphine was prepared by the standard Grignard route from $PMeCl_2$ (Hoest), and characterised by elemental analysis and ^{31}P-{H} NMR spectroscopy prior to use. Diethyl ether was stood over sodium wire for *ca.* 1 d and then distilled over CaH_2 in an inert atmosphere. The diethyl ether was subsequently distilled directly into the pre-dried reaction vessel.

Preparation of Complexes.—All manipulations were carried out using standard vacuum line and Schlenk techniques inside a Vacuum Atmospheres HE-493 glove-box (nitrogen atmosphere of < 100 ppm dioxygen). All glassware was heated to 200 °C for *ca.* 1 d before being transferred, hot, to the glove-box.

Crystalline $[MnI_2(PMeEt_2)]$ was prepared as follows. Anhydrous MnI_2 (1.90 g, 6.15 mmol) was added to a 100 cm^3 rotaflo tube to which dry degassed Et_2O (50 cm^3) and $PMeEt_2$ (0.81 cm^3, 6.2 mmol) were then added. The sealed vessel was heated to 60 °C for 48 h to give a pale pink solution of $[MnI_2(PMeEt_2)]$. Crystals of $[MnI_2(PMeEt_2)]$ formed after standing at 0 °C for *ca.* 7 d in essentially quantitative yield {Found (Calc.) for $[MnI_2(PMeEt_2)]$: C, 14.2 (14.5); H, 3.4 (3.1); I, 61.7 (61.5)%}.

Whilst $[MnBr_2(PEt_3)]$ is prepared in the same way, the complex is almost insoluble in Et_2O. Colourless crystals formed at the ether surface and on the side of the vessel after *ca.* 38 d at 0 °C. The crystals were present in very low yield and were separated from the free-flowing amorphous bulk product by filtration {Found (Calc.) for $[MnBr_2(PEt_3)]$: C, 21.3 (21.6); H, 4.2 (4.5); Br, 47.5 (48.0)%}.

Elemental analyses were performed by the Microanalytical Department of this laboratory. Electronic spectra and dioxygen-uptake measurements were performed as previously described.[7]

Single-crystal X-Ray Studies.—*Crystal data for* $[MnI_2(PMeEt_2)]$. $C_5H_{13}I_2MnP$, $M = 418.88$, monoclinic, space group $C2_2/c$, $a = 12.906(4)$, $b = 11.713(4)$, $c = 7.795(2)$ Å, $\beta = 100.63(2)°$, $U = 1158.1(6)$ Å^3, $Z = 4$, $D_c = 2.368$ Mg m^{-3}, $F(000) = 756$, λ(Mo-Kα) = 0.710 69 Å, $\mu = 6.453$ mm^{-1}, $T = 293$ K.

Table 3 Fractional atomic coordinates for the non-hydrogen atoms of $[MnI_2(PMeEt_2)]$

Atom	*x*	*y*	*z*
Mn(1)	0	0.055 74(18)	$\frac{1}{4}$
I(1)	−0.145 788(45)	−0.055 921(60)	0.006 732(70)
P(1)	0	0.275 76(30)	$\frac{1}{4}$
C(1)	−0.115 1(18)	0.348 8(19)	0.316 5(30)
C(2)	−0.005 7(18)	0.344 0(18)	0.025 3(27)
C(3)	−0.098 1(19)	0.312 9(22)	−0.105 7(30)
C(4)	0.112 9(16)	0.339 9(20)	0.373 2(31)
C(5)	0.130 4(21)	0.312 7(25)	0.567 8(36)

Table 4 Fractional atomic coordinates for the non-hydrogen atoms of $[MnBr_2(PEt_3)]$

Atom	*x*	*y*	*z*
Mn(1)	0.2303(10)	0.0215(5)	0.4580(6)
Br(1)	0.0439(8)	−0.1386(3)	0.4870(5)
Br(2)	0.4920(7)	0.0931(4)	0.6001(4)
P(1)	0.1702(24)	0.1240(12)	0.2916(14)
C(1A)	−0.0622(59)	0.1815(39)	0.2283(62)
C(2A)	−0.2010(73)	0.0790(59)	0.2013(92)
C(1B)	−0.0904(38)	0.1117(49)	0.2396(48)
C(2B)	−0.1164(108)	0.1418(71)	0.1208(52)
C(3A)	0.3459(71)	0.2273(36)	0.2850(53)
C(4A)	0.3652(124)	0.2912(54)	0.3906(68)
C(3B)	0.2057(77)	0.2658(22)	0.3174(52)
C(4B)	0.4373(89)	0.2760(47)	0.3570(93)
C(5A)	0.2132(94)	0.0226(35)	0.2029(43)
C(6A)	0.2189(137)	0.0891(63)	0.1014(38)
C(5B)	0.2735(90)	0.1017(51)	0.1815(41)
C(6B)	0.1945(132)	−0.0144(50)	0.1425(48)

A pale pink block crystal of dimensions 0.3 × 0.2 × 0.1 mm was mounted in a Lindeman tube under dry argon. Rigaku AFC6S diffractometer, graphite monochromated Mo-Kα radiation, unit-cell dimensions from the setting angles of 20 accurately centred reflections ($6.4 \leqslant \theta \leqslant 25°$), 1131 reflections measured, 1180 unique ($R_{int} = 0.034$), 710 observed [$I \geqslant 3\sigma(I)$], three intensity standards measured repeatedly at intervals of 150 reflections showed a 32% decline, decay and absorption (azimuthal scan techniques; maximum and minimum transmissions 1 and 0.61 respectively) corrections applied. The structure was solved by standard heavy-atom techniques. A two-fold axis coincided with the Mn–P bond, about which the $PMeEt_2$ ligand displayed rotational disorder. The Mn, P and some of the carbon atoms were subjected to anisotropic refinement (TEXSAN[19]). Hydrogen atoms were ignored. Maximum fluctuations in the final difference map fell in the range −0.55 to 0.88 e Å^{-3} and maximum shift/error was 0.01. Neutral-atom scattering factors were from ref. 20(*a*). Anomalous dispersion effects were included in F_{calc}; the values for $\Delta f'$ and $\Delta f''$ were those from ref. 20(*b*). All calculations were performed using the TEXSAN crystallographic software package of the Molecular Structure Corporation. Final residuals $R = 0.032$, $R' = 0.035$ {$w = 1/[\sigma^2(F) + 0.03F^2]$}. Fractional atomic coordinates are given in Table 3.

Crystal data for $[MnBr_2(PEt_3)]$. $C_6H_{15}Br_2MnP$, $M = 332.91$, monoclinic, space group $P2_1/c$, $a = 7.209(4)$, $b = 12.778(9)$, $c = 13.632(7)$ Å, $\beta = 103.65(4)$, $U = 1220.3$ Å^3, $Z = 4$, $D_c = 1.81$ Mg m^{-3}, $F(000) = 644.0$, λ(Mo-Kα) = 0.7103 Å, $\mu = 7.526$ mm^{-1}, $T = 293$ K.

A colourless block crystal of dimensions 0.3 × 0.15 × 0.15 mm was mounted in a Lindeman tube under dry argon. Nicolet R3m/V diffractometer, graphite monochromated Mo-Kα radiation, unit-cell dimensions from setting angles of 17 accurately centred reflections ($4.4 \leqslant \theta \leqslant 19.6°$), ω–2θ scan mode, scan width 0.6 below Kα, and 0.6 above Kα, and scan speed 1.0–5.0° min^{-1} according to the intensities gathered in a pre-scan, $0 \leqslant h \leqslant 8$, $0 \leqslant k \leqslant 15$, $0 \leqslant l \leqslant 15$, $0 \leqslant \theta \leqslant 25°$, 1120 reflections measured, 833 unique, 376 observed ($F \geqslant 5\sigma F$), intensity standards (1, 0, −4; −1, 0, 4; −2, 2, 3) measured every 200 reflections, 7% decomposition, Lorentz, polarisation corrections applied but absorption ignored. SHELXS 86[21] used to solve the phase problem, Fourier-difference maps revealed that each carbon atom semi-populated two sites, full-matrix least squares based on *F* using SHELX

76,[22] final $R = 0.081$, $R' = 0.081$, $w = 3.260\,40/[\sigma^2(F) + 0.000\,30F^2]$, anisotropic thermal parameters for heavier atoms, constraints applied to phosphine carbons with similar carbons sharing isotopic vibrational parameters, hydrogen atoms ignored. Maximum fluctuation in final ΔF map in the range -0.6 to 0.5 e Å^{-3}, maximum shift/error 0.02. Scattering factors were from International Tables.[20] Fractional atomic coordinates are given in Table 4.

Computations were carried out on the Amdahl 5890 system of the University of Manchester Regional Computing Centre.

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

Acknowledgements

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