Synthesis and Structure of a Polyphosphine Manganese(II) Complex *

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A new high-spin five-co-ordinated manganese(II) complex [Mn(tdpea)I]BPh$_4$·2CH$_2$Cl$_2$ with the tripod ligand tdpea = N(CH$_2$CH$_2$PPh$_2$)$_3$ has been prepared and characterized. Its molecular structure has been determined by single-crystal diffraction methods: monoclinic, space group $P2_1/n$, a = 34.511(9), b = 17.461(4), c = 10.753(3) Å, β = 95.45(2)°, and Z = 4. The metal atom is co-ordinated by one nitrogen and three phosphorus atoms of the tripod ligand and by the iodine ligand. The co-ordination geometry of the cation may be considered halfway between a trigonal bipyramid and a tetrahedron with the P–Mn–I angles averaging 104.3(5)° and the Mn–N distance 2.634(9) Å.

Among first-transition-series metal complexes those of high-spin manganese(II) are characterized by low stability and by the possibility to achieve several co-ordination numbers with different geometries. While the four- and six-co-ordination are rather common, five-co-ordinated manganese(II) complexes are still few in number,[1] and most are with porphyrins where interest stems from the biological implications of such systems. As regards manganese(II) complexes with phosphine ligands, which are still very scarce, no examples of five-co-ordination have been reported so far.

We report the synthesis and characterization of the high-spin manganese(II) phosphine complex [Mn(tdpea)I]BPh$_4$·2CH$_2$Cl$_2$ **1**, containing the tripodal tetradentate ligand tdpea = N(CH$_2$CH$_2$PPh$_2$)$_3$. The closely related amine tdmea = N(CH$_2$CH$_2$NMe$_2$)$_3$ has been previously found to form the trigonal-bipyramidal complex [Mn(tdmea)Br]BPh$_4$.[2,3]

Experimental

All reactions and manipulations were routinely carried out under a purified nitrogen atmosphere by using Schlenk-line techniques. Solvents were distilled from sodium, sodium–benzophenone, or lithium aluminium hydride under nitrogen. Literature routes were used for the preparation of tdpea[4] and anhydrous MnI$_2$.[5] The magnetic susceptibility was measured using apparatus and experimental techniques described elsewhere.[6] The ESR spectra were recorded by a Varian E-9 spectrometer at room temperature on polycrystalline powder.

Synthesis of [Mn(tdpea)I]BPh$_4$·2CH$_2$Cl$_2$ **1**.—A suspension of MnI$_2$ (0.308 g, 1 mmol) and tdpea (0.655 g, 1 mmol) in diethyl ether (50 cm^3) was stirred at room temperature, for 15 min, then a solution of NaBPh$_4$ (0.343 g, 1 mmol) in tetrahydrofuran (thf) (10 cm^3) was added. Stirring was continued for 2 h till a pale pink solid formed. The crude complex was dissolved in CH$_2$Cl$_2$ (50 cm^3), the resulting colourless solution filtered and diethyl ether (10 cm^3) added. Well shaped, pale pink, crystals of the complex were obtained by leaving the system, at room temperature, overnight. Yield 87% (Found: C, 61.45; H, 5.15; Mn, 4.25; N, 1.15. Calc. for C$_{68}$H$_{66}$BCl$_4$IMnNP$_3$: C, 61.65; H, 5.00; Mn, 4.15; N, 1.05%).

Crystallography.—Crystal data. C$_{66}$H$_{62}$BIMnNP$_3$·2CH$_2$Cl$_2$, M = 1324.68, monoclinic, space group $P2_1/n$, a = 34.511(9), b = 17.461(4), c = 10.753(3) Å, β = 95.45(2)°, U = 6450.4 Å^3, Z = 4, D_c = 1.364 g cm^{-3}, λ = 0.7107 Å, μ(Mo-Kα) = 9.49 cm^{-1}, F(000) = 2708.

Enraf Nonius CAD4 automatic diffractometer, pink prismatic crystal of dimensions 0.10 × 0.15 × 0.24 mm coated in paraffin, cell constants from 25 randomly selected reflections, $\bar{\omega}$ mode with scan width = 0.7 + 0.35 tanθ and a scan speed of 8.24° min^{-1}, graphite monochromated Mo-Kα radiation, background measurements equal to half the scan time, three standard reflections periodically measured, standard deviations $\sigma(I)$ calculated according to ref. 7. Of a total of 6344 reflections measured with $2\theta < 40°$, 4588 having $I > 3\sigma(I)$ were considered observed. The intensities were corrected for Lorentz-polarization effects. No absorption correction was applied.

Solution and refinement of the structure. All the calculations were carried out on a SEL 32/77 computer by using the SHELX 76[8] and ORTEP[9] programs. Atomic scattering factors for the non-hydrogen atoms were taken from ref. 10, those of the hydrogen atoms from ref. 11. Both $\Delta f'$ and $\Delta f''$ components of the anomalous dispersion were included for the non-hydrogen atoms.[12] The function minimized during the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$, the weights being defined as $w = 1/\sigma^2(F_o)$. Due to the isomorphism of this compound with [Pt(tdpea)(CH$_2$Cl)]BPh$_4$[13] the final positions of the platinum atom were used as starting parameters for the manganese complex. Full-matrix least-squares refinements were carried out by assigning anisotropic thermal parameters for the heavier atoms and treating the phenyl rings as rigid groups of D_{6h} symmetry. Hydrogen atoms were introduced in calculated positions (C–H 0.95 Å) but not refined. At convergence the final R and R' factors were 0.073 and 0.074 respectively. Final positional parameters are listed in Table 1.

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

Discussion

The tripod-like ligand tdpea has been used to co-ordinate a great number of transition metals ions, also in unusual oxidation states.[14] Through its particular steric requirements it has been found capable of stabilizing otherwise unstable groups (*i.e.* Co–Hg–Hg–Co,[15] Pt–Hg–Me$^+$,[16] *etc.*). However, no manganese(II) compounds with this ligand have so far been

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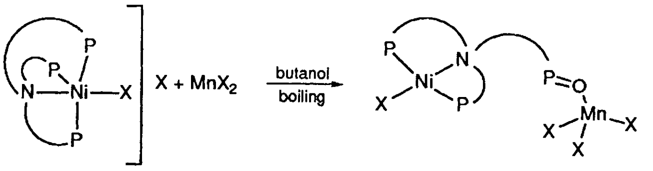
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Final positional (× 10^4) parameters for $[Mn(tdpea)I]BPh_4 \cdot 2CH_2Cl_2$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
I	1712(1)	1156(1)	−1297(1)	C(55)	610(2)	902(5)	2755(6)
Mn	1420(1)	2410(1)	−229(2)	C(65)	742(2)	1384(5)	1852(6)
P(1)	1754(1)	2438(2)	1988(3)	C(16)	437(2)	1911(4)	−1877(7)
P(2)	1613(1)	3512(2)	−1625(3)	C(26)	131(2)	2341(4)	−2456(7)
P(3)	686(1)	2183(2)	−380(3)	C(36)	−46(2)	2119(4)	−3621(7)
N	1146(3)	3654(5)	763(8)	C(46)	83(2)	1467(4)	−4206(7)
C(1)	1384(3)	3875(7)	1937(11)	C(56)	390(2)	1037(4)	−3627(7)
C(2)	1494(4)	3189(7)	2819(11)	C(66)	567(2)	1259(4)	−2462(7)
C(3)	1150(3)	4312(7)	−128(10)	C(17)	4252(2)	1334(4)	3853(5)
C(4)	1534(3)	4375(6)	−700(10)	C(27)	4566(2)	846(4)	4167(5)
C(5)	748(3)	3509(7)	1087(10)	C(37)	4754(2)	491(4)	3229(5)
C(6)	486(3)	3127(6)	20(10)	C(47)	4628(2)	625(4)	1977(5)
C(11)	2257(3)	2730(5)	2088(7)	C(57)	4314(2)	1113(4)	1663(5)
C(21)	2475(3)	2783(5)	3246(7)	C(67)	4126(2)	1468(4)	2601(5)
C(31)	2870(3)	2969(5)	3308(7)	C(18)	4303(2)	1683(4)	6340(7)
C(41)	3046(3)	3102(5)	2214(7)	C(28)	4271(2)	1025(4)	7059(7)
C(51)	2828(3)	3048(5)	1056(7)	C(38)	4514(2)	927(4)	8161(7)
C(61)	2434(3)	2863(5)	993(7)	C(48)	4788(2)	1486(4)	8544(7)
C(12)	1744(3)	1582(5)	2968(6)	C(58)	4820(2)	2144(4)	7825(7)
C(22)	1848(3)	889(5)	2443(6)	C(68)	4577(2)	2243(4)	6722(7)
C(32)	1844(3)	215(5)	3136(6)	C(19)	3989(2)	2752(5)	4641(7)
C(42)	1737(3)	232(5)	4355(6)	C(29)	3748(2)	3204(5)	5308(7)
C(52)	1634(3)	925(5)	4881(6)	C(39)	3728(2)	3993(5)	5102(7)
C(62)	1638(3)	1599(5)	4187(6)	C(49)	3950(2)	4329(5)	4229(7)
C(13)	2093(3)	3630(4)	−2113(8)	C(59)	4191(2)	3876(5)	3562(7)
C(23)	2241(3)	3038(4)	−2799(8)	C(69)	4211(2)	3088(5)	3768(7)
C(33)	2608(3)	3108(4)	−3228(8)	C(110)	3577(3)	1449(5)	5081(6)
C(43)	2828(3)	3770(4)	−2971(8)	C(210)	3360(3)	1154(5)	4027(6)
C(53)	2679(3)	4363(4)	−2285(8)	C(310)	2973(3)	942(5)	4090(6)
C(63)	2312(3)	4292(4)	−1856(8)	C(410)	2802(3)	1025(5)	5208(6)
C(14)	1296(3)	3623(4)	−3047(8)	C(510)	3019(3)	1319(5)	6262(6)
C(24)	1065(3)	3012(4)	−3507(8)	C(610)	3406(3)	1531(5)	6198(6)
C(34)	823(3)	3094(4)	−4614(8)	B	4027(4)	1792(8)	4967(12)
C(44)	812(3)	3787(4)	−5260(8)	Cl(1)	2750(3)	−165(5)	862(8)
C(54)	1043(3)	4399(4)	−4800(8)	Cl(2)	3225(3)	1062(6)	23(11)
C(64)	1285(3)	4317(4)	−3693(8)	Cl(3)	4036(4)	4224(6)	−1315(12)
C(15)	507(2)	1528(5)	747(6)	Cl(4)	3823(4)	2904(8)	−189(14)
C(25)	141(2)	1189(5)	545(6)	C(7)	2816(11)	756(21)	315(32)
C(35)	9(2)	706(5)	1448(6)	C(8)	3950(9)	3212(19)	−1262(30)
C(45)	243(2)	563(5)	2553(6)				

reported. Manganese(II) phosphine complexes are also relatively scarce probably due to preparative difficulties. McAuliffe *et al.*[17] have pointed out that the rigorous exclusion of moisture appears essential to avoid the formation of phosphine oxide or manganese(III) derivatives. The following previously reported[18] reaction, was found to result in the formation of a P=O–Mn linkage.



Now we have found that MnI_2 reacts with tdpea in the presence of $NaBPh_4$, in diethyl ether–thf solution, to form the complex $[Mn(tdpea)I]BPh_4 \cdot 2CH_2Cl_2$. Related reactions performed by using $P(CH_2CH_2PPh_2)_3$ or $MnBr_2$ in place of tdpea or MnI_2 respectively did not result in any detectable metal complex.

The complex appears exceptionally stable relative to other manganese(II) phosphine complexes: the crystals can be manipulated in air for minutes without decomposition. This finding must be ascribed to the well documented steric protection by the tdpea ligand.

The complex behaves as a 1 : 1 electrolyte in CH_2Cl_2 solution. The solid is high-spin d^5 at 295 K ($\mu = 5.83\ \mu_B$). The polycrystalline powder ESR spectrum recorded at X band at room temperature shows an intense band at $g_{eff} = 5.01$ and less-intense bands at $g_{eff} = 1.80$, 0.87 and 0.75 respectively. This is characteristic of a $S = \frac{5}{2}$ spin system split by a zero-field splitting larger than the microwave quantum of radiation.[19] Using the reported dependence of the transition fields,[19,20] the position of the high-field lines gives a zero-field splitting parameter $D = 0.53$–$0.58\ cm^{-1}$ and a rhombic parameter $\lambda = E/D = 0.26$–0.30.

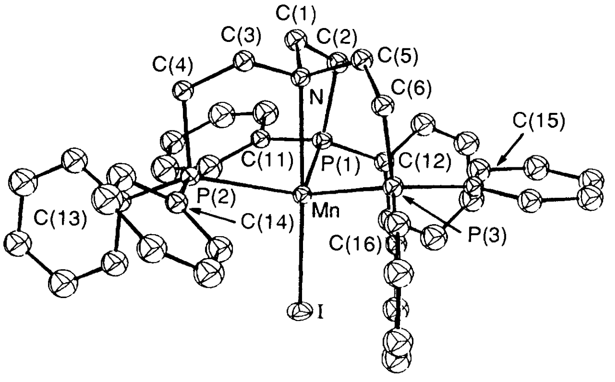


Fig. 1 Perspective view of the complex cation $[Mn(tdpea)I]^+$; ORTEP drawing with 30% probability ellipsoids

The molecular structure of complex **1** consists of discrete $[Mn(tdpea)I]^+$ cations, tetraphenylborate anions and inter-

Table 2 Selected bond distances (Å) and angles (°)

Mn–I	2.712(2)	P(3)–C(15)	1.81(1)
Mn–P(1)	2.548(3)	P(3)–C(16)	1.81(1)
Mn–P(2)	2.567(4)	N–C(1)	1.49(1)
Mn–P(3)	2.554(3)	N–C(3)	1.50(1)
Mn–N	2.634(9)	N–C(5)	1.47(1)
P(1)–C(2)	1.86(1)	C(1)–C(2)	1.55(2)
P(1)–C(11)	1.80(1)	C(3)–C(4)	1.52(2)
P(1)–C(12)	1.83(1)	C(5)–C(6)	1.54(2)
P(2)–C(4)	1.84(1)	B–C(17)	1.69(2)
P(2)–C(13)	1.80(1)	B–C(18)	1.69(1)
P(2)–C(14)	1.80(1)	B–C(19)	1.71(2)
P(3)–C(6)	1.85(1)	B–C(110)	1.68(2)
I–Mn–P(1)	104.9(1)	Mn–P(3)–C(15)	116.9(3)
I–Mn–P(2)	103.3(1)	Mn–P(3)–C(16)	118.7(3)
I–Mn–P(3)	104.7(1)	C(6)–P(3)–C(15)	104.3(5)
I–Mn–N	178.3(3)	C(6)–P(3)–C(16)	106.5(4)
P(1)–Mn–P(2)	114.4(1)	C(15)–P(3)–C(16)	105.4(3)
P(1)–Mn–P(3)	114.9(1)	Mn–N–C(1)	111.6(6)
P(1)–Mn–N	75.7(2)	Mn–N–C(3)	110.4(6)
P(2)–Mn–P(3)	113.0(1)	Mn–N–C(5)	109.4(6)
P(2)–Mn–N	75.0(2)	C(1)–N–C(3)	107.8(8)
P(3)–Mn–N	76.2(2)	C(1)–N–C(5)	107.1(8)
Mn–P(1)–C(2)	105.4(4)	C(3)–N–C(5)	110.4(8)
Mn–P(1)–C(11)	114.2(3)	C(2)–C(1)–N	113.6(9)
Mn–P(1)–C(12)	119.4(3)	C(1)–C(2)–P(1)	110.6(8)
C(2)–P(1)–C(11)	106.0(5)	C(4)–C(3)–N	112.1(9)
C(2)–P(1)–C(12)	105.2(5)	C(3)–C(4)–P(2)	109.9(7)
C(11)–P(1)–C(12)	105.5(4)	C(6)–C(5)–N	113.1(9)
Mn–P(2)–C(4)	103.7(4)	C(5)–C(6)–P(3)	110.6(7)
Mn–P(2)–C(13)	123.7(3)	C(17)–B–C(18)	107.8(8)
Mn–P(2)–C(14)	114.0(3)	C(17)–B–C(19)	110.4(8)
C(4)–P(2)–C(13)	104.6(4)	C(17)–B–C(110)	111.9(8)
C(4)–P(2)–C(14)	105.1(4)	C(18)–B–C(19)	108.3(8)
C(13)–P(2)–C(14)	104.0(4)	C(18)–B–C(110)	110.1(8)
Mn–P(3)–C(6)	103.6(4)	C(19)–B–C(110)	108.1(8)

spersed molecules of CH_2Cl_2. Fig. 1 shows a perspective view of the cation and Table 2 reports selected bond distances and angles. The metal atom is co-ordinated by one nitrogen and three phosphorus atoms of the tripod ligand and by the iodine ligand. However the geometry of the cation may be considered halfway between a trigonal bipyramid and a tetrahedron. The P–Mn–I angles average 104.3(5)° and the Mn–N distance is 2.634(9) Å, the latter value being *ca.* 0.5 Å larger than the sum of the corresponding atomic radii. The metal atom is 0.63 Å below the plane through the phosphorus atoms. The same distortion has been previously found in the high-spin cobalt compounds $[Co(tdpea)X]^+$ (X = Cl, Br or I), where the P–Co–X angles and the Co–N bonds fall in the ranges 101.3(2)–110.3(2)° and 2.67(1)–2.73(1) Å respectively.[21] On the other hand the tdpea ligand is able to wrap around a metal in a much more distorted fashion, with the central nitrogen being unco-ordinated.[22] For example the co-ordination of a d^{10} complex such as [Ni(tdpea)(CO)] can be considered as tetrahedral with the P–Ni–CO angles averaging 112.7° and the Ni–N distance 3.25(1) Å.[23]

In complex **1** the bond distances around the metal reflect the large size of the manganese(II) ion in the high-spin configuration as evidenced by Mn–P and Mn–I, 2.556(5) (av.) and 2.712(2) Å respectively. These values are very similar to those reported for high-spin tetrahedral manganese phosphine complexes.[24]

In the above context it is interesting that upon changing the donor set from NP_3X to N_4X the co-ordination geometry is drastically changed, although the flexibility and the chelating ability of the tripod remain approximately equal. On going from **1** to $[Mn(tdmea)Br]BPh_4$ **2**,[3] the metal appears more keen to accept the apical amine as a fifth donor and the former pseudo-tetrahedron becomes an almost regular trigonal bipyramid. While the mean $X–Mn–L_{eq}$ angle narrows from 104.3(5) to 99.3(6)°, the Mn–N apical bond shortens from 2.634(9) to 2.19(3) Å. Noteworthy in **2** is that the $Mn–N_{ap}$ distance is shorter than the $Mn–N_{eq}$ ones [2.19(3) *vs.* 2.27(2) Å].

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