

Mn(II)–I Bonds in Complexes in Solution and Crystalline Phases. Structural Studies by EXAFS and X-Ray Crystallography

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Following a recent upsurge of interest in systems with Mn(II)–I bonds, an attempt has been made to rationalize the bond lengths, which range between 2.5 and 3 Å. To add to the data available, EXAFS studies of MnI₂ in tetrahydrofuran (thf) solution and a crystallographic study of MnI₂(OPPh₃)₂ have been carried out. The latter has the average bond lengths Mn(II)–I = 2.668(1) Å and Mn(II)–O = 2.021(4) Å for the tetrahedrally coordinated Mn atom. The EXAFS studies employ [MnI₂(H₂O)₄] and MnI₂[PPh(CH₂CH₂Ph)₂]₂ as reference compounds; the results show that MnI₂ in thf solution has Mn(II)–I = 2.77(2) Å and Mn(II)–O = 2.24(2) Å, and suggest the existence of an equilibrium between octahedrally coordinated Mn(II) species of the type [MnI_nL_{6-n}]⁽²⁻ⁿ⁾⁺, with L = thf (*n* = 1, 2 and maybe 0); the average *n*, *n*_{av}, refined to 1.4(1).

All the observed Mn(II)–I bond lengths discussed in this paper (regardless of coordination at Mn) satisfactorily follow the Brown and Shannon relationship $s = s_0 (R/R_0)^{-p}$ with reference bond length $R_0 = 2.920$ Å and bond strength $s_0 = 0.333$, with $p = 5.1$, assuming the definitive data of Brown and Shannon themselves for Mn(II)–O bonds. Tentative Brown and Shannon parameters are also deduced for Mn(II)–P bonds.

Dedicated to Professor Otto Bastiansen on his 70th birthday

Until the present decade, structural data for systems containing Mn–I bonds were limited almost entirely to the results of the study¹ of anhydrous MnI₂, in which Mn(II) is octahedrally coordinated to six iodine atoms with Mn(II)–I = 2.92 (3) Å (CdI₂ structure-type). Inorganic systems studied more recently^{2–4} include CsMnI₃ and TlMnI₃; room temperature results from this work establish 2.920 Å as a reliable standard value for Mn(II)–I in systems with six I atoms around Mn(II). This length is also found in the complex⁵ [MnI₂(H₂O)₄], where the Mn–O distance is 2.177 Å.

Structural data for Mn–I bonds in organic complexes also began to appear around 1980. There are several carbonyl complexes whose

structural data have been reported^{6–10} and data on the Mn(III) complex MnI₃(PMe₃)₂ have appeared,¹¹ but of relevance to the present work are two studies of Mn(II) phosphine complexes: the first is of MnI₂(PPhMe₂), which we shall call the King structure¹² in memory of the late Professor T. J. King, and the second¹³ is of MnI₂(PEt₃)₂. The King structure¹² is unique not only in its stoichiometry as a monophosphine derivative of Mn(II) but it has Mn in both octahedral and tetrahedral coordination, as MnI₄ and MnI₄P₂. These forms link alternately through double Mn–I–Mn bridges forming chains parallel to the *c* crystal axis. Axial P–Mn–P configurations of the octahedra are alternately perpendicular to each other so that the repeat unit in the *c* direc-

Table 1. Lengths (Å) of Mn(II)–I and Mn(II)–P bonds in tetrahedral environments.

Molecule in crystal	Length Mn(II)–I	Length Mn(II)–P	Ref.
King structure	2.707 (mean of 8)	–	12
α -MnI ₂ (PEt ₃) ₂	2.662(2) 2.670(2)	2.528(4) 2.539(4)	13
β -MnI ₂ (PEt ₃) ₂	2.670(2) 2.675(2)	2.562(3) 2.568(4)	14
MnI ₂ (PPh ₃) ₂	2.632(2) 2.642(2)	2.596(3) 2.617(3)	14
MnI ₂ [PPh(CH ₂ CH ₂ Ph) ₂] ₂	2.653(2)×2	2.585(4)×2	14
Means:			
incl. King structure	2.682	–	
excl. King structure	2.657	2.573	

tion involves four Mn atoms, viz. those in MnI₄, MnI₄P₂, MnI₄ and MnI₄P₂, each adjacent unit being linked by the double Mn–I–Mn bridges. Voids between tetrahedral Mn sites of adjacent chains have been suggested as possible sites for small molecules such as dioxygen, which can bind reversibly to such monophosphine complexes,¹² under appropriate conditions. The stereochemistry provides eight independent octahedral Mn(II)–I bonds of mean length 2.971 Å. The latter is significantly longer than the 2.920 Å found for six equivalent Mn–I bonds in the inorganic compounds mentioned above, and the lengthening is undoubtedly due to the two Mn–P bonds to each octahedral Mn(II) atom. We shall return to the discussion of this lengthening later in this paper.

The crystals of MnI₂(PEt₃)₂ possess molecules of this formulation,¹³ which provide data for Mn(II) in tetrahedral coordination; we shall refer to this structure as α -MnI₂(PEt₃)₂. We have supplemented the information on MnI₂(PR₃)₂ molecules by crystal structure determinations¹⁴ of a second form of the R = Et compound, β -MnI₂(PEt₃)₂, and by studies of MnI₂(PPh₃)₂ and MnI₂[PPh(CH₂CH₂Ph)₂]₂. The data now available for Mn(II)–I and Mn(II)–P bonds with Mn in tetrahedral environments are summarized in Table 1. It may be noted that the Mn(II)–I bond length in the King structure is again significantly longer (2.707 Å) than the mean length (2.657 Å) for Mn(II) in comparable structures. Also, for Mn(II)–P, the length (2.573 Å) for Mn(II) in a

tetrahedral environment is (as expected) considerably shorter than the 2.671 Å (mean of 4) found in the octahedral environment of the King structure.¹²

The data presented above form the basis for any current discussion of Mn(II)–I bond lengths and are also needed in part or cumulatively as reference data for the interpretation of the EXAFS data reported in this paper. We are aware of no other EXAFS studies of Mn(II)–I systems.

The present work attempts to parameterize the EXAFS data, employing reference compounds selected from those mentioned above. Once parameterization has been achieved it is possible to use the EXAFS data to determine the structures of unknown systems such as that reported in this paper: MnI₂ in solution in tetrahydrofuran (thf). This solution is shown to possess complexes with Mn(II)–I and Mn(II)–O bonds.

An attempt to rationalize, particularly, the wide variations in Mn(II)–I bond lengths is made, and this is assisted by a crystallographic study of MnI₂(OPPh₃)₂, which like the species present in thf solutions of MnI₂ possesses Mn(II)–I and Mn(II)–O bonds, but of rather different lengths.

Experimental

EXAFS spectroscopy. EXAFS measurements at room temperature were made at the Synchrotron

Table 2. Crystal data and details of data collection.

Mol. formula	$C_{36}H_{30}I_2MnO_2P_2$
Mol. weight	865.34
Crystal system	Triclinic
$a/\text{\AA}$	10.105(4)
$b/\text{\AA}$	10.471(4)
$c/\text{\AA}$	10.703(5)
$\alpha/^\circ$	114.77(3)
$\beta/^\circ$	116.29(3)
$\gamma/^\circ$	90.14(3)
Space group	$P1$
$V/\text{\AA}^3$	897(1)
$F(000)$	423
$D_c/\text{g cm}^{-3}$	1.602
Z	1
Crystal dimension/mm	$0.2 \times 0.2 \times 0.2$
Diffractometer	Enraf-Nonius CAD4
Radiation	$\text{MoK}\alpha$; $\lambda = 0.71069 \text{ \AA}$ (graphite monochromatized)
$\mu(\text{MoK}\alpha)/\text{cm}^{-1}$	20.55
Scan type	$\omega/2\theta$
θ limit/ $^\circ$	0–25
No. of collected reflections	3536
No. of observed reflections	3129 [$F_o > 3\sigma(F_o)$]
$R(R = \sum F_o - F_c /\sum F_o)$	0.029
$R_w(R_w = [\sum w(F_o - F_c)^2/\sum w F_o ^2]^{0.5})$	0.039
w	$0.1337/[\sigma^2(F_o) + 0.001F_o^2]$

Radiation Source (SRS) at Daresbury Laboratory at the manganese K -edge (1.90 \AA , 6.54 keV). A wide variety of experimental conditions were employed over a period of time, as in our work on MnBr_2 complexes,¹⁵ where it was found that consistent results were obtained regardless of detection method or monochromator arrangement used. Data were reduced to χ -curves using the EXCALIB and EXBACK programs from the SRS program library,¹⁶ and transferred to UMIST for structure refinement.

X-Ray diffraction. Crystal data etc. for $\text{MnI}_2(\text{OPPh}_3)_2$ are given in Table 2. Unit cell parameters were determined by least-squares refinement based on diffractometer setting angles of 25 accurately centred reflections ($8 < \theta < 14^\circ$). L_p corrections were applied to the intensity data but absorption was ignored.

The structure was solved by normal heavy-atom techniques and refined to a final R of 0.029 using the SHELX76 computer program¹⁷ and neutral-atom scattering factors.¹⁸ All non-hydro-

gen atoms were subjected to anisotropic refinement and hydrogen atoms were constrained to chemically reasonable positions with a common isotropic vibrational parameter [$0.106(9) \text{ \AA}^2$]. The largest maxima in the final difference map were 0.78 e\AA^{-3} , near to an iodine atom, and 0.41 e\AA^{-3} elsewhere. Calculations were carried out on the computers of the University of Manchester Regional Computing Centre.* The molecule, including the atomic labelling scheme, is illustrated in Fig. 1, and fractional atomic coordinates of the non-hydrogen atoms are given in Table 3.

*Lists of observed and calculated structure amplitudes, anisotropic vibrational parameters and constrained hydrogen-atom coordinates are available from the authors on request, and pertinent structural data are deposited at the Cambridge Data Centre. Any request to the Director of the Cambridge Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW should be accompanied by the full literature citation for this publication.

Table 3. Fractional atomic coordinates ($\times 10^4$) and vibrational parameters ($\text{\AA}^2 \times 10^4$) for non-hydrogen atoms.

Atom	x/a	y/b	z/c	U_{eq}^*
I(1)	8436(1)	8795(1)	3617(1)	1050
I(2)	5188	9962		1428
Mn(1)	5671(1)	9243(1)	2254(1)	751
P(1)	2456(2)	6826(1)	951(1)	774
P(2)	5223(2)	12326(1)	4726(1)	776
O(1)	3997(5)	7576(4)	1427(5)	1045
O(2)	5525(6)	10860(4)	4051(5)	1092
C(1)	2369(7)	6982(6)	2638(6)	916
C(2)	1696(9)	5829(8)	2640(9)	1285
C(3)	1741(12)	6036(10)	4034(10)	1555
C(4)	2426(13)	7321(12)	5374(9)	1773
C(5)	3050(16)	8476(11)	5342(11)	1882
C(6)	3041(12)	8300(9)	3996(9)	1547
C(11)	2111(6)	4937(6)	-307(6)	831
C(12)	624(7)	4083(7)	-1363(8)	1043
C(13)	430(9)	2609(7)	-2253(9)	1221
C(14)	1649(11)	1993(7)	-2110(10)	1388
C(15)	3095(11)	2843(8)	-1105(11)	1488
C(16)	3326(8)	4319(7)	-206(8)	1105
C(21)	6121(7)	13586(6)	4454(6)	861
C(22)	5528(9)	14722(7)	4254(9)	1238
C(23)	6335(11)	15667(8)	4099(10)	1501
C(24)	7706(11)	15501(8)	4182(9)	1447
C(25)	8290(11)	14397(9)	4387(12)	1624
C(26)	7497(8)	13425(7)	4514(9)	1220
C(31)	6012(7)	13007(7)	6818(6)	952
C(32)	6178(11)	14443(9)	7792(9)	1462
C(33)	6792(13)	14919(14)	9399(11)	1866
C(34)	7221(13)	13952(21)	9991(11)	2233
C(35)	7085(12)	12376(21)	9037(14)	2286
C(36)	6471(8)	12042(11)	7409(9)	1447
C(41)	3256(6)	12251(5)	3882(6)	878
C(42)	2415(8)	12017(8)	2324(8)	1129
C(43)	907(9)	11783(9)	1589(9)	1297
C(44)	113(9)	11771(9)	2369(11)	1414
C(45)	875(9)	11991(10)	3882(12)	1634
C(46)	2465(8)	12247(8)	4663(9)	1228
C(51)	967(7)	7514(6)	-66(7)	900
C(52)	1070(10)	7843(8)	-1156(8)	1308
C(53)	-110(12)	8307(10)	-2016(9)	1462
C(54)	-1362(13)	8427(10)	-1829(12)	1651
C(55)	-1438(10)	8142(10)	-743(14)	1654
C(56)	-258(9)	7668(8)	147(10)	1335

$$*U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} \mathbf{a}_i \mathbf{a}_j \cdot \mathbf{a}_i^* \mathbf{a}_j^*$$

Theory

Bond length correlation. The work of Brown and Shannon¹⁹ has demonstrated that for bonds between many elements and oxygen, bond strength s and bond length R can be related by $s =$

$s_0(R/R_0)^{-p}$ where s_0 and R_0 are standard values for a reference system, and p is an empirical constant. For Mn(II)–O bonds in an octahedral environment, i.e. with $s_0 = 2/6 = 0.333$ valence units (vu), they quote $R_0 = 2.165 \text{ \AA}$ and $p = 5.1$. This R_0 value agrees well with the observed 2.177

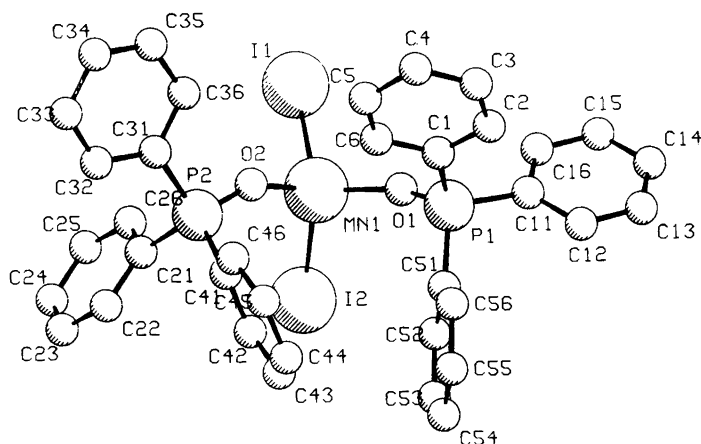


Fig. 1. View of $\text{MnI}_2(\text{OPPh}_3)_2$ showing numbering scheme.

Å found⁵ for Mn–O in $[\text{MnI}_2(\text{H}_2\text{O})_4]$ (see above). We have extended the approach to alkali halides quite successfully,²⁰ demonstrating that the equations can be applied to bonds to halogens just as effectively as to bonds to oxygen.

The data presented above for Mn(II)–I bonds enable the approach to be applied to the Mn(II)–I system. The appropriate empirical power parameter p can be derived using the lengths for octahedral and tetrahedral environments, 2.920 and 2.657 Å, respectively, with s values of 0.333 and 0.5 vu respectively. Thus, p is obtained from $0.5 = 0.333 (2.657/2.920)^{-p}$ to be 4.3. If, instead of 2.657 Å, the value of 2.707 Å from the King structure had been used, the estimated value of p obtained would have been 5.4. This may be preferable, because only the King structure (amongst the available data) has MnI_4 tetrahedra; the others have MnI_2P_2 tetrahedra. It is best, perhaps, to proceed bearing in mind that the value of p is subject to considerable error; however, the difference in bond lengths concerned is relatively small ($2.707 - 2.657 = 0.05$ Å) compared with the difference of about 0.25 Å between the values for Mn(II)–I bonds in octahedral and tetrahedral environments. EXAFS studies are quite capable of measuring bond lengths to ± 0.02 Å, so they will readily distinguish between such octahedral and tetrahedral environments. Observed differences in length of 0.05 Å will, however, be of only marginal significance, so that EXAFS will not be very sensitive to a difference in p of the magnitude referred to above.

EXAFS data are used below to demonstrate

that in solutions of MnI_2 in thf there are equilibria between octahedrally coordinated complexes of the type $[\text{MnI}_n\text{L}_{6-n}]^{(2-n)+}$ ($\text{L} = \text{thf}$). It is possible to carry out EXAFS curve-fitting calculations with the total number of bonds to Mn constrained to be exactly six, and refine n , whereupon an average value of n , n_{av} , is obtained; n_{av} represents the average number of iodine bonds to Mn, taking account of the equilibrium mixture of complexes with $n = 2, 1$ and 0. As, referring back to the Brown and Shannon treatment,¹⁹ the total number of valence units associated with an Mn(II) atom is two, the average individual iodine and oxygen (of thf) bond strengths s_{I} and s_{ox} are related by

$$n_{\text{av}}s_{\text{I}} + (6 - n_{\text{av}})s_{\text{ox}} = 2.$$

This expression may be used as a constraint in EXAFS refinements as follows. If n_{av} and $R(\text{Mn}-\text{I})$ are refined, s_{I} may be derived using $s_{\text{I}} = 0.333(R/2.920)^{-p}$. The above constraint, with known n_{av} and s_{I} enables the calculation of s_{ox} , and hence $R(\text{Mn}-\text{O})$ using the appropriate Brown and Shannon power equation; i.e. the constraint relates $R(\text{Mn}-\text{O})$ and $R(\text{Mn}-\text{I})$. Thus, EXAFS refinements which give good agreement between observation and calculation when this constraint is in use will help to confirm the validity of the structural model proposed.

EXAFS: Structure refinement. Refinements employed the UMIST software²¹ MOLEX85, which enables least-squares curve-fitting to be carried

$$\chi(k) = -\sum_j (N_j/k r_{ij}^2) |F_j(k, \pi)| \sin[2k(r_{ij} - \Delta r_{ij}) + \varphi_{ij}(k)] \times \exp(-2k^2 \sigma_{ij}^2 - 2r_{ij} \eta/k) \quad (1)$$

out using the modified plane wave equation (for K edges) given in eqn. (1). In this equation i is the absorber, j a back-scatterer, F_j is the back-scattering amplitude, φ_{ij} is a combined phase term adjusted to fit the experimental data for the reference compounds, N_j is the back-scatterer multiplicity, r_{ij} is an interatomic distance, Δr_{ij} the corresponding EXAFS phase correction, σ_{ij} is the corresponding Debye-Waller parameter and η is the mean free path parameter. The variable k is the photoelectron wave vector. The modified phase term $\varphi_{ij}(k) = 2\varphi_j(k) + \varphi_i(k) + \alpha_j(k - k_{\text{lim},j})$. The functions F_j , φ_j and φ_i were calculated from partial-wave phase shifts δ_l obtained from the Daresbury database in numerical form. Constants α_j and $k_{\text{lim},j}$ were adjusted during refinements for the reference compounds to give the best fit with experiment; $k_{\text{lim},j}$ is an upper k limit beyond which phase corrections are necessary. Below $k_{\text{lim},j}$, α_j was set at zero so that unmodified phases applied. All computations excluded data from the XANES region, i.e. $E < 2.5$ Hartree.

Results and discussion

EXAFS reference compounds. The key to solving unknown structures using EXAFS data is the successful treatment of related reference compounds. In the present case, two reference compounds were employed, viz. $[\text{MnI}_2(\text{H}_2\text{O})_4]$ and $\text{MnI}_2[\text{PPh}(\text{CH}_2\text{CH}_2\text{Ph})_2]_2$, for each of which

structural data were available from crystallographic studies.^{5,14} These two reference compounds provided the primary parameterization of the EXAFS equations for Mn(II)–I bonds in octahedral and tetrahedral environments, respectively. Parameterization in relation to Mn(II)–O and Mn(II)–P bonds in corresponding environments was also achieved. Three sets of EXAFS data were available for each of these two compounds. In all the least-square refinements, the bond lengths observed in the crystallographic studies were held constant and relevant adjustable parameters in the EXAFS χ -equation (see above) were refined. The results are presented in Table 4. The refined values for $\sigma(\text{Mn}–\text{O})$ and $\Delta r(\text{Mn}–\text{O})$ agree within their standard deviations with values obtained in work on $[\text{MnBr}_2(\text{H}_2\text{O})_4]$ and aqueous MnBr_2 solutions¹⁵ and on the Mn Tutton salt.²² Values obtained for the oxygen back-scatterer phase correction parameters $\alpha = 0.9(1) \text{ \AA}$ and $E_{\text{lim}} = 6.3(3)$ Hartree [$k_{\text{lim}} = 6.7(2) \text{ \AA}^{-1}$] are also in agreement with the work of Ref. 15. No such phase corrections appeared to be necessary for Mn–I and Mn–P. Typical least-squares fits for the two reference compounds are shown in Figs. 2a and 2b (the data for the phosphine complex were manually de-glitched at G; all data collected with the spectrometer configuration employed at the time the phosphine complex was studied unfortunately possessed the same glitch).

Table 4. Parameterization of EXAFS data with reference compounds.^a

	$[\text{MnI}_2(\text{H}_2\text{O})_4]$	$\text{MnI}_2[\text{PPh}(\text{CH}_2\text{CH}_2\text{Ph})_2]_2$
Mn coordination	octahedral	tetrahedral
Mn–I (cryst)	2.921	2.653
Mn–P (cryst)	–	2.585
Mn–O (cryst)	2.177	–
$\sigma(\text{Mn}–\text{I})$	0.121(3)	0.083(4)
$\sigma(\text{Mn}–\text{P})$	–	0.109(6)
$\sigma(\text{Mn}–\text{O})$	0.111(7)	–
$\Delta r(\text{Mn}–\text{I})$	0.28(2)	0.26(1)
$\Delta r(\text{Mn}–\text{P})$	–	0.44(2)
$\Delta r(\text{Mn}–\text{O})$	0.35(2)	–
Data range/Hartree	2.5–13	2.5–12

^aMean values for three independent data sets for each reference compound are given; distances in \AA .

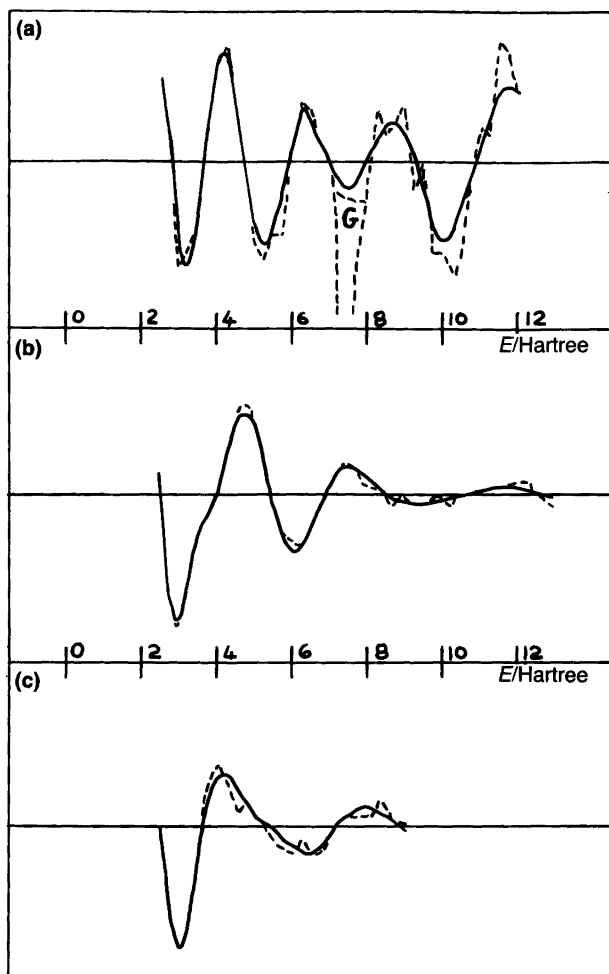


Fig. 2. EXAFS χ -curves; in each case one data set typical of three employed is shown. Solid lines: calculated; dashed lines: experimental. (a) Polycrystalline MnI_2 $[\text{PPh}(\text{CH}_2\text{CH}_2\text{Ph})_2]_2$; G indicates glitch which was corrected manually. (b) Polycrystalline $[\text{MnI}_2(\text{H}_2\text{O})_4]$. (c) MnI_2 in the thf solution.

Table 4 shows that $\Delta r(\text{Mn}-\text{I})$ is not significantly different for the two geometrically different environments. In subsequent refinements, the mean $\Delta r(\text{Mn}-\text{I})$ value and other parameters from Table 4 were held fixed.

MnI₂ in thf solution. Three sets of EXAFS data were collected for solutions of MnI_2 in dried thf. Comparison of the data (Fig. 2c) with that for $[\text{MnI}_2(\text{H}_2\text{O})_4]$ (Fig. 2b) reveals differences in details such as peak, trough and cross-over point positions. The data were also rather noisy, with no distinctive ripples beyond 9 Hartree. Preliminary structural refinements with Δr and σ parameters held fixed at the values obtained for the reference compounds suggested rather long

$\text{Mn}-\text{I}$ distances of ca. 2.8 Å and $\text{Mn}-\text{O}$ distances >2.2 Å, indicative of octahedral Mn coordination (long $\text{Mn}-\text{I}$) but with weaker $\text{Mn}-\text{O}$ bonds than found in $[\text{MnI}_2(\text{H}_2\text{O})_4]$. With the total coordination number $\sum N_j$ constrained to be six, good fits between calculation and experiment were obtained indicating rather less than 2 $\text{Mn}-\text{I}$ bonds and rather more than 4 $\text{Mn}-\text{O}$ bonds in the complex. These results were entirely consistent with our previous work on aqueous MnBr_2 solutions where equilibria between complexes of the type $[\text{MnX}_n\text{L}_{6-n}]^{(2-n)+}$ were postulated ($\text{X} = \text{Br}$, $\text{L} = \text{OH}_2$). Thus, MnI_2 in dry thf appears to exist as $[\text{MnX}_n\text{L}_{6-n}]^{(2-n)+}$ species in equilibrium [$\text{X} = \text{I}$, $\text{L} = \text{thf}$ ($n = 1, 2$ and maybe 0)]. The mean results obtained from the three sets of data

Table 5. Selected geometrical parameters for $\text{MnI}_2(\text{OPPh}_3)_2$.

Bond Lengths/Å			
Mn(1)–I(1)	2.670(1)	Mn(1)–I(2)	2.666(1)
Mn(1)–O(1)	2.014(5)	Mn(1)–O(2)	2.027(5)
O(1)–P(1)	1.502(5)	O(2)–P(2)	1.496(4)
P(1)–C(1)	1.785(8)	P(2)–C(21)	1.788(8)
P(1)–C(11)	1.787(5)	P(2)–C(31)	1.799(6)
P(1)–C(51)	1.783(6)	P(2)–C(41)	1.768(6)
Phenyl C–C			
Ring av. C(1)	1.379	Ring av. C(21)	1.375
Ring av. C(11)	1.383	Ring av. C(31)	1.378
Ring av. C(51)	1.373	Ring av. C(41)	1.380
Av. 3 rings	1.378	Av. 3 rings	1.378
Bond Angles/°			
I(1)–Mn(1)–I(2)	113.8(1)	O(1)–Mn(1)–O(2)	103.9(2)
I(1)–Mn(1)–O(1)	113.1(1)	I(2)–Mn(1)–O(1)	110.0(1)
I(1)–Mn(1)–O(2)	104.5(1)	I(2)–Mn(1)–O(2)	110.9(2)
Mn(1)–O(1)–P(1)	157.2(3)	Mn(1)–O(2)–P(2)	148.7(4)
O(1)–P(1)–C(1)	110.6(3)	O(2)–P(2)–C(21)	111.8(3)
O(1)–P(1)–C(11)	109.6(3)	O(2)–P(2)–C(31)	108.6(3)
O(1)–P(1)–C(51)	112.8(3)	O(2)–P(2)–C(41)	111.3(2)
Torsion Angles/°			
O(1)–P(1)–C(1)–C(6)	41.4(7)	O(2)–P(2)–C(21)–C(26)	–34.0(6)
O(1)–P(1)–C(11)–C(16)	24.7(4)	O(2)–P(2)–C(31)–C(36)	–12.1(5)
O(1)–P(1)–C(51)–C(52)	40.4(6)	O(2)–P(2)–C(41)–C(42)	–72.3(6)

were Mn–I = 2.77(2) Å and Mn–O = 2.24(2) Å with $n_{\text{av}} = 1.4(1)$. The Mn–O distance compares with 2.28 Å in a crystalline thf complex²³ of Mn(II) with octahedral coordination. Further refinements with ΣN_j constrained to be six and the distances constrained to fit the Brown and Shannon equations (see Theory section above) also give $n_{\text{av}} = 1.4$, but with only slightly shorter bond lengths of 2.74 and 2.22 Å, respectively. The similarity between the results from the free refinements and those constrained to fit the Brown and Shannon equations suggests a real strengthening of the Mn–I bonds accompanying a weakening (lengthening) of the Mn–O(thf) bonds compared with $[\text{MnI}_2(\text{H}_2\text{O})_4]$, where the lengths of the Mn–I and Mn–O(H₂O) bonds are 2.921 and 2.177 Å, respectively (Table 4). Furthermore, the consistent bond lengths and n_{av} values, with and without the Brown and Shannon constraints, reinforce the conclusion concerning the existence of octahedral species in equilibrium in the solution.

Crystalline $\text{MnI}_2(\text{OPPh}_3)_2$. Selected geometrical parameters are listed in Table 5. The structure consists of isolated asymmetrical molecules related only by the translational symmetry afforded by the *P1* triclinic space group. The mean Mn(II)–I distance of 2.668(1) Å is in the range of values covered by the other Mn(II)–I bonds in tetrahedral environments in Table 1. The mean Mn(II)–O distance of 2.021(4) Å is, however, predictably much shorter than the Mn(II)–O bond in the octahedral environments in $[\text{MnI}_2(\text{H}_2\text{O})_2]$, i.e. 2.177 Å, and in MnI_2 in thf solution, i.e. 2.24(2) Å. The angles of the ‘tetrahedral’ environment of Mn(II) range from 104–114°. The variability of the O–P–C–C torsion angles demonstrates the asymmetry of the molecules.

Bond length correlations. Applying the Brown and Shannon¹⁹ theory (see above) to the short 2.021 Å Mn(II)–O bonds in $\text{MnI}_2(\text{OPPh}_3)_2$, a strength of $s = 0.333 (2.021/2.165)^{-5.1} = 0.47$ vu is predicted, remarkably close to the value of 0.5

Table 6. Bond strength data for Mn(II)-X Bonds (X = O, I, P) for use with the expression $s = s_0(R/R_0)^{-p}$.

X	s_0	R_0	p	Ref.
O	0.333	2.165	5.1	19
	0.50	2.000		
I	0.333	2.920	5.1	This work
	0.50	2.697		
P	0.333	2.769	4.4	This work
	0.50	2.524		

which would occur if the two Mn-O and two Mn-I bonds shared the divalency of Mn(II) equally. However, the value of 0.47 vu suggests slightly unequal sharing of the divalency, and indicates a value for the strength of the 2.668 Å Mn(II) bonds of 0.53 vu. Calculating the p value for Mn(II)-I bonds from these data and the 2.920 Å length for $s = 0.333$ gives p from $0.53 = 0.333 (2.668/2.920)^{-p}$ as $5 \cdot 1$, exactly the same as for Mn(II)-O bonds and within the range 4.3 to 5.4 obtained previously for Mn(II)-I bonds (see above). If the Brown and Shannon data for Mn(II)-O bonds are assumed to be definitive, a value of $p = 5 \cdot 1$ for Mn(II)-I bonds from the present crystallographic data for $\text{MnI}_2(\text{OPPh}_3)_2$ can be taken to be more reliable than the previously calculated p values based on the phosphine derivatives listed in Table 1. Furthermore, a value of p for Mn(II)-P bonds can now be deduced as follows. Mn(II)-P bonds in an octahedral environment occur in the King structure, $\text{MnI}_2(\text{PPhMe}_2)_2$; the 2.971 Å "octahedral" Mn(II)-I bonds of the King structure will have a strength of $s = 0.333(2.971/2.920)^{-5.1} = 0.305$ vu, or 1.22 vu for four such Mn(II)-I bonds, leaving 0.78 vu for the two 2.671 Å Mn(II)-P "octahedral" bonds (0.39 vu each). For Mn(II)-P in a tetrahedral environment, a similar calculation can be performed for the averaged data in Table 2: Mn(II)-I = 2.657 Å with Mn(II)-P = 2.573 Å. Now $s(\text{Mn}-\text{I}) = 0.333 (2.657/2.920)^{-5.1} = 0.54$ vu, leaving 0.46 vu for each Mn-P bond. The value of p for Mn(II)-P bonds is now obtained from $0.46 = 0.39 (2.573/2.671)^{-p}$, giving $p = 4.4$.

Table 6 collects together the bond strength data now available for O, I and P bonded to Mn(II), although the data for P are tentative. The con-

stants in Table 6, used in conjunction with the standard Brown and Shannon equation,¹⁹ satisfactorily correlate the bond lengths in all the Mn species discussed in this paper. We have recently obtained crystallographic data²⁴ for the complex $[\text{MnI}(\text{OPPh}_3)_4]^+\text{I}_3^-$ in which the Mn(II)-I and average Mn(II)-O bond lengths are 2.745(4) and 2.123 Å. For the pentacoordinated Mn(II) atom in this cation, the data in Table 6 may be tested. The quoted bond lengths correspond to bond strengths of 0.46 and 0.37 vu, respectively. The sum $0.46 + 4(0.37) = 1.94$ vu is close enough to the requisite 2.0 vu to support the applicability of the data in Table 6 for pentacoordinated Mn(II).

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