Manganese(II) Complexes of Trialkylphosphine Oxide Ligands and Their Reaction with Sulfur Dioxide to form Ligand-bound Adducts†

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Manganese(II) complexes of the rarely studied ligands OPR_3 (R = Et, Pr^n or Bu^n), $[Mn(OPR_3)_2X_2]$ (R = Et, Pr^n or Bu^n) and $[Mn(OPR_3)_n(NCS)_2]$ (R = Et or Bu^n; n = 1, 2 or 4) have been prepared and characterised. The free ligands react rapidly with sulfur dioxide to form liquid 1 : 1 adducts $R_3PO{\cdot}SO_2$, and over a longer period to form $(R_3P{\cdot}SO_2)(SO_2)_{0.5}$. The adduct process is reversed by applying a vacuum; the stability of the $R_3PO{\cdot}SO_2$ adducts is in the order R = Bu^n > Pr^n, Et. The $[Mn(OPR_3)_2X_2]$ complexes do not react with SO_2 when slurried in toluene but take up 2 mol of SO_2 in the solid state. Moreover, $[Mn(OPR_3)_n(NCS)_2]$ (n = 2 or 4) take up 2 and 4 mol of SO_2, respectively, in the solid state, *i.e.* the number of SO_2 molecules bound is proportional to the number of ligands in the complex. Other evidence is presented which confirms ligand-bound SO_2, including the observation that $Bu^n{}_3PO{\cdot}SO_2$ reacts with $MnCl_2$ to form $[Mn\{O(SO_2)PBu^n{}_3\}_2Cl_2]$. Consistent with previous studies of ligand-bound SO_2, the binding is weak and the SO_2 is not activated to reaction with dioxygen. Aluminium trichloride replaces Mn from $[Mn(OPBu^n{}_3)_2Cl_2]$ to form $Bu^n{}_3PO{\cdot}AlCl_3$.

In contrast to the extensive use of triphenylphosphine oxide as a ligand, relatively little attention has been paid to the corresponding trialkyl derivatives. Long-chain alkylphosphine oxides have received attention as metal extractants in hydrometallurgy, and some trimethylphosphine oxide complexes have been characterised;[1-4] however, generally reports of complexes with first-row transition metals are scarce. One manganese(II) complex, tetrahedral $[Mn(OPBu^n{}_3)_4][ClO_4]_2$, is known.[5]

We have made extensive use of manganese(II)[6,7] and iron(III)[8] complexes containing $OPPh_3$ and $OAsPh_3$ ligands in binding and activating sulfur dioxide. In particular, manganese(II) iodide and thiocyanate complexes[6,7] co-ordinate up to two molecules of SO_2 and in some cases activate the SO_2 to oxidation by moist air to produce sulfuric acid which may be isolated and crystallographically characterised as the ligand hydrogen-bonded species $(PPh_3O)(PPh_3OH)(HSO_4)$[6] and $(AsPh_3OH)(HSO_4)$.[8] A good deal of complex redox chemistry goes on in these systems since highly unusual products, including $[AsPh_3I]I_3$,[9] $AsPh_3(I_2)$[10] and $[(AsPh_3O)_2H]I_3$[11] can be formed from complexes containing $OAsPh_3$. Indeed, the rare blue gas N_2O_3 has been detected as a product of the interaction of manganese(II) nitrate complexes of diphosphine dioxide and diarsine dioxide ligands with SO_2.[12] An extension of our work to a diphosphine dioxide ligand $Ph_2P(O)CH_2CH_2CH_2(O)PPh_2$ produced a 'Chinese lantern' type of cryptate molecule $[Mn_2\{Ph_2P(O)CH_2CH_2CH_2(O)PPh_2\}_4(NCS)_2][NCS]_2$ which can reversibly bind five molecules of SO_2, although in this case no activation of the SO_2 is observed.[13]

In view of this interesting chemistry we have extended our investigations to manganese(II) complexes containing $OPEt_3$, $OPPr^n{}_3$ and $OPBu^n{}_3$ ligands and have examined the interaction with sulfur dioxide in the solid state and as slurries in toluene.

Results and Discussion

Synthesis and Characterisation of the Complexes.—(*a*) *Manganese*(II) *Halides.* The complexes $[Mn(OPR_3)_2X_2]$ (R = Et, Pr^n or Bu^n; X = Cl, Br or I) are isolated from the reaction of MnX_2 with OPR_3 irrespective of the stoichiometries used, Table 1. No solvent dependence is observed and diethyl ether, toluene and hexane may all successfully be employed as solvents. Since both the anhydrous manganese(II) salts and trialkylphosphine oxide ligands are hygroscopic anhydrous reaction conditions need to be used; however, once isolated the final products are air stable. The complexes containing $OPEt_3$ are solids, whilst those of $OPBu^n{}_3$ are oils; those of the $OPPr^n{}_3$ ligand are intermediate, with the phase of the compound showing a secondary anion dependence, Table 1. The ESR spectra of the complexes provide little information, all exhibiting a strong $g = 2$ signal. The room-temperature magnetic moments are typical of spin-only values, Table 1, indicating monomeric species, as does the ready solubility of the complexes in most organic solvents. These pale yellow or green complexes are essentially non-conducting in nitrobenzene. All of these properties are consistent with a monomeric pseudo-tetrahedral structure and such a formulation concurs with the molecular weight obtained for $[Mn(OPPr^n{}_3)_2Br_2]$ of 497 (calc. 483) in dichloromethane. Crystals of the solid are readily grown, but the secondary evidence available is sufficient confidently to assign tetrahedral structures, making the complexes isostructural with their crystallographically characterised $OPPh_3$ analogues.[14-16]

An octahedral $[Mn(OPPh_3)_4I_2]$ complex is also known.[17] In view of the crystallographically characterised SO_2 insertion into the Mn–I bonds in this complex, $[Mn(OPPh_3)_4\{OS(O)I\}_2]$,[7] the isolation of an analogous six-co-ordinate trialkylphosphine oxide complex would be attractive. However, only the bis(ligand) complexes $[Mn(OPR_3)_2X_2]$ (R = Et, Pr^n or Bu^n) can be isolated under the same synthetic conditions.

(*b*) *Manganese*(II) *thiocyanates.* In contrast to the halide complexes, when $Mn(NCS)_2$ is used the ratio of reagents does influence the stoichiometry of the products formed: $[Mn(OPR_3)_n(NCS)_2]$ (R = Et or Bu^n; n = 1, 2 or 4) can be isolated using the appropriate $Mn(NCS)_2$: ligand ratio, Table 2. Large excesses of the ligand still only yield the tetrakis complex. Complexes with a tris(ligand) stoichiometry may be recovered

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* *Non SI unit employed:* emu = SI × $10^6/4\pi$.

Table 1 Some physical properties and elemental analyses of the manganese(II) halide trialkylphosphine oxide complexes

Complex	M.p./°C	Colour	μ_{eff}	ν(PO)[a]/ cm^{-1}	Λ[b]/S cm^2 mol^{-1}	Analysis (%)[c] C	H	Halide	P	Mn
$[Mn(OPEt_3)_2Cl_2]$	75–76	Pale green	5.97	1108s, 1140 (sh)	2	36.7 (36.5)	7.9 (7.6)	17.7 (18.0)	16.0 (15.7)	
$[Mn(OPEt_3)_2Br_2]$	88–89	Pale green	5.99	1108s, 1140 (sh)	3	29.5 (29.8)	5.9 (6.2)	32.9 (33.1)	12.6 (12.8)	11.2 (11.4)
$[Mn(OPEt_3)_2I_2]$	79–80	Pale yellow	5.96	1108s, 1130m	6	25.2 (25.0)	5.4 (5.2)	43.8 (44.0)	10.6 (10.7)	9.1 (9.5)
$[Mn(OPPr^n{}_3)_2Cl_2]$	63–64	Pale green	5.94	1120s	2	45.0 (45.2)	9.0 (8.8)	14.8 (14.9)	13.0 (13.0)	10.8 (11.5)
$[Mn(OPPr^n{}_3)_2Br_2]$	Oil	Pale green	5.98	1112s, 1135 (sh)	2	38.1 (38.1)	7.6 (7.4)	28.2 (28.2)	11.2 (10.9)	9.2 (9.7)
$[Mn(OPPr^n{}_3)_2I_2]$	Oil	Orange	5.94	1115s	9	32.9 (32.7)	6.4 (6.4)	38.1 (38.4)	8.9 (9.4)	8.3 (7.8)
$[Mn(OPBu^n{}_3)_2Cl_2]$	Oil	Pale green	5.91	1115s	3	51.1 (51.2)	9.9 (9.6)	12.5 (12.6)	11.2 (11.0)	9.9 (9.8)
$[Mn(OPBu^n{}_3)_2Br_2]$	Oil	Pale green	5.94	1117s	6	43.9 (44.2)	8.6 (8.3)	24.5 (24.6)	9.9 (9.5)	8.3 (8.4)
$[Mn(OPBu^n{}_3)_2I_2]$	Oil	Orange	5.91	1120s	6	38.5 (38.7)	7.4 (7.2)	34.4 (34.1)		

[a] ν(PO): $OPEt_3$, 1155s; $OPPr^n{}_3$, 1160s; $OPBu^n{}_3$, 1157s cm^{-1}. [b] In nitrobenzene. [c] Calculated values in parentheses.

Table 2 Some physical properties and elemental analyses of the manganese(II) thiocyanate trialkylphosphine complexes

Complex	M.p./°C	Colour	μ_{eff}	ν(PO)[a]/ cm^{-1}	ν(CN)/ cm^{-1}	Λ[b]/S cm^2 mol^{-1}	Analysis (%)[c] C	H	N	P	S	Mn
$[Mn(OPEt_3)(NCS)_2]$[d]	131 (decomp.)	White	5.39	1118s	2105s, 2060m		32.5 (31.5)	5.5 (4.9)	9.0 (9.2)	10.3 (10.2)	20.5 (21.0)	17.2 (18.0)
$[Mn(OPEt_3)_2(NCS)_2]$	Oil	Pale green	5.89	1125s	2060s	4	38.6 (38.3)	6.9 (6.8)	6.1 (6.4)	14.3 (14.1)		
$[Mn(OPEt_3)_4(NCS)_2]$	62–64	Pale green	6.08	1140s	2060s	5	43.8 (44.1)	8.3 (8.5)	4.0 (4.0)	17.2 (17.5)	9.1 (9.5)	8.3 (7.8)
$[Mn(OPBu^n{}_3)(NCS)_2]$[d,e]	238 (decomp.)	White	5.42	1145s	2105s, 2060s		40.1 (43.2)	6.9 (6.9)	7.3 (7.3)	7.8 (8.0)	16.7 (16.5)	13.8 (14.1)
$[Mn(OPBu^n{}_3)_2(NCS)_2]$	Oil	Pale green	5.95	1118s	2060s	6	51.4 (51.4)	9.2 (9.0)	4.5 (4.6)	10.0 (10.2)	10.2 (10.5)	8.9 (9.0)
$[Mn(OPBu^n{}_3)_4(NCS)_2]$	32–33	White	5.89	1130s	2060s	5	57.8 (57.5)	10.7 (10.4)	2.6 (2.7)	11.9 (11.9)	5.7 (6.1)	5.0 (5.3)

[a] ν(PO), $OPEt_3$ 1155s; $OPPr^n{}_3$, 1160s; $OPBu^n{}_3$, 1157s cm^{-1}. [b] In nitrobenzene. [c] Calculated values in parentheses. [d] Insoluble in $PhNO_2$ or $MeNO_2$. [e] Consistently low carbon analyses, but the total C + O (by difference) is 47.5 (47.3)%, suggesting a systematic error in analysis.

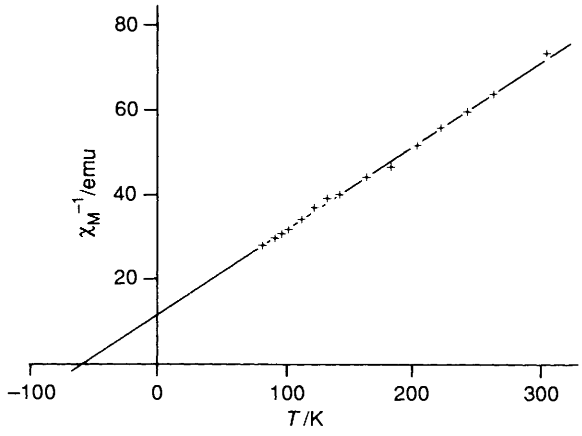


Fig. 1 Plot of $1/\chi_M$ *versus* temperature for $[Mn(OPEt_3)(NCS)_2]$

from a reaction of $Mn(NCS)_2$:OPR_3 ratio 1:3; however, GLC analyses show that these are mixtures of the bis and tetrakis complexes. Infrared spectra of the $[Mn(OPR_3)(NCS)_2]$ complexes, Table 2, exhibit ν(CN) bands indicative of both terminal and bridging anions and thus a dinuclear structure is pointed to, in agreement with the reduced room-temperature magnetic moment due to the antiferromagnetism arising from bridging anions, Table 2. Low-temperature magnetic susceptibility studies for $[Mn(OPEt_3)(NCS)_2]$ indicate a marked temperature dependence. This complex obeys the Curie–Weiss law, Fig. 1, with $\theta = -59$ K and $2J = -6.9$ cm^{-1}. These values suggest a small, but significant, antiferromagnetic exchange. Crystallographic characterisation has been prevented by the extreme insolubility of these monoligand complexes. The bis(ligand) complexes exhibit only a terminal ν(CN) band and magnetic moments consistent with a high-spin complex with a monomeric pseudo-tetrahedral structure.

The $[Mn(OPR_3)_4(NCS)_2]$ complexes have infrared[18,19] and magnetic properties which mirror those of *trans*-octahedral $[Mn(OPPh_3)_4(NCS)_2]$.

There appears to be a marked difference between the monomeric $[Mn(OPR_3)_2(NCS)_2]$ (R = Et or Bu^n) reported here {the molecular weight of $[Mn(OPBu^n{}_3)_2(NCS)_2]$ is 590 (calc. 617 for a monomer) in dichloromethane} and the previously reported complex $[Mn(OPPh_3)_2(NCS)_2]$. The latter exhibits both bridging and terminal ν(CN) bands and has been shown by X-ray crystallography to have a five-co-ordinate dinuclear structure.[6] This is somewhat surprising since less, rather than more, steric crowding would be anticipated for the trialkylphosphine oxide complexes. However, the trialkyl-substituted ligands are significantly more basic than $OPPh_3$ (K_b: $OPBu^n{}_3$, 4.92; $OPPh_3$, 3.72),[20] and this suggests that the stronger σ donors stabilise the bis complex without the need to dimerise.

All the thiocyanate complexes are air stable, save for the monoligand complexes $[Mn(OPEt_3)(NCS)_2]$ and $[Mn(OPBu^n{}_3)(NCS)_2]$ which are hygroscopic. After exposure to air, infrared bands at 3400 and 1640 cm^{-1} are observed; moreover, the ν(CN) bands show major changes. The terminal ν(CN) bands shift to lower energy by 5–10 cm^{-1}, but the bridging bands show vastly increased intensity. Karl–Fischer analyses indicate the presence of one H_2O molecule, *e.g.* $Mn(OPEt_3)(H_2O)(NCS)_2$ (Found: H_2O, 5.6. Calc.: 6.0%). Other hygroscopic

Table 3 Sulfur dioxide uptake by the trialkylphosphine oxide ligands

Ligand	Amount g	Amount 10^{-4} mol	Increase in mass/g	Ar/SO_2 Corr./g	Amount absorbed g	Amount absorbed 10^{-4} mol	SO_2/Mn ratio
$OPEt_3$	0.1581	11.80	0.0825	0.0077	0.0784	11.69	1:0.99
$OPPr^n_3$	0.4592	26.09	0.1921	0.0199	0.1722	26.90	1:1.03
$OPBu^n_3$	0.8998	41.28	0.3011	0.0233	0.2778	43.41	1:1.05

Table 4 Infrared absorptions (cm^{-1}) for ligand–sulfur dioxide adducts (all clear liquids)

Adduct	$\nu_{sym}(SO)$	$\nu_{asym}(SO)$	$\delta(SO)$	$\nu(PO)$[b]
$Et_3PO{\cdot}SO_2$	1310s	1115s	525s	1150s
$Pr^n_3PO{\cdot}SO_2$	1310s	1112s	525s	1150s
$Bu^n_3PO{\cdot}SO_2$	1315s	1120s	528s	1150s

[a] For SO_2: $\nu(SO)$ 1340, 1150, $\delta(SO)$ 524s cm^{-1}. [b] $\nu(PO)$: $OPEt_3$, 1155s; $OPPr^n_3$, 1160s; $OPBu^n_3$, 1157s cm^{-1}.

Table 5 The ^{31}P NMR shifts for trialkylphosphine oxide ligands after exposure to sulfur dioxide

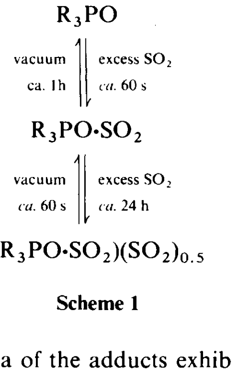
Ligand	Literature value[27,28]	In CCl_4	In SO_2-saturated CCl_4	Neat adduct	In 98% H_2SO_4
$OPEt_3$	48.3	48.3	53.0	52.8	96.8
			(Δ = 4.7)	(Δ = 4.5)	(Δ = 48.5)
$OPPr^n_3$	—	42.6	49.3	47.9	91.9
			(Δ = 6.7)	(Δ = 5.3)	(Δ = 49.3)
$OPBu^n_3$	43.2	43.1	53.7	54.1	93.0
			(Δ = 10.6)	(Δ = 11.0)	(Δ = 49.9)

All values are quoted in ppm relative to H_3PO_4.

tertiary phosphine oxide complexes have been characterised; for example $[Mn(dppoe)(NCS)_2]$ [dppoe = $Ph_2P(O)CH_2CH_2(O)PPh_2$] on recrystallisation from acetone yields the five-co-ordinate polymeric complex $[\{Mn(dppoe)(H_2O)(NCS)_2{\cdot}dppoe\}_n]$.[21]

Reactivity of Unco-ordinated Trialkylphosphine Oxide Ligands with Sulfur Dioxide.—The reversible formation of a 1:1 adduct between Me_3PO and SO_2 was established as long ago as 1951.[22] The solid ligand rapidly forms a liquid on exposure to SO_2, and the interaction is fairly weak since there is always a low partial pressure of SO_2 above the liquid, eventually leading to total loss of SO_2 and the reformation of the solid Me_3PO.

We have explored the possibility of similar interactions of $OPEt_3$, $OPPr^i_3$ and $OPBu^n_3$ with SO_2, applying quantitative 'solid state' techniques. When the argon atmosphere above the ligands is replaced by one of dry SO_2 an almost instantaneous liquefaction of all three compounds occurs. Maintaining an atmosphere of SO_2 above these liquids results in a stable mass increase after *ca.* 60 s. After correcting for the greater density of SO_2 compared to that of argon, the weight increase is commensurate with 1:1 $R_3PO{\cdot}SO_2$ adducts, Table 3. On standing for 24 h this value increases to *ca.* 1.5 mol of SO_2 per mol of ligand. This additional 0.5 SO_2 seems much more weakly bound, since it is lost by even a slight application of a vacuum to leave the 1:1 adduct. Much longer evacuation, *ca.* 1 h, is required to remove the remaining SO_2 (Scheme 1).



Scheme 1

The infrared spectra of the adducts exhibit smaller shifts in their $\nu(PO)$ bands from those of the free ligands, Table 4. Whilst such shifts to lower energy are frequently associated with ligand co-ordination, solvation effects can also be responsible for relatively small movements.[23] Intense bands due to the $\nu_{sym}(SO)$ and $\delta(SO)$ modes of SO_2 are also observed, Table 4, and $\nu_{asym}(SO)$ appears as a shoulder on the more prominent $\nu(PO)$ band. The two assignable bands are shifted to lower energy from those of free SO_2 and are consistent with weak reversible co-ordination.[24,25]

However, ^{31}P NMR spectroscopy has proven to be a more informative technique. Previous studies with $OPPh_3$ show that certain solvents can significantly displace the ^{31}P signal as a result of even weak interactions with the ligand. Carbon tetrachloride has little effect, whereas concentrated H_2SO_4 causes the largest known shifts.[26] We have thus used these two solvents as references in this study.

Phosphorus-31 NMR shifts of 5–10 ppm to low frequency from those in CCl_4 are recorded for the ligands in SO_2-saturated CCl_4, Table 5. If solvation rather than genuine co-ordinative bonding were occurring a more dilute SO_2–CCl_4 mixture should result in significantly small shifts from the free-ligand values. In fact the resultant spectra are remarkably similar, suggesting that $R_3PO{\cdot}SO_2$ adducts are formed in each case. Numerically, the displacements from the free-ligand values are small compared to those in sulfuric acid and a rapid $R_3PO{\cdot}SO_2 \rightleftharpoons R_3PO + SO_2$ equilibrium may be envisaged, but cooling to −17 °C in CCl_4 and −78 °C in CH_2Cl_2 fails to produce any line broadening or splitting, reducing the case for such an equilibrium.

Lewis-acid and -base behaviour by the SO_2 and ligand, respectively, is the logical form of bonding, and this is confirmed by the ^{31}P NMR shifts to lower frequency on adduct formation. Such movements imply deshielding of the phosphorus, commensurate with electron donation by the adjacent oxygen. Although both oxygen and sulfur atoms in SO_2 can function as Lewis bases, only the sulfur can function as an acid by donation into the empty $2b_1$ molecular orbital, which is essentially sp^2 in character.

The precise upfield shift is indicative of the strength of the co-ordination. That of $Bu^n_3PO{\cdot}SO_2$ is significantly greater, *ca.* 10 ppm, than its triethyl and tri-*n*-propyl analogues. This is reflected in its relative stability during elemental analysis [Found (Calc.): C, 51.4 (51.1); H, 9.9 (9.6); S, 10.9 (11.3)%], and a weak parent ion (m/z = 282) is observed in its mass spectrum. Similar results could not be recorded for the $Pr^n_3PO{\cdot}SO_2$ and $Et_3PO{\cdot}SO_2$ adducts.

Affinity of Trialkylphosphine Oxide Complexes of Manganese(II) *for Sulfur Dioxide.*—(*a*) *Manganese*(II) *halides.* The $[Mn(OPR_3)_2X_2]$ complexes take one of two physical forms: the low-molecular-weight compounds (R = Et, X = Cl, Br or I;

Table 6 Mass changes on exposure of the manganese(II) halide complexes to sulfur dioxide

Complex	Amount		Increase in mass/g	Ar/SO_2 Corr./g	Amount absorbed		SO_2/Mn ratio
	g	10^{-4} mol			g	10^{-4} mol	
$[Mn(OPEt_3)_2Cl_2]$	0.1806	4.58	0.0829	0.0233	0.0596	9.31	1:2.03
$[Mn(OPEt_3)_2Br_2]$	0.1833	3.58	0.0686	0.0199	0.0487	7.61	1:2.00
$[Mn(OPEt_3)_2I_2]$	0.3916	6.79	0.1033	0.0167	0.0866	13.53	1:1.99
$[Mn(OPPr^n{}_3)_2Cl_2]$	0.3550	7.43	0.1205	0.0233	0.0972	15.19	1:2.05
$[Mn(OPPr^n{}_3)_2Br_2]$	0.3441	5.89	0.1088	0.0346	0.0742	11.59	1:1.97
$[Mn(OPPr^n{}_3)_2I_2]$	0.2239	3.39	0.0527	0.0087	0.0440	6.88	1:2.02
$[Mn(OPBu^n{}_3)_2Cl_2]$	0.1059	1.88	0.0360	0.0128	0.0232	3.63	1:1.92
$[Mn(OPBu^n{}_3)_2Br_2]$	0.2675	4.11	0.0860	0.0525	0.0535	8.36	1:2.00
$[Mn(OPBu^n{}_3)_2I_2]$	0.3290	4.42	0.0613	0.0047	0.0566	8.84	1:2.00

Table 7 Infrared absorptions (cm^{-1}) for $[Mn\{OP(SO_2)R_3\}_2X_2]$ adducts (X = Cl, Br or I)

Complex	Colour	$\nu_{sym}(SO)$	$\delta(SO)$	$\nu(PO)$
$[Mn\{O(SO_2)PEt_3\}_2Cl_2]$	Green	1323s	524s	1108s, 1140s
$[Mn\{O(SO_2)PEt_3\}_2Br_2]$	Green	1321s	521s	1108s, 1140s
$[Mn\{O(SO_2)PEt_3\}_2I_2]$	Red	1322s	523s	1108s, 1130s
$[Mn\{O(SO_2)PPr^n{}_3\}_2Cl_2]$	Green	1322s	521s	1120s
$[Mn\{O(SO_2)PPr^n{}_3\}_2Br_2]$	Green	1320s	521s	1112s, 1135
$[Mn\{O(SO_2)PPr^n{}_3\}_2I_2]$	Red	1320s	523s	1115s
$[Mn\{O(SO_2)PBu^n{}_3\}_2Cl_2]$	Green	1320s	524s	1115s
$[Mn\{O(SO_2)PBu^n{}_3\}_2Br_2]$	Green	1320s	521s	1115s
$[Mn\{O(SO_2)PBu^n{}_3\}_2I_2]$	Red	1320s	522s	1117s

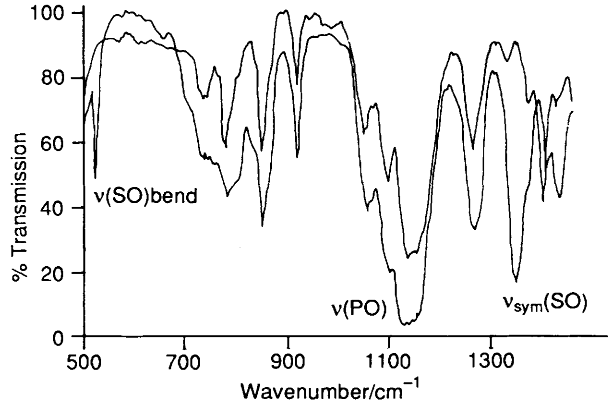


Fig. 2 The infrared spectra (1300–500 cm^{-1} region) of $[Mn(OPPr^n{}_3)_2Br_2]$ (upper) and $[Mn\{O(SO_2)PPr^n{}_3\}_2Br_2]$ (lower) illustrating the strong ν(SO) absorptions in the latter

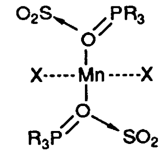
R = Pr^n, X = Cl) are solids, whilst the remainder of the complexes are oils. Exposure of the latter to SO_2 as toluene slurries produces no visible change and the oils may be recovered with no apparent SO_2 co-ordination. The solid complexes rapidly become oily when slurried in SO_2-saturated toluene; however, on isolation the oils resolidify and no SO_2 is detectable either by elemental analyses or infrared spectroscopy.

Quantitative 'solid state' exposures to SO_2 are more informative. All complexes rapidly increase in weight to a maximum commensurate with the co-ordination of two SO_2 moieties, Table 6. The solid complexes become intensely coloured oils.

Parallels are strong with the ligand reactivity already discussed. Co-ordination is reversible and empirical observations suggest that SO_2 binds even more weakly than to the free ligands. Such weak interactions explain the difficulties encountered in isolating the adducts formed in toluene slurries: solvent cannot be removed without the concurrent loss of sulfur dioxide, and this acute lability effectively prevents the elemental analysis of the adducts. In such analyses some sulfur and reduced carbon and hydrogen values are recorded, but the results are variable and at best only confirmed *ca.* 50% of the total SO_2 present.

The infrared spectra of the adducts, Table 7, exhibit very strong $\nu_{sym}(SO)$ and δ(SO) bands, Fig. 2. These are typical of ligand-, rather than metal-, co-ordinated SO_2 [29] and are very similar to those of the $R_3PO{\cdot}SO_2$ adducts, Table 4. Hence, the SO_2 is co-ordinated to the R_3PO ligands in the $[Mn(OPR_3)_2X_2]$ complexes, but it is somewhat surprising that this occurs without decomposition of the complex. Complexation of the R_3PO ligands with the MnX_2 salts results in shifts to lower energy of the ν(PO) band of *ca.* 40–50 cm^{-1} compared to the free R_3PO ligand value, whereas co-ordination to SO_2 by R_3PO causes only shifts of *ca.* 10 cm^{-1}. On the other hand, co-ordination of SO_2 to the $[Mn(OPR_3)_2(NCS)_2]$ complexes results in no detectable shift in ν(PO), Table 7, compared to that of the complexes, Table 1.

It is thus most likely that the phosphine oxide ligand must co-ordinate to both SO_2 and the metal through a single oxygen centre. Assuming that the $[Mn(OPR_3)_2X_2]$ complexes are isostructural with their crystallographically characterised $[Mn(OPPh_3)_2X_2]$ analogues, the co-ordinating oxygen will be essentially sp^2 hybridised.[14–16] This leads to bent Mn–O–P bonds of *ca.* 145°, which leaves a second sp^2 lone pair free to co-ordinate to SO_2 without steric hindrance.



(*b*) *Manganese*(II) *thiocyanates.* The activity of both bis $[Mn(OPR_3)_2(NCS)_2]$ and tetrakis $[Mn(OPR_3)_4(NCS)_2]$ complexes (R = Et or Bu^n) mirrors that of the halide complexes, inasmuch as 'solid state' exposure to SO_2 turns all the compounds to oils, with weight increases corresponding to 2 and 4 mol of SO_2 per Mn, respectively, Table 8. Clearly, the number of SO_2 moieties co-ordinated is dependent on the number of phosphine oxide ligands present, strengthening our deduction of SO_2 binding at these ligands.

The rapid reversibility of SO_2 binding is once again observed. Strong bands at *ca.* 1312 and 525 cm^{-1} are evidence for SO_2 co-ordination and these rapidly disappear on the application of a vacuum. The ν(CN) bands of the $[Mn(OPR_3)_n(NCS)_2]$ (*n* = 2 or 4) complexes are not affected by SO_2 binding, Table 9, discounting the possibility of binding to the thiocyanate ion (such binding to thiocyanate has previously been observed [21,30]). Thus, we once more propose weak ligand–SO_2 binding in these complexes.

The oligomeric monoligand complexes $[Mn(OPR_3)(NCS)_2]$ (R = Et or Bu^n) behave very differently, however. No weight increases are observed on exposure to SO_2, Table 8, and no change in infrared spectra, Table 9. Since we have observed that co-ordination of the ligand to manganese(II) reduces the ligand

Table 8 Mass changes on exposure of the thiocyanate complexes to SO_2

Complex	Amount g	Amount 10^{-4} mol	Increase in mass/g	Ar/SO_2 Corr./g	Amount absorbed g	Amount absorbed 10^{-4} mol	SO_2/Mn ratio
$[Mn(OPEt_3)(NCS)_2]$	0.1072	3.51	0.0100	0.0096	0.0004	0.06	1: <0.1
$[Mn(OPEt_3)_2(NCS)_2]$	0.1073	2.44	0.0479	0.0167	0.0312	4.88	1:2.00
$[Mn(OPEt_3)_4(NCS)_2]$	0.3372	4.78	0.1372	0.0146	0.1227	19.17	1:4.02
$[Mn(OPBu^n{}_3)(NCS)_2]$	0.2443	6.28	0.0150	0.0146	0.0004	0.06	1: <0.1
$[Mn(OPBu^n{}_3)_2(NCS)_2]$	0.5735	9.45	0.1433	0.0233	0.1200	18.75	1:1.99
$[Mn(OPBu^n{}_3)_4(NCS)_2]$	0.5707	5.47	0.1607	0.0186	0.1421	22.20	1:4.05

Table 9 Infrared data (cm^{-1}) for $[Mn\{OP(SO_2)R_3\}_n(NCS)_2]$ adducts and $[Mn(OPR_3)(NCS)_2]$ complexes (n = 2 or 4, R = Et or Bu^n)

Complex	Colour	$\nu_{sym}(SO)$	$\delta_{def}(SO)$	$\nu(PO)$	$\nu(CN)$
$[Mn(OPEt_3)(NCS)_2]$	White			1120s	2105s, 2060s
$[Mn\{O(SO_2)PEt_3\}_2(NCS)_2]$	Green	1315s	523s	1125s	2060s
$[Mn\{O(SO_2)PEt_3\}_4(NCS)_2]$	Green	1315s	527s	1140s	2065s
$[Mn(OPBu^n{}_3)(NCS)_2]$	White			1145s	2105s, 2060m
$[Mn\{O(SO_2)PBu^n{}_3\}_2(NCS)_2]$	Green	1312s	520s	1118s	2060s
$[Mn\{O(SO_2)PBu^n{}_3\}_4(NCS)_2]$	Green	1310s	525s	1130s	2060s
$[Mn(OPEt_3)(H_2O)(NCS)_2]$	White			1120s	2110s, 2050s
$[Mn(OPBu^n{}_3)(H_2O)(NCS)_2]$	White			1145s	2105s, 2060s

Table 10 NMR data for the $R_3PO{\cdot}AlCl_3$ adducts and their R_3PO precursors

Compound	$\delta(^{31}P)$	$\delta(^{27}Al)$
Ph_3PO[31]	29.3	
$Ph_3PO{\cdot}AlCl_3$[31]	44.9	90 ($\nu_{\frac{1}{2}}$ = 40 Hz)
$Bu^n{}_3PO$	43.2	
$Bu^n{}_3PO{\cdot}AlCl_3$	75.5	90 ($\nu_{\frac{1}{2}}$ = 50 Hz)

affinity for SO_2, the expected greater manganese–ligand interaction in the monoligand complexes appears to render these complexes totally inactive to SO_2 binding.

(*c*) *Exposure under aerobic conditions.* Exposure of the complexes to air, after slurrying in SO_2-saturated toluene, produces no evidence of oxidation of the sulfur dioxide: the complexes are recovered unchanged and no sulfuric acid derivative can be isolated even on concentration of the solution. This is not altogether surprising since SO_2 activation is generally thought to require direct co-ordination to a metal.[29] We thus see the quite drastic effect which the nature of the R group in manganese(II) tertiary phosphine oxide complexes has on the co-ordination of sulfur dioxide. Where this happens the complexes containing triarylphosphine oxide ligands induce a Mn–OSO bond, characterised by ν(SO) at *ca.* 1265 cm^{-1}, which tends to activate the bound SO_2 to oxidation, whilst the complexes of trialkylphosphine oxides induce ligand-bound SO_2, ν(SO) *ca.* 1320 cm^{-1}, where the binding is weak and activation to oxidation does not occur.

Reaction of Manganese(II) *Chloride with* $Bu^n{}_3PO{\cdot}SO_2$.—We have seen that co-ordination of Mn to the O donor of OPR_3 does not prevent subsequent binding by SO_2, but would the opposite also prevail, *i.e.* will binding of SO_2 to OPR_3 subsequently block binding to the manganese?

To the neat liquid $Bu^n{}_3PO{\cdot}SO_2$ was added 0.5 mol equivalent of anhydrous $MnCl_2$ and after 7 d the pink salt was totally consumed to leave a pale green oil {*cf* the conventional synthesis of $[Mn(OPBu^n{}_3)_2Cl_2]$ in toluene appears complete after *ca.* 1 d}. The infrared spectrum of the product is identical to that of $[Mn\{O(SO_2)PBu^n{}_3\}_2Cl_2]$ [ν(PO) 1115, ν(SO) 1320, δ(SO) 524 cm^{-1}] prepared by exposure of $[Mn(OPBu^n{}_3)_2Cl_2]$ to SO_2. Whilst the lability of the co-ordinated SO_2 once again prevented accurate elemental analysis, nonetheless loss of the gas yields stable $[Mn(OPBu^n{}_3)_2Cl_2]$ [Found (Calc.): C, 51.5 (51.6); H, 9.9 (9.6); Cl, 12.7 (12.6)%].

Reactivity of Aluminium Trichloride with $[Mn(OPBu^n{}_3)_2Cl_2]$.—We have observed that the interaction between SO_2 and manganese(II) complexes of trialkylphosphine oxide is a finely balanced system. Could a stronger Lewis acid than SO_2, but of similar size, for example $AlCl_3$, yield a solid adduct?

The addition of 2 mol equivalents of $AlCl_3$ to a dichloromethane solution of $[Mn(OPBu^n{}_3)_2Cl_2]$ under anaerobic conditions gives an almost immediate milky pink suspension. No further change occurs after 2 d and filtration and concentration of the resultant filtrate quantitatively yields $Bu^n{}_3PO{\cdot}AlCl_3$ [Found (Calc.): C, 41.3 (41.0); H, 8.0 (7.7); Cl, 29.8 (30.3)%]. Work-up of the insoluble component in air gives $[Mn(H_2O)_4Cl_2]$ [Found (Calc.): Cl, 30.3 (30.3); Mn, 23.3 (23.5)%].

Clearly, aluminium trichloride is a more effective Lewis acid than is $MnCl_2$ and displaces the latter. Similar aluminium, gallium and boron adducts have been isolated by direct reaction with $OPPh_3$.[31] Comparisons of the ^{31}P NMR data for $Ph_3PO{\cdot}AlCl_3$ and $Bu^n{}_3PO{\cdot}AlCl_3$, Table 10, suggest similar aluminium environments. Greater upfield shifts for $Bu^n{}_3PO{\cdot}AlCl_3$ arise from the more basic nature of the ligand. The crystal structure of $Ph_3PO{\cdot}AlCl_3$ shows linear P–O–Al bonding, implying an sp-hybridised oxygen.[31] Such a change in the hybridisation of an isostructural $Bu^n{}_3PO{\cdot}AlCl_3$ adduct from the sp^2 configuration of oxygen in $[Mn(OPBu^n{}_3)_2Cl_2]$ would remove the second lone pair required for simultaneous co-ordination of manganese and $AlCl_3$.

Experimental

Reagents.—Hydrated manganese(II) salts (X = Cl, Br or NCS, Aldrich; X = I, Ross Chemicals) were dried according to published methods[32] down to Karl–Fischer water analysis <0.02%. The ligands $OPEt_3$, $OPPr^n{}_3$ (Strem Chemicals) and $OPBu^n{}_3$ (Fluka) were used as received.

Preparation of $[Mn(OPR_3)_2X_2]$ (R = Et, Pr^n *or* Bu^n; X = Cl, Br *or* I).—All the complexes were synthesised under strictly anaerobic and moisture-free conditions, since both the anhydrous manganese(II) salts and the trialkylphosphine oxide ligands are hygroscopic. The method is illustrated for $[Mn(OPEt_3)_2Cl_2]$. Manganese(II) chloride (1.10 g, 8.7 × 10^{-3} mol) was placed in a flame-dried round-bottomed flask (250 cm^3) fitted with a side-arm and a ground-glass tap. Triethylphosphine oxide (2.90 g, 17.5 × 10^{-3} mol) in freshly distilled toluene (100 cm^3) was added against a stream of dry argon. The flask was then evacuated and then the vacuum let down against a stream of dry argon. The flask was sealed and the slurry was briskly stirred for *ca.* 7 d. The complex was then isolated using standard Schlenk techniques. [When the product was an oil, the flask was transferred to an argon-filled dry-box. The product was then pipetted from the flask, washed with dry hexane (2 × 25 cm^3) and separated by the use of a small separating funnel.] The product was eventually dried *in vacuo* for *ca.* 24 h.

Preparation of $[Mn(OPR_3)_n(NCS)_2]$ R = Et *or* Bu^n; *n* = 1, 2 *or* 4).—These preparations were achieved in the same way as that described above, except that the ratio of reagents influences the stoichiometry of the product formed. An exact stoichiometric ratio of $Mn(NCS)_2$ and the trialkylphosphine oxide (either 1 : 1, 1 : 2 or 1 : 4) was employed to synthesise the mono, bis and tetrakis complexes, respectively.

The $R_3PO{\cdot}SO_2$ *Adducts.*—The trialkylphosphine oxide ligand (*ca.* 2.0 g) was placed in a round-bottomed flask (100 cm^3) equipped with a side-arm under dry argon. The argon was evacuated and an atmosphere of dry sulfur dioxide introduced. A rapid reaction occurred which led to a liquid product being formed. The flask was sealed until further use.

Reactions of the Manganese(II) *Complexes with Sulfur Dioxide in the Solid State.*—Complexes were exposed to SO_2 in the solid state under anaerobic conditions. The techniques and conditions used have been published.[6]

Elemental analyses were performed by the University of Manchester Institute of Science and Technology (UMIST) Microanalytical Service. Infrared spectra were obtained for Nujol mulls on KBr plates over the 4000–200 cm^{-1} range on a Perkin-Elmer 598 spectrometer. NMR spectra were obtained in 5 mm sealed tubes on a Bruker WP80 NMR spectrometer at 32.4 MHz, relative to concentrated phosphoric acid external standard.

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