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The Co-ordination of Small Molecules by Manganese(II) Phosphine Complexes. Part 1.† The Reversible Co-ordination of Dioxygen by [MnX$_2$(PR$_3$)] (X = Cl, Br, or I; R$_3$ = Bu$^n{}_3$ or PhBu$^n{}_2$) Complexes in Solution and an Infrared Criterion for predicting Dioxygen Binding Activity in the Di-isothiocyanato(phosphine)manganese(II) Complexes

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The reversible binding of dioxygen by the novel manganese(II) phosphine complexes [MnX$_2$(PR$_3$)] (X = Cl, Br, or I; R$_3$ = Bu$^n{}_3$ or PhBu$^n{}_2$) in solution in tetrahydrofuran (thf), toluene, and 1,2-dichloroethane has been studied. Quantitative absorption of dioxygen to form [MnX$_2$(PR$_3$)(O$_2$)] complexes is observed, and gas chromatographic methods have been used to measure desorption. Repeated cycling of dioxygen absorption has been shown to be possible, *e.g.* [MnI$_2$(PBu$^n{}_3$)] absorbed and desorbed dioxygen in thf at −20 °C more than 400 times without any complex deterioration. Colourless solutions of [MnX$_2$(PR$_3$)] become intensely coloured as [MnX$_2$(PR$_3$)(O$_2$)] forms, and changes in $\varepsilon_{\text{max.}}$ with p(O$_2$) employed allow construction of dioxygen binding curves. Using the Hill equation, equilibrium data have been deduced. Tentative conclusions have been drawn relating the nature of the phosphine, the halide, and the solvent to the ability of the [MnX$_2$(PR$_3$)] complexes to bind dioxygen. The solid-state dioxygen binding by bis(isothiocyanato)(phosphine)manganese(II) complexes [Mn(NCS)$_2$(PPh$_{3-n}$R$_n$)] (n = 0—3; R = alkyl) have been studied and only the [Mn(NCS)$_2$(PR$_3$)] compounds are found reversibly to bind dioxygen. The compounds are characterised by their different i.r. spectra [ν(CN)] and magnetic moments to those of the inactive compounds. The phosphine oxide complexes [Mn(NCS)$_2$(OPR$_3$)] (OPR$_3$ = OPPhMe$_2$, OPPr$^n{}_3$, or OPBu$^n{}_3$) have also been synthesised. Their i.r. and magnetic properties are similar to those of the inactive phosphine complexes and they do not bind dioxygen.

We recently reported [2–5] some preliminary data of our discovery of a novel series of manganese(II) complexes of tertiary phosphines, [MnX$_2$(PR$_3$)], which not only reversibly co-ordinate dioxygen under very mild conditions, but can also bind carbon monoxide,[6,7] carbon dioxide, nitric oxide,[8] sulphur dioxide,[9] ethylene,[10] and dihydrogen.

These complexes are easily synthesized but, as pointed out recently by Wilkinson and co-workers,[11] probably have a number of different structures in the solid state. This coincides with the fact that some of the [MnX$_2$(PR$_3$)] complexes are observed not to bind dioxygen, and some do in a 1 : 1 ratio to form [MnX$_2$(PR$_3$)(O$_2$)] both in the solid state and in solution. We have tentatively suggested that the dioxygen molecule is bound in a ' bent, end-on ' fashion, based on e.s.r. measurements,[5] but confirmation of this must await crystal structure determinations.

In this paper we report our observations of the reversible binding of dioxygen to some of these complexes. For ease of discussion, we separate the [MnX$_2$(PR$_3$)] (X = Cl, Br, or I) from the [Mn(NCS)$_2$(PR$_3$)] complexes.

Results and Discussion

(1) *Complexes of Manganese*(II) *Halides.*—Although we have extensively studied the reversible co-ordination of dioxygen to a large number of [MnX$_2$(PR$_3$)] species (R$_3$ = trialkyl, phenyldialkyl, diphenylalkyl; X = Cl, Br, or I), in this paper we report the solution properties of a few of these complexes, Table 1. These complexes are easily prepared by the reaction of anhydrous manganese(II) halides with phosphines in a 1 : 1 molar ratio in anhydrous solvents in an inert atmosphere. Complete preparative details have been published.[1,‡] Once isolated, the complexes can be stored indefinitely under dry, inert conditions.

Dioxygen Uptake Measurements.—The apparatus and method used to study the uptake of dioxygen and its subsequent release are fully described in the Experimental section (essentially a gas burette, gas reservoir, and uptake flask immersed in a constant-temperature bath). Those parts of the apparatus through which gas passed which were not immersed in the constant-temperature bath were kept to a minimum and were fully lagged. In order to ensure that studies were performed on real solutions in tetrahydrofuran (thf), light scattering measurements were made to determine optimum concentrations; for toluene and 1,2-dichloroethane a saturated solution was made, filtered three times by Schlenk techniques and then analyzed by atomic absorption for manganese concentrations.

Dioxygen uptake by the solvent blanks were determined. For example, 100 cm^3 of thf was found to absorb 5.2×10^{-4}

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† Taken as Part 8 of the Co-ordination Chemistry of Manganese.[1]
Non-S.I. units employed: Torr = (101 325/760) Pa; B.M. = 9.27×10^{-24} J T^{-1}.

‡ A referee has requested that we comment on the controversy generated by Green and co-workers.[12] The approach to the synthesis of these simple [MnX$_2$(PR$_3$)] complexes taken by Green and co-workers differs significantly from our own, and the conditions employed by them almost certainly would give rise to the oxidized products they describe. Almost all of their observations [colour changes, production of ν(P=O) bands in the i.r. spectrum] on manganese(III)–phosphine oxide complexes had previously been reported by us [13–16] in papers not cited by Green and co-workers.[12] A full response to the findings of Green has now been published.[6] Although Green has argued strongly that the [MnX$_2$(PR$_3$)] complexes do not exist, Wilkinson and co-workers [11] have recently published the *X*-ray crystal structure of the dimeric complex [{Mn(CH$_2$SiMe$_3$)$_2$(PMe$_3$)}$_2$] and Worley *et al.*[17] have isolated [MnBr$_2$(PPhMe$_2$)].

Table 1. Analytical data (%)[a] for the manganese(II) complexes

Complex	C	H	X[b]	P	Mn
$[MnCl_2(PBu^n_3)]$	43.8	8.2	22.0	9.7	16.9
	(43.9)	(8.2)	(21.7)	(9.5)	(16.8)
$[MnBr_2(PBu^n_3)]$	34.5	6.5	38.5	7.4	13.1
	(34.6)	(6.5)	(38.4)	(7.4)	(13.3)
$[MnI_2(PBu^n_3)]$	28.4	5.4	49.4	6.6	10.9
	(28.2)	(5.3)	(49.7)	(6.1)	(10.8)
$[MnCl_2(PPhBu^n_2)]$	48.3	6.6	20.4	8.9	15.8
	(48.0)	(6.4)	(20.6)	(8.3)	(16.0)
$[MnBr_2(PPhBu^n_2)]$	38.5	5.3	36.6	7.1	12.4
	(38.8)	(5.2)	(37.0)	(6.9)	(12.3)
$[MnI_2(PPhBu^n_2)]$	31.6	4.3	5.8	5.8	10.4
	(32.0)	(4.4)	(5.7)	(5.7)	(10.4)
$[Mn(NCS)_2(PMe_3)]$	23.8	3.7	11.2	12.4	
	(24.3)	(3.6)	(11.3)	(12.5)	
$[Mn(NCS)_2(PEt_3)]$	32.9	5.2	9.7	10.6	
	(33.2)	(5.2)	(9.7)	(10.7)	
$[Mn(NCS)_2(PPr^n_3)]$	39.9	6.2	8.6	9.6	
	(39.9)	(6.3)	(8.5)	(9.3)	
$[Mn(NCS)_2(PBu^n_3)]$	45.1	7.3	7.4	8.0	
	(45.0)	(7.2)	(7.5)	(8.3)	
$[Mn(NCS)_2(PPhMe_2)]$	38.8	3.8	3.9	10.3	
	(38.8)	(3.6)	(9.1)	(10.0)	
$[Mn(NCS)_2(PPhEt_2)]$	42.4	4.9	7.7	8.8	
	(42.7)	(4.9)	(8.3)	(9.2)	

Complex	C	H	X[b]	P
$[Mn(NCS)_2(PPhPr^n_2)]$	45.4	5.2	7.3	8.4
	(46.0)	(5.2)	(7.6)	(8.5)
$[Mn(NCS)_2(PPhBu^n_2)]$	49.1	5.2	7.2	7.4
	(48.8)	(5.8)	(7.1)	(7.8)
$[Mn(NCS)_2(PPh_2Me)]$	48.8	3.2	7.5	7.9
	(48.5)	(3.2)	(7.5)	(8.3)
$[Mn(NCS)_2(PMe_3)(O_2)]$	21.7	3.4	9.9	11.0
	(21.5)	(3.2)	(10.0)	(11.1)
$[Mn(NCS)_2(PEt_3)(O_2)]$	29.8	4.9	8.9	9.4
	(29.9)	(4.7)	(8.9)	(9.3)
$[Mn(NCS)_2(PPr^n_3)(O_2)]$	36.5	5.6	7.9	8.4
	(36.4)	(5.8)	(7.7)	(8.5)
$[Mn(NCS)_2(PBu^n_3)(O_2)]$	41.3	6.6	7.0	7.5
	(41.5)	(6.7)	(6.9)	(7.6)
$[Mn(NCS)_2(PPh_3)]$	55.3	3.7	6.8	7.3
	(55.3)	(3.5)	(6.5)	(7.1)
$[Mn(NCS)_2(OPPr^n_3)]$	38.2	6.1	8.3	8.8
	(38.3)	(6.1)	(8.1)	(8.9)
$[Mn(NCS)_2(OPBu^n_3)]$	43.4	7.0	7.4	7.9
	(43.1)	(6.9)	(7.2)	(8.0)
$[Mn(NCS)_2(OPPhMe_2)]$	46.5	3.1	7.2	7.8
	(46.4)	(3.3)	(7.2)	(8.0)

[a] Calculated values are in parentheses. [b] X = Halogen or nitrogen.

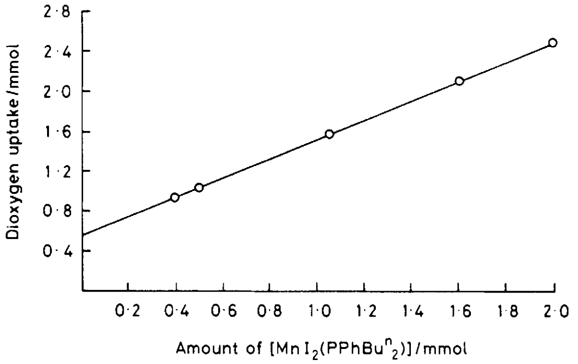

Figure 1. Dioxygen uptake as a function of $[MnI_2(PPhBu^n_2)]$ concentration in 100 cm^3 thf at 0 °C

mol of dioxygen under the conditions we employed at 0 °C. All of the complexes $[MnX_2(PR_3)]$ (X = Cl, Br, or I; R_3 = Bu^n_3 or $PhBu^n_2$) take up 100 mol % dioxygen in thf and toluene and form the coloured $[MnX_2(PR_3)(O_2)]$ species. For example, at 0 °C, 3.8×10^{-3} mol $[MnI_2(PBu^n_3)]$ in 100 cm^3 thf absorbed 97 cm^3 of dioxygen, equivalent to 85 cm^3 by the complex and 12 cm^3 by the solvent (blank). The reaction (i)

$$[MnX_2(PR_3)] + O_2 \rightleftharpoons [MnX_2(PR_3)(O_2)] \qquad \text{(i)}$$

may be reversed by lowering the pressure above the oxygenated solution or by warming to room temperature.

That the $[MnX_2(PR_3)]$ complexes do bind dioxygen in thf solution is further shown by plots of dioxygen absorbed against complex concentration, Figure 1 and Table 2. The slopes of all these plots are 0.94—0.98, indicative of a 1 : 1 complex, $[MnX_2(PR_3)(O_2)]$, in solution. The values of the intercepts, (5.2—5.3) $\times 10^{-4}$ mol dioxygen is equivalent to that amount of dioxygen which a blank of 100 cm^3 thf absorbs under the same conditions and coincides with our independent measurements.

Table 2. Data from the plots of dioxygen uptake at 0 °C as a function of complex concentration (see Figure 1)

Complex	Slope	Intercept (10^{-4} mol)
$[MnCl_2(PBu^n_3)]$	0.94	5.3
$[MnBr_2(PBu^n_3)]$	0.96	5.2
$[MnI_2(PBu^n_3)]$	0.98	5.2
$[MnCl_2(PPhBu^n_2)]$	0.98	5.2
$[MnBr_2(PPhBu^n_2)]$	0.96	5.3
$[MnI_2(PPhBu^n_2)]$	0.96	5.2

Recycling (100 mol % uptake, successively) and stability of the complexes in solution were followed by accurate successive gas burette measurements and the examination of the electronic spectrum associated with each complex on completion of uptake. We have observed quantitative dioxygen cycling in great detail for the complex $[MnI_2(PBu^n_3)]$ in thf: more than five cycles at $p(O_2)$ = 760 Torr at −20 °C, whilst only two cycles are possible at $p(O_2)$ = 760 Torr at 0 °C, and more than 400 cycles are possible at $p(O_2)$ = 150 Torr at −20 °C.

Observations on storage of the oxygenated complexes in thf again indicated that the stability of the $[MnX_2(PR_3)(O_2)]$ species is sensitive to $p(O_2)$ above the solution and the temperature. For example, it was possible to store $[MnI_2(PBu^n_3)(O_2)]$ for 24 h under $p(O_2)$ = 100 Torr at −20 °C with no detectable deterioration of the oxygenated species, whilst under the same $p(O_2)$ but at 0 °C a similar solution of $[MnI_2(PBu^n_3)(O_2)]$ began to deteriorate perceptibly after only 6 h. Similar observations of the chloro- and bromo-complexes suggest slightly more stability than for the iodo-species. We have evidence that the major decomposition product of $[MnI_2(PBu^n_3)(O_2)]$ is $[MnI_2(OPBu^n_3)]$. After removing the thf solvent from an inactive (' deteriorated ') system, the bluish white oil remaining was washed with dry toluene to yield a white-yellow solid, the elemental analyses of which closely correspond to $[MnI_2(OPBu^n_3)]$ [Found: C, 27.2; H, 5.3; I, 47.9; Mn, 10.6; O (by difference), 2.9; P, 6.1.

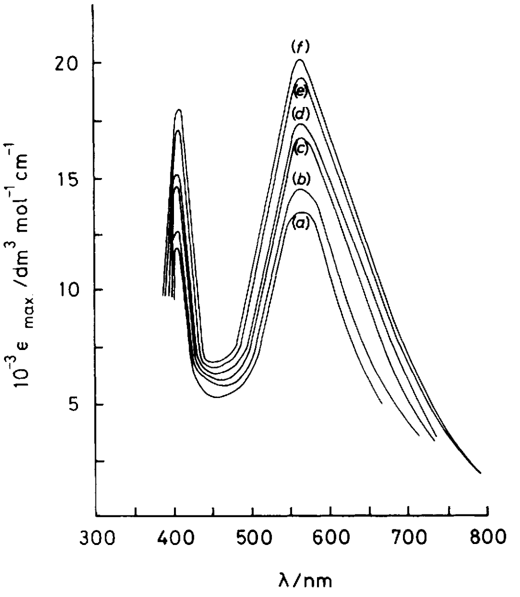

Figure 2. Variation of the electronic spectrum of [$MnBr_2(PBu^n_3)$] in toluene with dioxygen partial pressure at 20 °C: $p(O_2)$ = 10 (*a*), 20 (*b*), 50 (*c*), 70 (*d*), 100 (*e*), and 150 Torr (*f*)

Calc. for $C_{12}H_{27}I_2MnOP$: C, 27.2; H, 5.1; I, 48.1; Mn, 10.6; O, 3.0; P, 5.9%]. The i.r. spectrum exhibits a strong absorption at 1 150 cm^{-1}, assignable to ν(P=O), which is absent in the i.r. spectrum of [$MnI_2(PBu^n_3)$], and is shifted approximately 25 cm^{-1} from the value recorded for ν(P=O) in free PBu^n_3O. We can tentatively assign a band at 296 cm^{-1} to ν(Mn–O), which is absent in [$MnI_2(PBu^n_3)$]. On heating the white-yellow solid *in vacuo* to *ca.* 180 °C a white, waxy sublimate was obtained, which proved to be PBu^n_3O (by elemental analysis and i.r. spectrum).

Electronic Spectral Measurements.—Upon contact with dioxygen, colourless solutions of [$MnX_2(PR_3)$] begin to colour intensely as [$MnX_2(PR_3)(O_2)$] forms. (There is a *linear relationship* between the magnitude of the absorption coefficient and the degree of dioxygenation for *all* complexes we have studied, *i.e.* the intense colour is due to the [$MnX_2(PR_3)(O_2)$] complex and is not due to the presence of any other coloured species.) These colours essentially reflect the nature of the halide ion and not the phosphine: *i.e.*, the chloro-complexes are purple and exhibit band maxima at 395 and 530 nm, the bromo-complexes are blue and exhibit band maxima at 414 and 570 nm, and the iodo-complexes are green or green-brown and exhibit band maxima at 455 and 620 nm. The spectral profiles (band maxima) of any particular complex are solvent independent, but the absorption coefficients do vary with solvent, being largest in non-co-ordinating solvents.

Solution Isotherms (Dioxygen Binding Curves).—The formation of the [$MnX_2(PR_3)(O_2)$] complex is a function of $p(O_2)$, and this may be followed spectrophotometrically. The percentage saturation of the [$MnX_2(PR_3)$] complex was calculated from the ratio of the absorption intensity at $\lambda_{max.}$ at any $p(O_2)$ relative to that at 100% saturation, which was in turn judged by the constancy of the spectrum upon further increase in $p(O_2)$; typically this equilibrium was reached in 20—30 s. The band maxima followed were 530 nm (chlorides), 570 nm (bromides), and 455 nm (iodides). The data given below emerged from the isotherms constructed from graphs of the variation of the electronic spectrum with $p(O_2)$, see Figure 2.

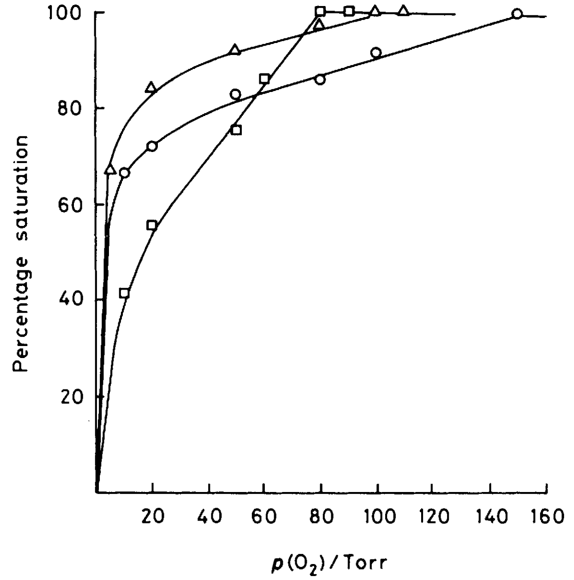

Figure 3. Solution isotherms for [$MnBr_2(PBu^n_3)$] at 20 °C: in 1,2-dichloroethane (△), toluene (○), and thf (□)

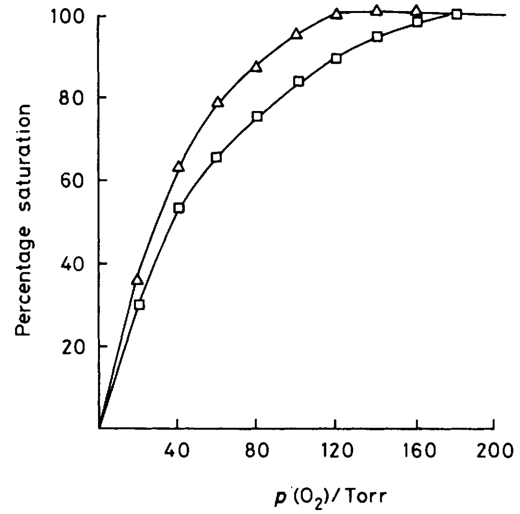

Figure 4. Solution isotherms for [$MnX_2(PPhBu^n_2)$] in 1,2-dichloroethane: X = Cl (△) and Br (□)

Isotherms constructed by this method for [$MnBr_2(PBu^n_3)$] in three solvents are shown in Figure 3, from which it can be seen that the position and shape of the curves in the non-co-ordinating solvents toluene and 1,2-dichloroethane are hyperbolic. It is seen that the isotherm moves to the right for [$MnBr_2(PBu^n_3)$] in thf; the affinity of [$MnBr_2(PBu^n_3)$] for dioxygen thus varies with solvent. Another variation we observe is that, in general, for the same solvent and for the same manganese-bound phosphine, affinity for dioxygen varies with halide, in the order Cl > Br > I. This is illustrated for the complexes [$MnX_2(PPhBu^n_2)$] (X = Cl or Br) in Figure 4. The isotherm for [$MnI_2(PBu^n_3)$] in thf is shown in Figure 5 and equilibrium data derived are listed in Table 3.

On the other hand, for a constant halide and solvent the isotherm moves to the right as the phosphine changes from

Table 3. Equilibrium data for dioxygen uptake by the manganese(II) complexes

Complex	Solvent	Temperature/°C	log (K/Torr^{-1})	$10^2K_{O_2}$/Torr^{-1}	$P_{\frac{1}{2}}(O_2)$/Torr	Slope
$[MnBr_2(PBu^n_3)]$	thf	20	−1.32	4.79	20.9	1.1
	Toluene	20	−0.43	37.24	2.7	0.7
	$ClCH_2CH_2Cl$	20	−0.42	38.2	2.6	0.9
$[MnI_2(PBu^n_3)]$	thf	−40	−1.47	3.37	29.7	1.8
$[MnCl_2(PPhBu^n_2)]$	Toluene	20	−2.22	0.60	165.6	1.2
	$ClCH_2CH_2Cl$	20	−2.25	0.56	179.5	1.2
$[MnBr_2(PPhBu^n_2)]$	Toluene	20	−2.30	0.50	199.5	1.3

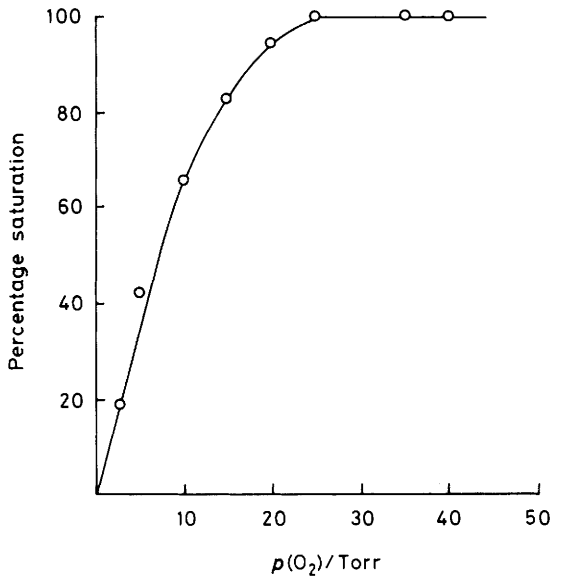

Figure 5. Solution isotherm for $[MnI_2(PBu^n_3)]$ in thf at −40 °C

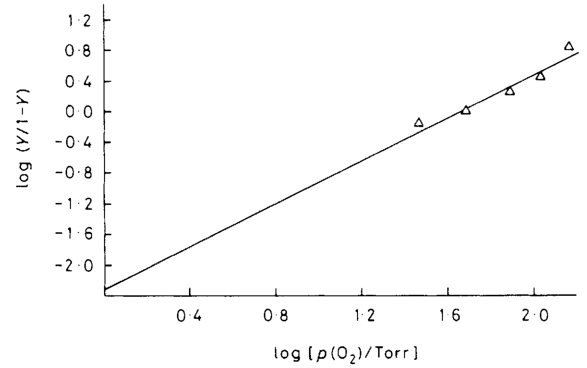

Figure 6. Hill plot for $[MnBr_2(PPhBu^n_2)]$ in toluene at 20 °C

alkyl (R) to phenyl: thus dioxygen affinity increases in the order $PR_3 > PPhR_2 > PPh_2R > PPh_3$ (no affinity). This is partly illustrated in Table 3 for the complexes $[MnBr_2(PBu^n_3)]$ and $[MnBr_2(PPhBu^n_2)]$ in toluene; $P_{\frac{1}{2}}(O_2)$ values [the $p(O_2)$ at which 50% of the manganese sites are dioxygenated] for these complexes are 2.7 and 199.5 Torr, respectively.

Equilibrium Constants for Binding of Dioxygen.—The equilibrium constants for binding of dioxygen by the manganese complexes, K_{O_2}, equation (ii), were calculated from the isotherms using the Hill equation [equation (iii)] where Y is

$$[MnX_2(PR_3)] + O_2 \overset{K_{O_2}}{\rightleftharpoons} [MnX_2(PR_3)(O_2)] \qquad \text{(ii)}$$

$$\frac{Y}{1-Y} = \frac{[MnX_2(PR_3)(O_2)]}{[MnX_2(PR_3)]} = K_{O_2}\,.\,p(O_2)^n = [P_{\frac{1}{2}}(O_2)]^{-1}\,.\,p(O_2)^n \qquad \text{(iii)}$$

the fraction of the dioxygenated sites, K_{O_2} is the equilibrium constant for the reaction, and $P_{\frac{1}{2}}(O_2)$ is the partial pressure at half-oxygenation, *i.e.* $p(O_2)$ at which 50% of the sites are oxygenated.

A plot of log ($Y/1 - Y$) *versus* log $p(O_2)$ is the Hill plot, and yields a line of slope n, the Hill coefficient. The values of log K_{O_2} are obtained from the intercept of the best straight line. A Hill plot for $[MnBr_2(PPhBu^n_2)]$ in toluene is shown in Figure 6. The equilibrium data, log K_{O_2}, K_{O_2}, $P_{\frac{1}{2}}(O_2)$, and the slopes of the Hill plots are listed in Table 3.

(2) *Complexes of Manganese*(II) *Thiocyanate.*—The complexes studied are listed in Table 1. In the solid state, reactions with dioxygen were observed only for the complexes $[Mn(NCS)_2(PR_3)]$ (R = Me, Et, Pr^n, or Bu^n), whereas the complexes $[Mn(NCS)_2(PPhR_2)]$ (R = Me, Et, Pr^n, or Bu^n) and $[Mn(NCS)_2(PPh_2Me)]$ show no ability to form $[Mn(NCS)_2(phosphine)(O_2)]$ adducts. No reaction of dioxygen with the complexes $[Mn(NCS)_2(OPR_3)]$ was observed. It is predicted [18] that all complexes of metals with a $^6A_1$ ground term show magnetic moments very close to the spin-only value of 5.92 B.M. We have obtained room-temperature magnetic moments and these are listed in Table 4. As can be seen, they fall into two distinct classes: the $[Mn(NCS)_2(PR_3)]$ complexes exhibit $\mu_{eff.}$ *ca.* 6.0 B.M., whereas those containing phenyl-substituted phosphines or phosphine oxides exhibit moments in the range 5.2—5.4 B.M. These latter low values suggest a considerable degree of spin pairing in these complexes.

The magnetic susceptibility data and the i.r. data to a certain extent complement one another. The mull i.r. spectra relating to the NCS^- group are listed in Table 4. The i.r. spectra of this ambidentate group have been well studied and some useful, although by no means absolutely convincing correlations between complex structure and ν(CN) and ν(CS) band energies have been made.[19-21] It is clear from the results in Table 4 and Figure 7 (which shows spectral profiles typical of the two types of complex) that there is an abrupt rise of some 30—40 cm^{-1} in the high-energy ν(CN) band in going from the complexes with PR_3 groups to those with $PPhR_2$, PPh_2R, or OPR_3 groups. It is unwise to speculate too much about how the NCS^- groups are bound in these complexes, but it is undoubtedly significant that the $[Mn(NCS)_2(PPh_{3-n}R_n)]$ complexes and the phosphine oxide complexes all exhibit a very high-energy absorption at *ca.* 2 130—2 140 cm^{-1} and, generally, bands at 2 100 and 2 080 cm^{-1}, whilst the profile and band energies of the spectra of the $[Mn(NCS)_2(PR_3)]$ complexes are quite different.

We thus observe in this study not only a structure/reactivity relationship ‘ fine-tuned ’ by the presence or absence of phenyl groups in the phosphine ligand, but, in addition, there appears to be an i.r. criterion to indicate whether a [Mn-

Table 4. I.r. data for $[Mn(NCS)_2L]$ complexes

Complex	ν(CN)/cm^{-1}				ν(P=O)/cm^{-1}	$\mu_{eff.}$/B.M.
$[Mn(NCS)_2(PMe_3)]$	2 100	2 080	2 040		770	5.7
$[Mn(NCS)_2(PEt_3)]$	2 115	2 100	2 080		768	5.9
$[Mn(NCS)_2(PPr^n_3)]$	2 108	2 085			775	6.0
$[Mn(NCS)_2(PBu^n_3)]$	2 100	2 085			775	6.0
$[Mn(NCS)_2(PPhMe_2)]$	2 130	2 100	2 080		780	5.4
$[Mn(NCS)_2(PPhEt_2)]$	2 140	2 100	2 085		775	5.4
$[Mn(NCS)_2(PPhPr^n_2)]$	2 130	2 100	2 080	2 060	780	5.4
$[Mn(NCS)_2(PPhBu^n_2)]$	2 130	2 100	2 080		790	5.3
$[Mn(NCS)_2(PPh_2Me)]$	2 140	2 100	2 080		780	5.3
$[Mn(NCS)_2(PMe_3)(O_2)]$	2 100	2 080	2 040		770	6.8
$[Mn(NCS)_2(PEt_3)(O_2)]$	2 115	2 100	2 080		768	6.8
$[Mn(NCS)_2(PPr^n_3)(O_2)]$	2 108	2 085			775	6.8
$[Mn(NCS)_2(PBu^n_3)(O_2)]$	2 100	2 085			775	6.9
$[Mn(NCS)_2(PPh_3)]$	2 140				790	5.3
$[Mn(NCS)_2(OPPr^n_3)]$ [a]	2 140	2 100			780	5.2
$[Mn(NCS)_2(OPBu^n_3)]$ [a]	2 140	2 100			780	5.2
$[Mn(NCS)_2(OPPhMe_2)]$ [b]	2 130	2 100	2 080		780	5.3

[a] ν(P=O) at 1 145 cm^{-1}. [b] ν(P=O) at 1 160 cm^{-1}.

Table 5. Gas chromatographic analysis of desorbed dioxygen

Total uptake (cm^3)	Complex uptake (cm^3)	Percentage saturation	Total peak	Complex peak	Percentage desorption
82.7	70.8	98.7	43.8	37.5	97.0
39.4	27.5	38.4	22.4	16.1	29.6
26.4	14.4	20.1	11.3	5.0	9.2
19.2	7.3	10.2	8.1	1.8	3.3
11.9	0	0	6.3	0	0

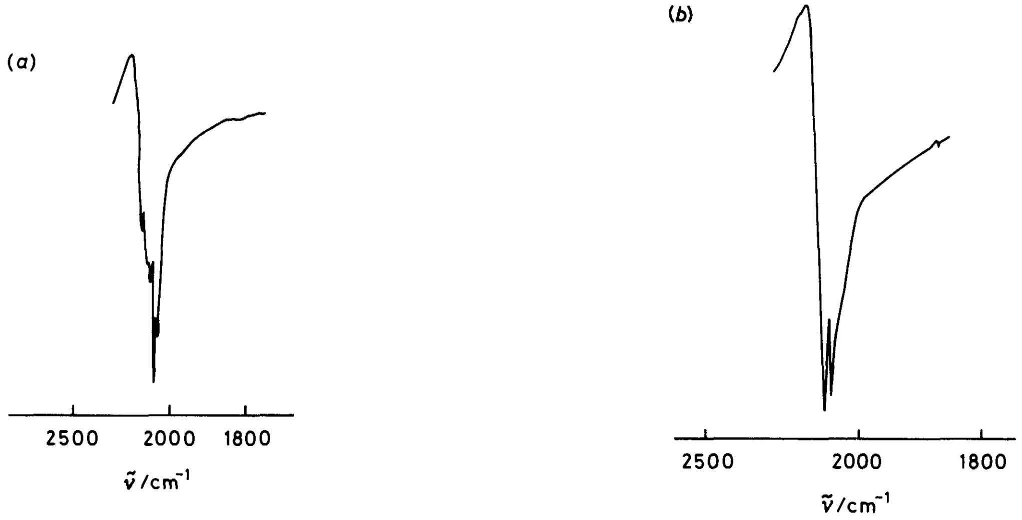

Figure 7. I.r. spectra of $[Mn(NCS)_2(PPhPr^n_2)]$ (*a*) and $[Mn(NCS)_2(PPr^n_3)]$ (*b*)

$(NCS)_2L]$ complex will be dioxygen-transport active, namely the presence of a band in the i.r. spectrum of the complex at 2 130—2 140 cm^{-1} indicates no activity.

Further essential differences between the dioxygen-active and the non-active complexes are currently being demonstrated by *X*-ray powder diffraction measurements. These indicate that $[Mn(NCS)_2(PR_3)]$ (R = Pr^n or Bu^n) are isomorphous and have patterns quite different from their OPR_3, $PPhR_2$, and PPh_2R counterparts.

Upon exposure to dry dioxygen or dry air, the colour of the active complexes changes to deep red-pink almost instantaneously. This initial reaction is on the surface only and the rate at which further dioxygenation takes place depends upon the surface area exposed. For a tightly packed material, for example, when magnetic susceptibility measurements are made by the Gouy method, 1.0 g of $[Mn(NCS)_2(PPr^n_3)]$ ($M = 331$) tightly packed in the Gouy tube and allowed to stand in dry dioxygen slowly gains weight for *ca.* 24 h until the weight reaches 1.09 g, corresponding to $[Mn(NCS)_2(PPr^n_3)(O_2)]$ ($M = 363$). No further weight gain occurs.

We have investigated the $[Mn(NCS)_2$(phosphine)] complexes and their dioxygen adducts in the solid state because we hoped that the i.r. spectra of the NCS^- group would prove to be a more revealing probe than the bands due to halide

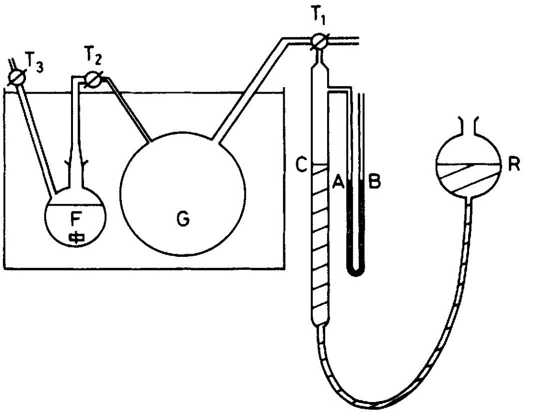

Figure 8. Thermostatted apparatus for dioxygen uptake measurements on the manganese(II) complexes using a gas burette

linkages, which are much more difficult to assign. To a certain extent we have been successful in being able to see distinct differences in ν(CN) for the dioxygen-active and -inactive complexes. However, we must admit that the i.r. spectra of the $[Mn(NCS)_2(PR_3)]$ and the $[Mn(NCS)_2(PR_3)(O_2)]$ complexes are almost identical; we observe no bands assignable to $Mn-O_2$ interactions, although we realise that few metal–dioxygen vibrational spectra have been published for systems which facilely bind dioxygen.

Experimental

Complex Preparation.—Absolutely crucial to the preparation of the manganese(II) phosphine complexes is the use of strictly anhydrous solvents and manganese(II) salts, the reaction of the MnX_2 and phosphine in a 1 : 1 ratio, and the employment of dioxygen-free atmospheres. The methods have been published in detail [1] and will not be repeated here. Yields were quantitative.

Measurement of Dioxygen Uptake.—The essential features of the apparatus employed are illustrated in Figure 8. The flask containing the solution under study and the large gas reservoir bulb (G) were maintained at the same temperature by means of a large cooling bath. The remainder of the apparatus consisted of a standard gas burette fitted with a three-way tap (T_1). A typical experiment is described below.

The flask (F) was flame dried *in vacuo* and, upon cooling, was charged with 100 cm³ of the solution of $[MnX_2L]$ (L = phosphine) to be studied. It was then placed in the bath and connected to the rest of the apparatus *via* tap joint T_2. The gas reservoir G was then evacuated *via* T_1 and the inert gas above the solution was removed *via* T_3; tap T_2 was kept closed throughout this procedure. Dioxygen was then introduced into reservoir G and into the gas burette *via* T_1. The apparatus was usually filled to a pressure of approximately 1.1×10^5 Pa at 20 °C. Upon cooling the gas contracted and the mercury levels A and B changed. Thermal equilibrium was attained when no further gaseous contraction occurred, *i.e.* when A and B gave a steady reading of the pressure in the apparatus (usually 20—30 min). Once thermal equilibrium was attained, the uptake could be performed. Tap T_2 was opened and the mercury in A and B adjusted by means of the reservoir R until they were level and the initial reading on the burette was taken from level C. Under the conditions employed, dioxygen absorption was complete after 5—10 min depending on stirrer speed and the nature of the complex.

A typical experiment using 3.2×10^{-3} mol of $[MnI_2(PBu^n_3)]$ in 100 cm³ thf (*i.e.* 3.2×10^{-2} mol dm^{-3}) resulted in the absorption of 82.7 cm³ dioxygen at −20 °C over *ca.* 6 min; no further dioxygen absorption occurred. The blank thf (100 cm³) absorbed 11.9 cm³ of dioxygen under identical conditions, resulting in 70.8 cm³ O_2 being attributable to the reaction $[MnI_2(PBu^n_3)] + O_2 \longrightarrow [MnI_2(PBu^n_3)(O_2)]$. The 70.8 cm³ O_2 is equivalent to 98.7% of the theoretical 1 : 1 absorption.

On removal of the flask F from the bath (tap T_1 closed) desorption could be examined. On warming the deeply green-purple solution to room temperature under vacuum the dioxygen rapidly desorbed from solution and the vivid colour completely disappeared. Any thf vapour leaving the flask was trapped out and fresh thf was added to the flask periodically to maintain the concentration of the solution. We have been able to follow this desorption quantitatively by g.c. methods.

Several solutions of $[MnI_2(PBu^n_3)]$ were allowed to absorb dioxygen to give various percentage saturations (0, 10, 20, 38, and 100) at −20 °C. A vacuum was applied to the flask and it was allowed to warm to room temperature. The 'dead space' in the flask and attachments was then returned to atmospheric pressure by the introduction of dinitrogen. The resultant gas mixture was then analyzed by g.c. and the percentage composition $N_2 : O_2$ determined. By knowing the 'dead space' volume and the percentage O_2 in the gas mixture it is a simple matter to determine the volume of O_2 evolved from the solution in the desorption cycle. The results are listed in Table 4. A typical calculation is as follows: total dead space = 184 cm³; we have 37.5% O_2 in 184 cm³ of an $O_2 : N_2$ sample, therefore release from solution = (37.5/100) × 184 = = 69.0 cm³.

This represents 97% of the dioxygen taken up. Within experimental error, these observations may be taken to represent quantitative 1 : 1 dioxygen : manganese and desorption and mirror the mass spectral results obtained by Barber *et al.*[3]

Molecular Weight Measurements.—We have been unable to obtain reliable molecular weight data on the deoxygenated complexes, even though e.s.r. measurements in thf are consistent with a monomeric $[MnX_2(PR_3)(thf)]$ formulation.[5] The problem is the insolubility of the complexes in solvents suitable for our vapour phase osmometry. However, Dr. Hill (Auburn University) has recently obtained molecular weight measurements on $[MnI_2(PBu^n_3)]$ in thf using a Chromatix KM-16 laser differential refractometer. The result, 546, indicates a monomeric formulation {calc. for $[MnI_2(PBu^n_3)]$, 511}, and this method does not reflect any co-ordinated thf, since this is probably rapidly exchanging with free thf at room temperature.[22]

Conductivity Measurements.—These were made on 10^{-3}—10^{-4} mol dm^{-3} solutions of the oxygenated and deoxygenated complexes in thf and toluene employing a Cambridge Instruments Ltd conductivity bridge. All species are non-conducting in these solvents.

Solution Isotherm Measurements at 20 °C.—A u.v. gas cell (*i.e.* a cell with a bulb stopper and a side-inlet), together with a syringe which was used to transfer the sample, were dried in the oven at 130 °C, filled with dry argon, and transferred to a glove-box filled with argon. A sample of the solution of the complex under investigation was syringed out from the deoxygenated mother solution (which was stored in a 250 cm³ flask in the glove-box) and put into the gas cell while in the glove-box. After obtaining the spectrum of the deoxygenated solution, the gas cell was connected to the vacuum line and evacuated by opening and closing the cell's side-inlet five times

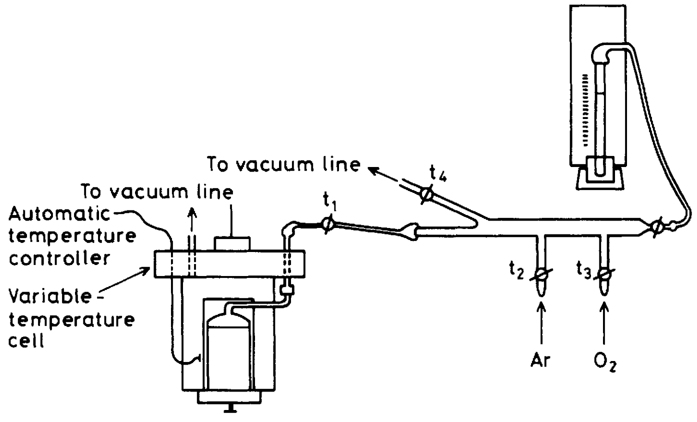

Figure 9. Apparatus used for the electronic spectral measurements at low temperatures

very quickly. Dry dioxygen was admitted to the vacuum line, the pressure being measured with a line manometer, and the pressure made up to atmospheric with dry argon. The gas mixture was then introduced into the cell and the cell inlet kept open for 10 min to ensure that the required $p(O_2)$ was obtained inside the gas cell. After that, the cell was disconnected from the vacuum line and shaken for 5 min before being placed in the spectrophotometer. After the spectrum had been obtained the cell was removed from the spectrophotometer, cleaned, dried and filled with argon and transferred to the glove-box to take a fresh sample for another pressure of dioxygen. 100% Saturation was judged by the constancy of the spectra upon further increases in $p(O_2)$. Care was taken to ensure that no solvent was removed from the sample during the gas evacuation from the cell. Removal of the solvent would increase the concentration of the complex and lead to an error in the calculation of $\varepsilon_{max.}$.

Low-temperature Measurements.—A specially built vacuum system (Figure 9) was connected to the variable-temperature cell of the spectrophotometer in order to follow the change in the spectra of the solutions with different partial pressures of oxygen. A specially built u.v. cell was cleaned, dried, and loaded as previously described. The cell was then placed inside the variable-temperature device and maintained at the required temperature. The inert gas above the solution was removed by turning tap t_1 to the vacuum. The cell was left for 15 min to equilibrate at the required temperature. After this time tap t_4 was closed and an oxygen–argon mixture was introduced into the vacuum line. Tap t_1 was then opened to introduce the gas mixture into the cell. After each spectrum at a given partial pressure had been recorded, the cell was evacuated and the spectrum rerun to ensure the solution was completely deoxygenated before a new partial pressure of oxygen was introduced into the cell.

Light Scattering Measurements.—These were made in order to ensure that the solutions being studied could be considered as ' real '. The turbidities of solutions of the complexes were determined in a Brice-Phoenix Light Scattering Photometer. A cylindrical light scattering cell was dried by the usual procedure and put into the glove-box where it was filled with deoxygenated sample and its inlet closed tightly with a piece of nylon and a rubber band. The photometer was checked by a water standard, then the cell containing the solution was shaken and placed into the photometer and the measurement performed quickly, for two reasons: (1) to measure the turbidity before the undissolved solid (if any) precipitated to the bottom of the cell and (2) to avoid any possibility of air diffusion into the cell which would lead to oxgenation of the complex. Turbidity of every sample was measured at least four times and an average value was obtained. The method of calculation was described in the instruction manual for the photometer.

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