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THE COORDINATION OF DIOXYGEN AND OTHER SMALL MOLECULES BY MANGANESE(II) PHOSPHINE COMPLEXES

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Summary

The synthesis and structures of the Mn(phosphine)X_2 (X = Cl, Br, I, NCS) complexes are described. Their reactivity towards molecular oxygen:

$$\text{Mn(phosphine)}X_2 + O_2 \rightleftharpoons \text{Mn(phosphine)}X_2(O_2)$$

in both the solid state and in solution in a number of organic solvents (toluene, tetrahydrofuran, 1,2-dichloroethane) is discussed; equilibrium data for reactions in THF show, for example, that the affinity for dioxygen decreases in the order $X = Cl > Br > I$ and phosphine = trialkyl > phenyldialkyl > diphenylalkyl ≫ triphenyl. An empirical relation between K_{O_2} and θ, the cone angle of the phosphine, has been developed. Other small molecules are capable of being bound reversibly (ethylene, carbon monoxide, nitric oxide) or irreversibly (sulphur dioxide, carbon disulphide, tetracyanoethylene). The use of these complexes in gas separations (dioxygen from air, carbon monoxide from CO/H_2 mixtures) is described.

Introduction

Dioxygen interactions with metal complexes

In addition to binding nitric oxide, a number of manganese complexes have been shown to function as dioxygen carriers [1, 2]. A dioxygen carrier can be defined as a metal complex which absorbs molecular oxygen (dioxygen) without either the metal (M) or the ligand (L) being irreversibly oxidised and will, under appropriate conditions, release the absorbed dioxygen to yield the metal complex (eqn. 1):

$$M(L)_n + O_2 \rightleftharpoons [M(L)_n(O_2)] \qquad (1)$$

In practice, the reverse reaction can be initiated by lowering the partial pressure of O_2, heating the adduct or by the addition of a ligand capable of replacing bound dioxygen.

Several other metals apart from manganese have been identified as dioxygen carriers including iron [2 - 4], cobalt [2, 5], chromium [6], nickel

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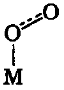
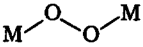
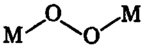
TABLE 1

Comparison of O—O stretching frequencies in metal–dioxygen complexes

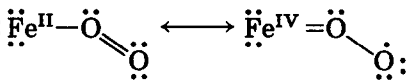
Type of complex	M:O	Structure	Range of ν(O—O) (cm^{-1})
superoxide-like			
Ia	1:1		1130 - 1195
Ib	2:1		1122 - 1075
peroxide-like			
IIa	1:1		932 - 800
IIb	2:1		884 - 790
ionic dioxygen compounds		$K^+O_2^-$ $2Na^+O_2^{2-}$	1145 842

[7], copper [8, 9], titanium [10] and a number of Group VIII metals [11 - 13]. Almost all currently known metal–dioxygen complexes can be divided into two types depending upon the characteristics of the dioxygen ligand, these being either superoxo (I) or peroxo (II) complexes. A further subdivision can be made according to whether the dioxygen is coordinated to one or two metal atoms [14]. A comparison of the O—O stretching frequencies, obtained from metal–dioxygen complexes, Table 1, shows that the metal–dioxygen adducts have O—O stretching frequencies similar to those obtained from compounds containing ionic superoxide or peroxide species.

Type IA

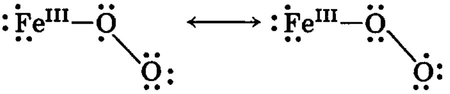
It has long been believed that the bonding of O_2 in dioxygenated haemoglobin (HbO_2) and myoglobin (MbO_2) is of type Ia. Recently reported values for (O—O) (1103 cm^{-1} for MbO_2 [15] and 1107 cm^{-1} for HbO_2 [16]) together with single crystal X-ray studies of model systems [17] lend support to this formulation. Synthetic type Ia complexes have been prepared by the reaction of dioxygen with metal complexes containing Cr(II), Fe(II) and Co(II).

In terms of simple valence bond theory, bonding in these complexes has been described in two ways: (1) The first approach, proposed by Pauling [18, 19] to explain the diamagnetism of HbO_2, assumes an even number of electrons about dioxygen and is represented as a resonance hybrid of structures A and B:



A B

Following the conventional method of assigning oxidation states, the canonical forms of A and B have valencies corresponding to $M^{II}(O_2)$ and $M^{IV}(O_2^{2-})$ respectively; (2) The second approach, proposed by Weiss [20] for the bonding of O_2 in HbO_2, assumes an odd number of electrons on the coordinated dioxygen and is represented by the structures C and D. For either of these two structures, the metal is in a +3 oxidation state, with coordinated O_2 being formally O_2^-.



C D

For this bonding model, the unpaired spins on Fe(III) and O_2^- are reputedly coupled, thus allowing for the observed diamagnetism of the FeO_2 system.

Dioxygen has been observed to form Ia type adducts with a large number of Co(II) complexes, with the most common examples being the five-coordinated Schiff base complexes Co^{II}(SB)(B), where B represents a neutral donor ligand, and porphyrinato–cobalt(II) complexes Co^{II}(por)(B). Magnetic susceptibility measurements on the cobalt–dioxygen adducts formed from these low-spin d^7 Co(II) complexes show the presence of only one unpaired electron [21]. EPR studies using ^{17}O-labelled dioxygen have shown that the electron spin density on the coordinated dioxygen is close to 100% [22]. On the basis of these results, it is clear that the unpaired electron resides on the dioxygen moiety and that the complexes are correctly formulated as $Co^{III}(O_2^-)$. Recent molecular orbital calculations also lend support to this formulation [23, 24]. These calculations show that (1) bonding between Co and O_2 arises primarily from the overlap of a dioxygen π-$^*O_2$ orbital with the d_{z^2} orbital of cobalt, (2) there is negligible Co—O_2 π-overlap and (3) the unpaired electron resides in the π-$^*O_2$ orbital.

The situation for chromium–dioxygen and iron–dioxygen complexes is not as clear as in the case of the Co—O_2 adducts. Experimental evidence has been collected on iron–dioxygen systems that has been interpreted in terms of an electron transfer from the iron(II) centre to the dioxygen ligand to form an Fe—O_2 bond which can be formulated as an $Fe^{III}(O_2^-)$ adduct. The evidence can, however, also be interpreted in terms of delocalisation of paired electron density from the iron to the coordinated dioxygen, suggesting a bonding scheme similar to the Fe(II) $\longleftrightarrow$ Fe(IV) formalisation proposed by Pauling for HbO_2 [17, 18]. These inconsistencies regarding the formulation of iron–dioxygen systems have yet to be fully resolved. As with the iron–dioxygen systems, the O_2 adducts of chromium complexes can be formulated as either a Cr(II) $\longleftrightarrow$ Cr(IV) or a Cr(III) configuration [25].

Type Ib

At the present time, the only complexes of type Ib characterised are those which contain cobalt. These compounds are paramagnetic with μ_{eff} *ca.* 1.6 μ_B and their EPR spectra are consistent with there being two equivalent cobalt nuclei having the majority of the electron density residing on the dioxygen bridge [26].

Type IIa

A large number of type IIa metal–dioxygen complexes have been prepared including the Group VIII metal–O_2 compounds formed by the addition of O_2 to low-valent coordinatively unsaturated organometallic compounds [12]. The salient differences between this type of bonding and that observed in type Ia complexes are: (1) the coordination geometry, with the dioxygen being bound to the metal centre in a symmetric, triangular fashion; and (2) the ν(O—O) values are similar to those observed for free peroxide ion, Table 1. The only synthetic dioxygen carriers of biological interest in which this type of bonding has been identified are the porphyrinato–manganese–dioxygen complexes Mn(por)(O_2).

Type IIb

The bonding of dioxygen in IIb complexes is believed to be similar to that of the natural systems of haemerythrin and haemocyanin. Bonding of O_2 in these natural systems involves two metal centres, with the bound O_2 being in a reduced 'peroxide-like' state with a concomitant one-electron oxidation of both metal centres. With the exceptions of some rhodium [27] and molybdenum [28] complexes, which are not strictly type IIb complexes since there is multiple M—(O_2)—M bridging and the coordination number of dioxygen is higher than two, the predominant number of synthetic type IIb complexes contain cobalt centres [2, 5].

Manganese dioxygen carriers

Manganese has been found to play an important role in the dioxygen evolution stage of photosystem(II) [29, 30], and this has coincided with much of the present research into manganese dioxygen complexes.

In 1936 Barrett *et al.* [31] and Linstead and Robertson [32] first reported that a pyridine solution of manganese(II)phthalocyanine absorbed dioxygen, the colour changing from olive green to dark blue. Boiling the solution regenerated the olive green colour of manganese(II)phthalocyanine and, once cool, the solution would absorb further amounts of dioxygen. These observations were investigated further in 1959 by Elvidge and Lever [33], who found that oxidation of pyridine solutions of [Mn^{II}(Pc)] (Pc = phthalocyanato) with molecular oxygen resulted in the precipitation of crystals they formulated as [Mn^{IV}(Pc)(py)(O)]. This was, however, shown to be in error by Vogt and coworkers [34], who showed the material to be $[Mn^{III}(Pc)(py)]_2O$, i.e. an oxo-bridged manganese(III) dimer. More recently, Lever and coworkers [35, 36] have reported that [Mn(Pc)] does not react with dioxygen in rigorously purified dry pyridine solution. Reaction does, however, occur in pure *N,N'*-dimethylacetamide to yield a solution of a dioxygen adduct. Deoxygenation can be achieved by flushing the solution with dinitrogen or by freeze–thaw degassing. The reaction can also be reversed more rapidly by exposing the solution to white light or by the addition of an electron donor *in vacuo*. Employing visible spectroscopy, a plot of $\log(A - A_0/A_0 - A)$ *vs.* pO_2 produced a slope of unity, indicating [37] formation of a 1:1 complex $[Mn(Pc)(O_2)]$ in solution, and yielded a $P_{50}(O_2)$ of 0.2 torr at 24 °C. A solution of the dioxygen adduct in *N,N'*-dimethylacetamide can be converted into the μ-oxo species by the addition of either imidazole or *N*-methylimidazole; Lever has postulated the following mechanism for the reaction:

$$Mn^{II}(Pc) + O_2 \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} Mn(Pc)(O_2) \qquad (2)$$

$$Mn(Pc)(O_2) + Mn^{II}(Pc) \rightleftharpoons (Pc)Mn^{III}{-}O_2{-}Mn^{III}(Pc) \qquad (3)$$

$$(Pc)Mn^{III}{-}O_2{-}Mn^{IV}(Pc) \rightleftharpoons 2Mn^{IV}(Pc)O \qquad (4)$$

$$Mn^{IV}(Pc)O + Mn^{II}(Pc) \rightleftharpoons (Pc)Mn^{III}{-}O{-}Mn^{III}(Pc) \qquad (5)$$

Analysis, infrared (^{18}O isotopic substitution), electronic spectra, magnetism ($S = 3/2$) and EPR studies all appear consistent with the formulation of the dioxygen adduct as $[Mn^{III}(Pc)(O_2^-)]$, that is, a bound superoxide species.

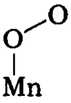
Until quite recently, the only synthetic complexes of biological interest which had been observed to reversibly bind dioxygen were those containing cobalt(II) [2, 5] and iron(II) [2, 4]. Recently, however, *meso*-tetraphenylporphyrinatomanganese(II) complexes of the form $Mn^{II}(TPP)(L)$, where L represents a coordinating ligand such as pyridine, have been shown to act as reversible dioxygen carriers in toluene solution at −79 °C [38 - 41]. This reversible dioxygenation was also observed independently using Mn(TPP) in a toluene/THF solution at −90 °C [42]. In these experiments, the use of aprotic solvents and low temperatures inhibits reversible oxidation and stabilises the dioxygen adduct. At −70 °C, up to 70% of the initial manganese(II) porphyrin complex can be regenerated by flushing the solution with dinitrogen after exposure of the system to dioxygen at atmospheric pressure for 14 h [43].

The reaction of dioxygen in toluene, with a series of *para*-substituted *meso*-tetraphenylporphyrinatomanganese(II) complexes $[Mn^{II}(T(p\text{-}X)PP)(B)]$ containing an axial base B has recently been studied [44]. Spectrometric titrations of toluene solutions of these complexes at −78 °C with molecular oxygen confirm that at low temperature an equilibrium between the five-coordinated monoligated species [Mn(T(*p*-X)PP)(B)], and the dioxygen complex [Mn(T(*p*-X)PP)(O_2)] is established (eqn. 6):

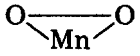
$$Mn^{II}(T(p\text{-}X)PP)(B) + O_2 \rightleftharpoons Mn(T(p\text{-}X)PP)(O_2) + B \qquad (6)$$

A comparison can be made of the properties observed for the dioxygen adducts of tetraphenylporphyrinatomanganese(II) complexes with those expected on the basis of an assigned d^3 Mn(IV) ground state. A recent study on the chemical and spectroscopic properties of [Cr^{III}(TPP)Cl], which contains a d^3 metal centre, has shown that this five-coordinate complex has an exceptionally large affinity toward the binding of a sixth N-donor axial ligand [45]. In contrast with this behaviour, no tendency for the presumed d^3 Mn(IV) centre in [Mn(TPP)(O_2)] to bind an axial ligand at −78 °C has been observed [44]. This large difference in the affinities of the d^3 metalloporphyrin complexes [Cr^{III}(TPP)Cl] and [Mn(TPP)(O_2)] for an axial ligand can be interpreted as arising from either of two factors: (1) repulsive steric interaction between the coordinated dioxygen and the porphyrinato ring in [Mn(TPP)(O_2)] that results in the manganese centre lying out of the plane of the porphyrin toward the coordinated dioxygen; (2) differences in the ground state electronic configuration of the chromium and manganese centres which favour the [Mn(TPP)(O_2)] structure.

Two geometric conformations have been suggested for the bonding of dioxygen to the manganese–porphyrins (E) and (F):



(E)



(F)

On the basis of the formal $Mn^{IV}(O_2^{2-})$ ground state configuration, it has been suggested [41] that the Griffin conformation (F) is to be preferred. This structural assignment is also consistent with the observation that the porphyrinatomanganese–dioxygen complexes do not bind an axial ligand. The binding of an axial ligand on the dioxygen complex would tend to draw the manganese centre into the plane of the porphyrin. This would be expected to result in severe repulsive interaction between the coordinated dioxygen ligand and the porphyrinato ring. For Pauling geometry (E), however, this repulsive interaction would not occur, and the dioxygen complex of such a structure would be expected to bind an axial ligand readily.

Hanson and Hoffman have recently reported charge-interactive extended Hückel calculations on both Griffin and Pauling bonding models [46]. The authors concluded that all the experimental results [40, 41, 47] can be explained in terms of a d^3 configuration and Griffin binding of the dioxygen.

Additional evidence for the Griffin mode of coordination has been afforded recently by Urban and coworkers [48]. Using matrix isolation techniques, they were able to record the IR spectrum of the dioxygen adduct [Mn(TPP)(O_2)]. They assigned the $\nu(O_2)$ bands for both $^{18}O_2$ and $^{16}O_2$ adducts at 933 and 983 cm^{-1} respectively. The authors also carried out an oxygen isotope scrambling experiment to provide further evidence on the structure of the dioxygen adduct. They observed three bands at 983, 958 and 933 cm^{-1} when [Mn(TPP)] was co-condensed with a mixture of $^{16}O_2$, $^{16}O^{18}O$ and $^{18}O_2$. The bands at 983 and 933 cm^{-1} corresponded to $\nu(O_2)$ of the $^{16}O_2$ and $^{18}O_2$ adducts respectively. The remaining band at 958 cm^{-1} was assigned to the $^{16}O^{18}O$ species. Since only one band was observed for this species, the O_2 moiety must be side-on coordinated. End-on coordination would lead to splitting of the central band into a doublet due to the presence of both (Mn—$^{16}O^{18}O$) and (Mn—$^{18}O^{16}O$) species [49].

Apart from the phthalocyanine and porphyrin systems, probably the most intensely studied manganese system is the tris(3,5-t-butylcatecholato)-manganese(IV) complex of Sawyer *et al.* [50 - 54]. Although several manganese–catechol complexes have been reported [50 - 62], most of the studies concerned the comparison of metal–catechol formation constants [51, 59, 61, 62] and metal-catalysed autoxidation of catechol [60, 63]. The aqueous chemistry of tris(catecholato) complexes of manganese(II) and (III) has been described, as well as the reversible oxidation of tris(3,5-di-t-butylcatecholato)manganese(III), $[Mn^{III}(DTBC)_3]^{3-}$ [52]. Sawyer has reported [53] that the oxidation product of $[Mn^{III}(DBTC)_3]^{3-}$ reversibly binds dioxygen at room temperature in a number of solvents, although reversibility is reported as optimal in acetonitrile [54].

Recent work by Cooper and Hartman has however cast doubt on Sawyer's conclusions [64]. These authors report that they are able to produce solutions with spectroscopic properties identical to those of Sawyer's O_2-adduct merely by the oxidation of the catechol in the absence of manganese. Sawyer has, however, reaffirmed his claim of reversible dioxygen binding and has presented further spectroscopic evidence in support of this claim [65].

Manganese(II)–tertiary phosphine complexes

Thus far the discussion has included the well-characterised manganese(II)phthalocyanine and porphyrin systems, both of which have clearly been shown to bind dioxygen reversibly, and also the $[Mn(DBTC)_3]^{3-}$ system about which doubts have been cast. There is evidence that salen [66] or sorbitol [67] manganese(II) systems also form dioxygen adducts, and one could also include the somewhat esoteric $(O_2)Mn(CO)_5$ [68]. However, whilst these systems appear to form dioxygen adducts, there is little evidence to support their classification as dioxygen carriers and they can therefore only be considered as peripheral to any discussion of true reversible coordination of the O_2 molecule [1].

TABLE 2

Typical colours of [$MnLX_2$] and [$MnL(O_2)X_2$] complexes

Complex	[$MnLX_2$]	[$MnL(O_2)X_2$]
X = Cl	white	purple
X = Br	off-white	blue
X = I	pale orange	green
X = NCS	yellow	red

In 1979, McAuliffe *et al.* [69] reported the preparation and characterisation of a large number of manganese(II) tertiary phosphine complexes of general formula [$MnLX_2$] (L = tertiary phosphine, but not PPh_3, and X = Cl, Br, I or NCS). These simple complexes reversibly bound dioxygen in a manner which quite closely resembled the properties of both haemoglobin and myoglobin. These complexes were shown to bind dioxygen in a 1:1 molar ratio, forming [$MnL(O_2)X_2$] species in both the solid state and in a number of organic solvents [69 - 74]. The [$MnLX_2$] complexes were found to be pale in colour, but upon contact with dioxygen, rapidly developed deep colours which appeared to depend on the anion, Table 2.

Synthesis of the Mn(II) phosphine complexes

The failure of some workers to synthesise the manganese(II) phosphine complexes [75, 76] leads us to stress the stringently anhydrous conditions necessary for their preparation — both manganese(II) salts and solvents must be rigorously dried. Reliable synthetic methods have been reported in full [77 - 79].

X-ray crystal structures of Mn(phosphine)X_2 complexes

Although tertiary phosphine alkyls are common ligands for transition metals [80 - 82], manganese is an exception; the only compound known, other than those reported by McAuliffe *et al.* [69], is the σ-bonded aryl derivative {$MnPh_2[P(c\text{-}C_6H_{12})_3]$}; but again, no structural data was reported for this complex [83]. Recently, however, Davies and coworkers [84] have isolated the air-sensitive orange complex bis(trimethylphosphine) bis(trimethylsilylmethyl)bis(μ-trimethylsilylmethyl)dimanganese(II), [$Mn_2(CH_2SiMe_3)_4(PMe_3)_2$] in crystalline form by interaction of [$Mn(CH_2SiMe_3)_2]_n$ with PMe_3 in toluene. Figure 1 shows the centrosymmetric dimeric structure of this complex.

Each manganese atom is coordinated to a terminal PMe_3 group (Mn—P distance of 2.650 Å), a terminal CH_2SiMe_3 group, and to two bridging CH_2SiMe_3 groups. The coordination geometry about manganese is distorted tetrahedral, with bond angles in the range 99.8 - 125.0°. The methylene bridge is asymmetric, with an Mn—C(1) distance of 2.369 Å and Mn′—C(1) distance of 2.209 Å. This can be compared with the Mn—C(2) distance of 2.11 Å. The Si—CH_3 distances in the two groups also significantly differ,

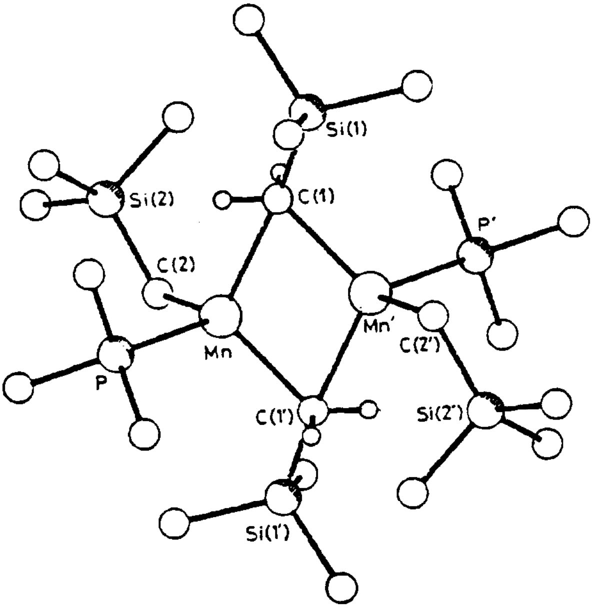
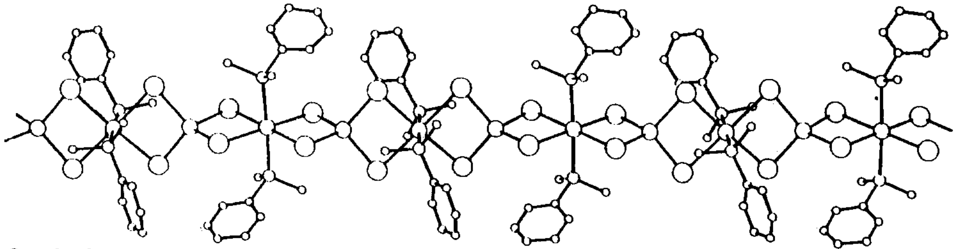


Fig. 1. Molecular structure of the centrosymmetric dimer $Mn_2(CH_2SiMe_3)_4(PMe_3)_2$. Hydrogen atoms have been omitted, with the exception of those on the bridging CH_2 groups.



Octahedra		Tetrahedra
Mn—I	2.97 - 3.00	Mn—I 2.96 - 2.72
Mn—P	2.65 - 2.68	

Fig. 2. Crystal structure of $Mn(PPhMe_2)I_2$.

with Si(1)—C(1) 1.863 Å in the bridging group, and Si(2)—C(2) 1.825 Å in the terminal group.

This complex represents, then, the first crystallographically characterized unidentate phosphine complex of manganese(II). It has since been shown that the complex $[Mn(PPhMe_2)I_2]$ has a rather remarkable crystal structure different from that reported by Wilkinson's group. The overall single crystal structure is shown in Fig. 2.

As can be seen from Fig. 2, the crystal structure of this complex at once presents a radical difference to that of Wilkinson's compound, $[Mn_2(CH_2SiMe_3)_4(PMe_3)_2]$. The overall 3-D structure is best described as an infinitely long, halide-bridged polymer consisting of tetrahedral 4-coordinate and octahedral 6-coordinate subunits in a regularly repeating

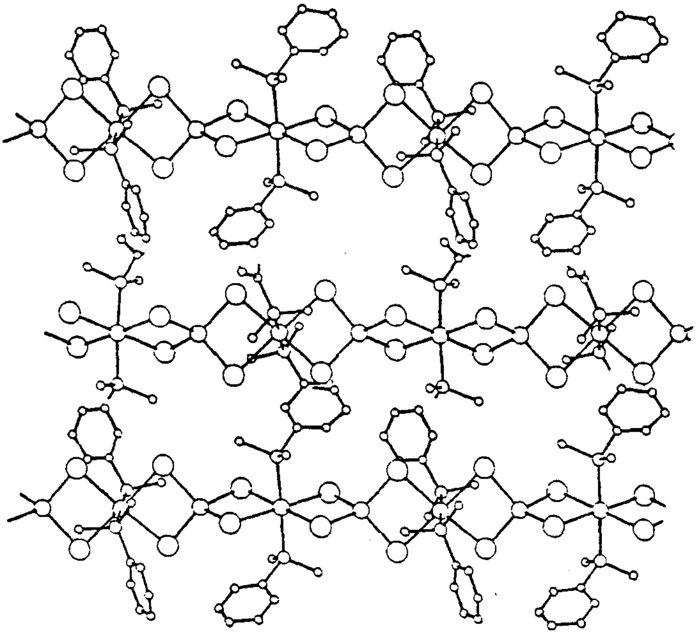


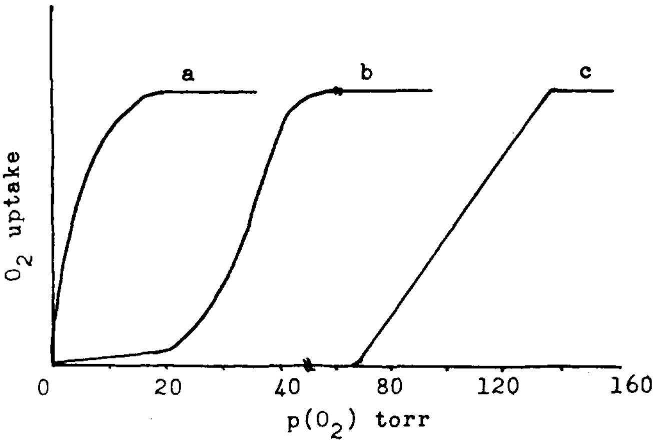
Fig. 3. The proposed unit cell of $Mn(PPhMe_2)I_2$; some phenyl groups have been omitted for clarity.

O_h, T_d, O_h, T_d etc. pattern. The cell unit is shown in Fig. 3, from which it can be seen that there are distinct spaces above and below the coordinatively unsaturated Mn sites. These 'spaces' can be fine-tuned by changing either the bridging halide or by changing the steric requirements of the phosphine group. Thus, our experience of being able to discriminate binding between O_2, CO, SO_2, NO and ethylene may be attributed to fine tuning of the vacant spaces about the T_d manganese atom.

Reaction with dioxygen

Reaction of the manganese(II) phosphine complexes with dioxygen in the solid state is almost instantaneous at the surface; complete dioxygenation is diffusion controlled and can take 2 - 24 h to complete, depending upon particle size. Some solid state isotherms, representing equilibria on the surface, are shown in Fig. 4 and illustrate well the way in which changes in X and R in the $[Mn(PR_3)X_2]$ molecule affect the interaction of the molecule with dioxygen.

For dioxygen uptake measurements in solution, the apparatus has been fully described [85] (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 concentra-



a = $[Mn(PPhMe_2)Br_2]$
b = $[Mn(PPhEt_2)Br_2]$
c = $[Mn(PBu_3)(NCS)_2(THF)_2]$

Fig. 4. Some solid state O_2 isotherms for the $[MnLX_2]$ complexes.

tions; 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} mol of dioxygen under the conditions we employed at 0 °C. All of the complexes $[MnX_2(PR_3)]$ (X = Cl, Br or I; $R_3 = Bu_3^n$ or $PhBu_2^n$) 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 $[MnI_2(PBu_3^n)]$ in 100 cm^3 THF absorbed 97 cm^3 of dioxygen, equivalent to 85 cm^3 absorbed by the complex and 12 cm^3 by the solvent (blank). Reaction (7) may be reversed by lowering the pressure above the oxygenated solution or by warming to room temperature.

$$MnX_2(PR_3) + O_2 \rightleftharpoons MnX_2(PR_3)(O_2) \qquad (7)$$

That the $[MnX_2(PR_3)]$ complexes do bind dioxygen in THF solution is further evidenced by plots of dioxygen absorbed against complex concentration, Fig. 5 and Table 3. 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 value 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.

Recycling (100 mol% uptake, successively) and stability of the complexes in solution were followed by accurate successive gas burette measurements and 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 $[MnI_2(PBu_3^n]$ in THF: more than

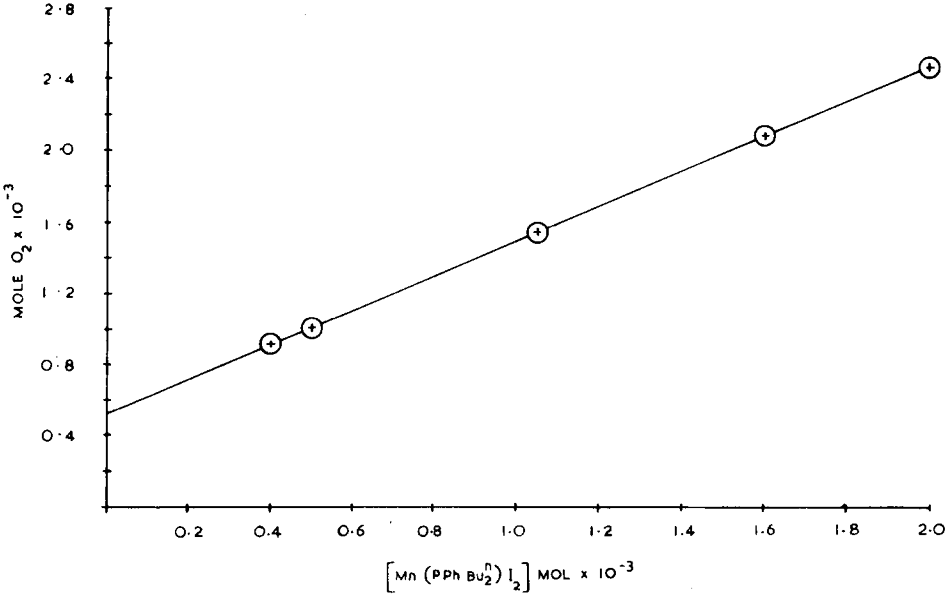


Fig. 5. Dioxygen uptake as a function of $Mn(PPhBu_2^n)I_2$ concentration in 100 ml THF at 0 °C.

TABLE 3

Data from the plots of dioxygen uptake at 0 °C as a function of complex concentration (see Fig. 5)

Complex	Slope	Intercept (10^{-4} mol)
$[MnCl_2(PBu_3^n)]$	0.94	5.3
$[MnBr_2(PBu_3^n)]$	0.96	5.2
$[MnI_2(PBu_3^n)]$	0.98	5.2
$[MnCl_2(PPhBu_2^n)]$	0.98	5.2
$[MnBr_2(PPhBu_2^n)]$	0.96	5.3
$[MnI_2(PPhBu_2^n)]$	0.96	5.2

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 to the temperature. For example, it was possible to store $[MnI_2(PBu_3^n)(O_2)]$ 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 $[MnI_2(PBu_3^n)(O_2)]$ 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 $[MnI_2(PBu_3^n)(O_2)]$ is $[MnI_2(OPBu_3^n)]$. 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 $[MnI_2(OPBu_3^n)]$ (Found: C, 27.2; H, 5.3; I, 47.9; Mn, 10.6; O (by difference), 2.9; P, 6.1%. 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 IR spectrum exhibits a strong absorption at 1150 cm^{-1} assignable to $\nu(P{=}O)$, which is absent in the IR spectrum of $[MnI_2(PBu_3^n)]$, and is shifted approximately 25 cm^{-1} from the value recorded for $\nu(P{=}O)$ in free PBu_3^nO. We can tentatively assign a band at 296 cm^{-1} to $\nu(Mn{-}O)$, which is absent in $[MnI_2(PBu_3^n)]$. On heating the white-yellow solid *in vacuo* to *ca.* 180 °C a white, waxy sublimate was obtained, which proved to be PBu_3^nO (by elemental analysis and IR 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 exhibits 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-coordinating 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 λ_{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 in the electronic spectrum with $p(O_2)$, see Fig. 6.

Isotherms constructed by this method for $[MnBr_2(PBu_3^n)]$ in three solvents are shown in Fig. 7, from which it can be seen that the position and shape of the curves in the non-coordinating solvents toluene and 1,2-dichloroethane are hyperbolic. It is seen that the isotherm moves to the right

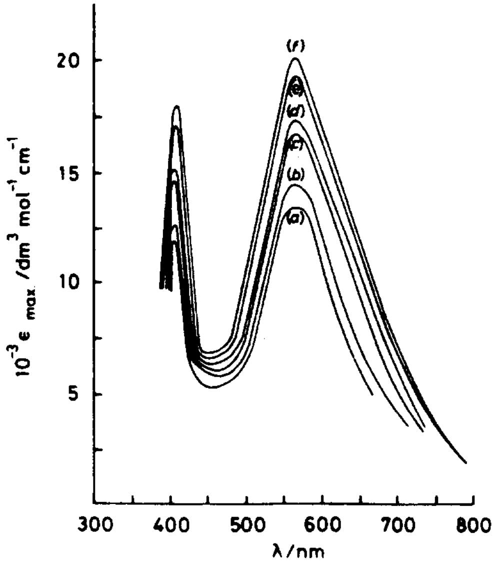


Fig. 6. Variation of the electronic spectrum of [$MnBr_2(PBu_3^n)$] in toluene with dioxygen partial pressure at 20 °C: $p(O_2)$ = 10(a), 20(b), 50(c), 70(d), 100(e) and 150 torr (f).

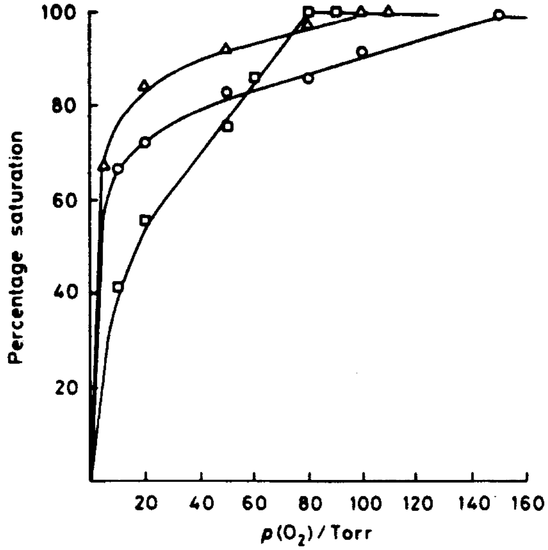


Fig. 7. Solution isotherms for [$MnBr_2(PBu_3^n)$] at 20 °C: in 1,2-dichloroethane (△), toluene (○) and THF (□).

for [$MnBr_2(PBu_3^n)$] in THF; the affinity of [$MnBr_2(PBu_3^n)$] 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 [$MnX_2(PPhBu_2^n)$] (X = Cl or Br) in Fig. 8. The isotherm

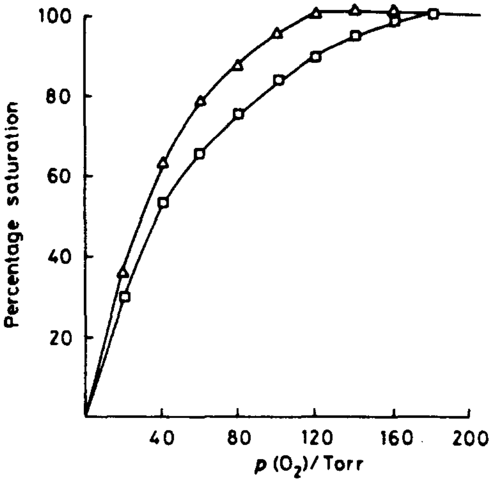


Fig. 8. Solution isotherms for $[MnBr_2(PBu_3^n)]$ at 20 °C in 1,2-dichloroethane: X = Cl (△) and Br (□).

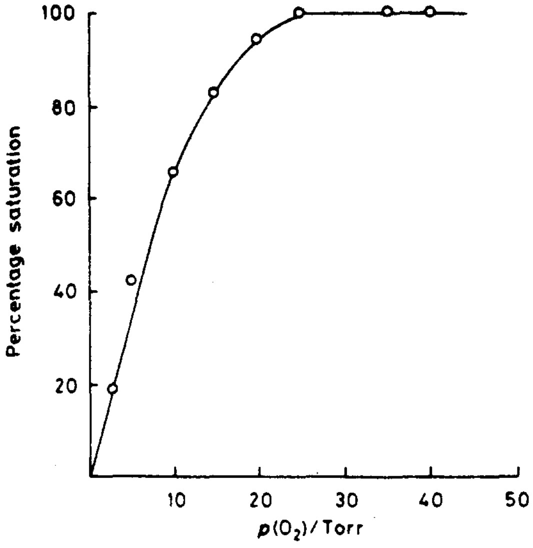


Fig. 9. Solution isotherm for $[MnI_2(PBu_3^n)]$ in THF at −40 °C.

for $[MnI_2(PBu_3^n)]$ in THF is shown in Fig. 9 and equilibrium data derived are listed in Table 4.

On the other hand, for a constant halide and solvent, the isotherm moves to the right as the phosphine changes from 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 4 for the complexes $[MnBr_2(PBu_3^n)]$ and $[MnBr_2(PPhBu_2^n)]$ in toluene; $p_{1/2}(O_2)$ values (the $p(O_2)$ at

TABLE 4

Equilibrium data for dioxygen uptake by manganese(II) complexes

Complex	Solvent	Temperature (°C)	log K (torr^{-1})	$10^2 K_{O_2}$ (torr^{-1})	$p_{1/2}(O_2)$ (torr)	Slope
$[MnBr_2(PBu_3^n)]$	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
$[MnI_2(PBu_3^n)]$	THF	−40	−1.47	3.37	29.7	1.8
$[MnCl_2(PPhBu_2^n)]$	toluene	20	−2.22	0.60	165.6	1.2
	$ClCH_2CH_2Cl$	20	−2.25	0.56	179.5	1.2
$[MnBr_2(PPhBu_2^n)]$	toluene	20	−2.30	0.50	199.5	1.3

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} (eqn. 8), were calculated from the isotherms using the Hill equation (eqn. 9), where Y is the fraction of the dioxygenated sites, K_{O_2} is the equilibrium constant for the reaction, and $p_{1/2}(O_2)$ is the partial pressure at half-oxygenation, *i.e.* $p(O_2)$ at which 50% of the sites are oxygenated.

$$[MnX_2(PR_3)] + O_2 \overset{K_{O_2}}{\rightleftharpoons} [MnX_2(PR_3)(O_2)] \tag{8}$$

$$\frac{Y}{1-Y} = \frac{[MnX_2(PR_3)(O_2)]}{[MnX_2(PR_3)]} = \frac{K_{O_2}p(O_2)^n}{[O_2]} = [p_{1/2}(O_2)]^{-1}p(O_2)^n \tag{9}$$

Fuller equilibrium data is given in Table 5. In general, in THF solution we have found that the affinity for dioxygen is for halide X = Cl > Br > I and for phosphine R_3 = trialkyl > phenyldialkyl > diphenylalkyl ≫ triphenyl.

Other small molecules

Sulphur dioxide [86]

The reaction of the complexes $[MnX_2(PR_3)]$ (X = Cl, Br or I; R_3 = $PhMe_2$, $PhEt_2$, $PhPr_2^n$, $PhBu_2^n$, $PhBu_2^i$, Pr_3^n or Ph_3) with sulphur dioxide in the solid state, in toluene slurries and in THF has been studied. In all three systems a strong dependence on the nature of the halide is observed. For X = Cl, no reaction takes place; for X = I, all complexes irreversibly absorb SO_2; for X = Br a borderline exists and the nature of the phosphine

TABLE 5

Equilibrium data for dioxygen uptake by $[Mn(PR_3)X_2]$ complexes

Complex	Solvent	Temp. (°C)	Log K ($torr^{-1}$)	$K_{O_2} \times 10^2$ ($torr^{-1}$)	$p_{1/2}(O_2)$ (torr)	Slope
$[Mn(PEt_3)Br_2]$	THF	20	−1.054	8.83	11.3	0.88
$[Mn(PEt_3)Cl_2]$	THF	20	−1.073	8.45	11.83	0.86
$[Mn(PEt_3)I_2]$	THF	−40	−1.109	8.45	12.9	1.62
$[Mn(PPr_3^n)Br_2]$	THF	20	−1.073	8.45	11.8	0.86
$[Mn(PPr_3^n)Br_2]$	toluene	20	−0.251	56.1	1.78	0.54
$[Mn(PPr_3^n)Cl_2]$	THF	20	−2.707	0.196	509.0	1.35
$[Mn(PPr_3^n)Cl_2]$	toluene	20	−1.565	2.72	36.73	1.02
$[Mn(PPr_3^n)I_2]$	THF	−40	−1.361	4.35	22.9	1.77
$[Mn(PBu_3^n)Br_2]$	THF	20	−1.320	4.79	20.9	1.12
$[Mn(PBu_3^n)Br_2]$	toluene	20	−0.429	37.23	2.69	0.69
$[Mn(PBu_3^n)Br_2]$	1,2-$C_2H_4Cl_2$	20	−0.418	38.19	2.62	0.94
$[Mn(PBu_3^n)I_2]$	THF	−40	−1.472	3.373	29.7	1.8
$[Mn(PPhMe_2)I_2]$	toluene	20	−0.853	14.03	7.13	0.92
$[Mn(PPhMe_2)I_2]$	THF	−40	−1.431	3.707	26.98	1.43
$[Mn(PPhEt_2)Br_2]$	toluene	20	−2.099	0.796	125.6	1.22
$[Mn(PPhEt_2)Br_2]$	1,2-$C_2H_4Cl_2$	20	−2.105	0.966	103.5	1.4
$[Mn(PPhEt_2)Cl_2]$	toluene	20	−2.162	0.688	145.2	1.16
$[Mn(PPhEt_2)Cl_2]$	1,2-$C_2H_4Cl_2$	20	−2.139	0.726	137.7	1.17
$[Mn(PPhBu_2^n)Br_2]$	toluene	20	−2.300	0.501	199.5	1.36
$[Mn(PPhBu_2^n)Br_2]$	1,2-$C_2H_4Cl_2$	20	−2.055	0.881	113.5	1.34
$[Mn(PPhBu_2^n)Cl_2]$	toluene	20	−2.219	0.604	165.6	1.19
$[Mn(PPhBu_2^n)Cl_2]$	1,2-$C_2H_4Cl_2$	20	−2.254	0.557	179.5	1.24

is important, *viz.* trialkylphosphines promote SO_2 binding, whereas complexes containing phenyl-substituted phosphines (except $PPhMe_2$) are inactive towards SO_2. The reaction stoichiometry is unusual, $[MnX_2(PR_3)(SO_2)_x]$ (for measurements in the solid state $x = 0.66$, for THF solution $x = 0.65 - 0.76$). Although $[MnI_2(PPh_3)]$ does not bind dioxygen, it forms an adduct with sulphur dioxide in the solid state and in THF.

Ethylene [87]

The complexes $[MnX_2PR_3]$ ($X = Cl$, $Pr_3 = PPr_3^n$, PBu_3^n, $PPhMe_2$, $PPhEt_2$; $X = Br$, $L = PBu_3^n$) react with ethylene in THF solution at 0 °C to give 1:1 adducts. None of the iodide complexes, nor $[MnX_2(PPh_3)]$ ($X =$ Cl, Br or I), reacts with ethylene under these conditions. The order of stability of the ethylene adducts (*i.e.* $Cl > Br > I$ and $PR_3 > PPhR_2 > PPh_3$) is probably due to a combination of both steric and electronic effects. Thus, the order of decreasing stability is the same as the order of decreasing ligand size and also the same as the order of decreasing electronegativity of the halide. If the electronic effect were the dominant factor, this would imply that the σ-component of the manganese(II)–ethylene bond is more important than the π-component, since increasing electron-withdrawing ability of the halide will promote donation of electron density from the ethylene, thereby increasing the strength of the manganese(II)–ethylene σ-bond.

Nitric oxide [88]

The complexes $[MnX_2(PR_3)]$ (X = Cl, Br, I; $PR_3 = PPr_3^n$, PBu_3^n, $PPhMe_2$ or $PPhEt_2$) have been shown to react with nitric oxide both in the solid state and in THF solution. For X = Cl or Br, the reaction is reversible and $[MnX_2(PR_3)(NO)]$ species are formed. For X = I, the reaction is irreversible even at low temperatures, with the phosphine ligand being oxidised. For the reversible reaction in the solid state the complexes have ν(NO) at 1600 cm^{-1}, the magnetic moment and EPR data indicate the $[MnX_2(PR_3)(NO)]$ species have four unpaired electrons and are formulated as Mn^{III}—NO^- moieties. In THF solution, the formation of 1:1 Mn:NO adducts has been confirmed by quantitative gas absorption measurements. These adducts are also highly coloured, and NO binding isotherms have been constructed. Cycling experiments have shown the adducts to be more stable at lower temperatures. The decomposition product has been studied, with phosphine oxides being formed both in the solid state and solution decomposition. It is postulated that NO oxidation of the PR_3 ligand occurs at higher temperature.

Carbon disulphide [89]

The $[Mn(PR_3)X_2]$ and $[Mn(PR_3)X_2(THF)_2]$ complexes ($PR_3 = PPr_3^n$, PBu_3^n, $PPhMe_2$, $PPhEt_2$ or $PPhPr_2^n$; X = Cl, Br or I) react with carbon disulphide in diethyl ether to form the insoluble $\{[Mn(PR_3)X_2]_2(CS_2)\}$ and $\{[Mn(PR_3)X_2(THF)_2]_2(CS_2)\}$ complexes. Electron paramagnetic and electronic spectra are consistent with pseudotetrahedral and pseudooctahedral coordination geometries, respectively, for the carbon disulphide complexes. The IR spectra are consistent with bridging CS_2 ligands. The carbon disulphide moieties are bound strongly; heating $\{[Mn(PR_3)X_2]_2(CS_2)\}$ *in vacuo* at 80 °C for long periods does not displace the CS_2. Heating $\{[Mn(PR_3)X_2(THF)_2]_2(CS_2)\}$ displaces the THF, and $\{[Mn(PR_3)X_2]_2(CS_2)\}$ is formed. The CS_2 ligands cannot be displaced by dioxygen, but dioxygen is displaced from $[Mn(PR_3)X_2(O_2)]$ by carbon disulphide to form $\{[Mn(PR_3)X_2]_2(CS_2)\}$.

Tetracyanoethylene [90]

When $[MnX_2PR_3]$ (X = Cl, Br or I; $PR_3 = PPr_3^n$, PMe_2Ph or PPh_3) complexes react with tetracyanoethylene (tcne) in toluene slurries, the 1:1 adducts $[MnX_2PR_3(tcne)]$ are formed. The magnetic moments of the adducts at room temperature, $\mu_{eff} = 4.6 - 4.9\ \mu_B$, are consistent with a d^4 manganese(III) species, and IR, visible and EPR spectroscopic data are also consistent with the transfer of an electron from manganese(II) to tcne on adduct formation, resulting in a manganese(III)–$tcne^{\cdot -}$ species. The tcne coordinates via a nitrile nitrogen.

Trends in dioxygen activity

In an attempt to show structure/reactivity relationships, we have examined the difference in K_{O_2} for the reaction with dioxygen as the phosphine varies in the $[Mn(PR_3)Cl_2]$ and $[Mn(PR_3)Br_2]$ systems in the non-coordinating solvent toluene. Thus, we have (empirically) constructed 3-D graphs incorporating the cone angle of the phosphine [91], Strohmeir's electronic parameter [92] and K_{O_2}. These are illustrated in Tables 6 and 7 and Figs. 10 and 11.

Designating the x, y and z axes to be θ, ν and K_{O_2} (see Tables 6 and 7) respectively, we find a graph in which overall reactivity appears to fall inside a narrow steric and electronic parameter range. It is clear, however, that the value of K_{O_2} is not determined simply in terms of either a single steric parameter or a single electronic parameter.

We can envisage this activity surface as a 'hill" in a 'Z plain' of no activity. Seen in this light, dioxygen coordination is a very special phenomenon. In terms of a 'hill' and 'plain' concept, if we define activity in terms of only ν and θ, then there should be other 'hills of activity' for complexes of the type $[Mn(ER_3)X_2]$ (E = As or Sb). However, in the case of As and Sb complexes these ligands are slightly smaller than their phosphorus analogues [93]. Models show that increasing M—E or E—C bond lengths by approximately 0.1 Å decreases θ by 30 - 50 [94]. It should be borne in mind that, although the carbonyl stretching frequencies in $M(CO)_n(ER_3)_m$ complexes are really independent of E, the M—E bond strengths can be very different, and fall rapidly in the order P > As > Sb > Bi [95, 96]. With this in mind,

TABLE 6

K_{O_2} values, ν and cone angles of complexes of the type $Mn(PR_3)Cl_2$ at 20 °C in toluene solution

Complex	θ [87] (°)	ν [87] (cm^{-1})	K_{O_2} ($torr^{-1}$)
$[Mn(PPhMe_2)Cl_2]$	122	2065.3	0.95×10^{-2}
$[Mn(PPhEt_2)Cl_2]$	136	2063.7	0.69×10^{-2}
$[Mn(PPhBu_2^n)Cl_2]$	135	2063.2	0.61×10^{-2}
$[Mn(PEt_3)Cl_2]$	132	2061.7	69.2×10^{-2}
$[Mn(PPr_3^n)Cl_2]$	132	2060.9	2.7×10^{-2}
$[Mn(PBu_3^n)Cl_2]$	132	2060.3	1.0×10^{-2}
$[Mn(PPh_2Me)Cl_2]$	136	2065.3	—
$[Mn(PPh_2Et)Cl_2]$	140	2066.7	—
$[Mn(PPh_3)Cl_2]$	145	2068.9	—
$[Mn(P[benzyl]_3)Cl_2]$	165	2066.4	—
$[Mn(PPr_3^n)Cl_2]$	160	2059.2	—
$[Mn(PCy_3)Cl_2]$	170	2056.4	—
$[Mn(PBu_3^t)Cl_2]$	182	2056.1	—

TABLE 7

K_{O_2} values, ν and cone angles of complexes of the type $Mn(PR_3)Br_2$ at 20 °C in toluene solution

Complex	θ [86] (°)	ν [87] (cm^{-1})	K_{O_2} ($torr^{-1}$)
$[Mn(PPhMe_2)Br_2]$	122	2065.3	14.03×10^{-2}
$[Mn(PPhEt_2)Br_2]$	136	2063.7	0.79×10^{-2}
$[Mn(PPhBu_2^n)Br_2]$	135	2063.2	2×10^{-2}
$[Mn(PEt_3)Br_2]$	132	2061.7	94.6×10^{-2}
$[Mn(PPr_3^n)Br_2]$	132	2060.9	56.1×10^{-2}
$[Mn(PBu_3^n)Br_2]$	132	2060.3	37.2×10^{-2}
$[Mn(Pamyl_3^n)Br_2]$	132	2060	8×10^{-2}
$[Mn(PPh_2Me)Br_2]$	136	2065.3	0.0132×10^{-2}
$[Mn(PPh_2Et)Br_2]$	140	2066.7	—
$[Mn(PPh_3)Br_2]$	145	2068.9	—
$[Mn(P[benzyl]_3)Br_2]$	165	2066.4	—
$[Mn(PPr_3^i)Br_2]$	160	2059.2	—
$[Mn(PCy_3)Br_2]$	170	1056.4	—
$[Mn(PBu_3^t)Br_2]$	182	2056.1	—

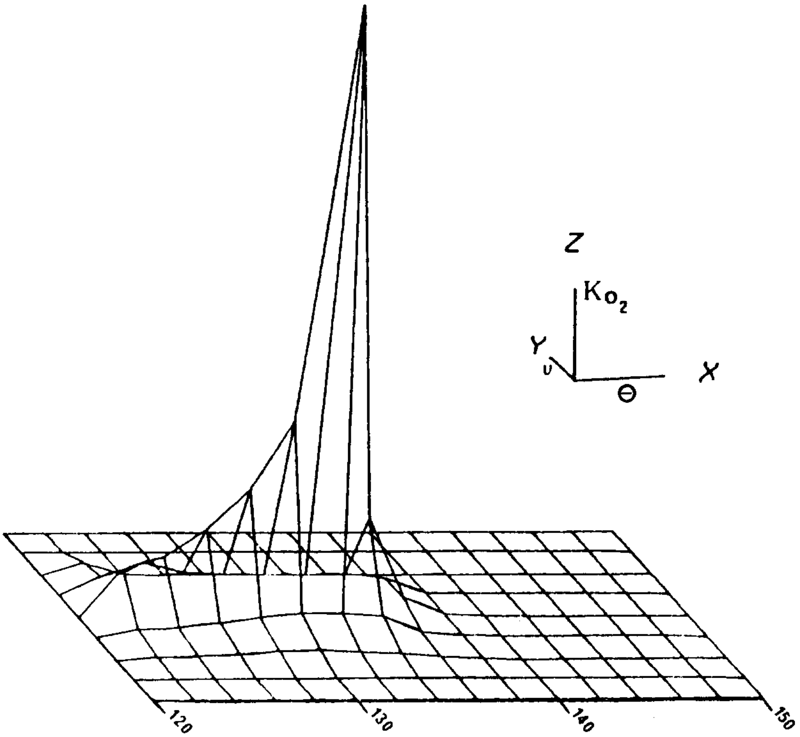


Fig. 10. The 3-D or spatial diagram of K_{O_2} vs. θ vs. ν for $Mn(PR_3)Cl_2$ complexes in toluene solution at 20 °C.

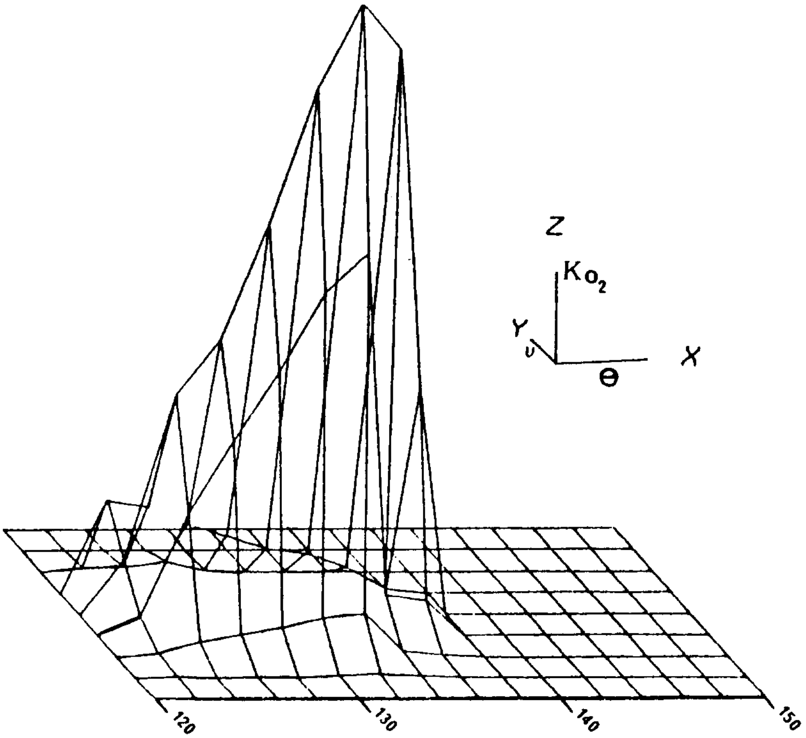


Fig. 11. The 3-D or spatial diagram of K_{O_2} *vs.* θ *vs.* ν for $Mn(PR_3)Br_2$ complexes in toluene solution at 20 °C.

the parameters for dioxygen activity appear to be extremely rare or even non-existent with other Group V donor sets.

Use of the complexes in gas separations

We have been able to demonstrate that two important separations are possible, *viz.* H_2/O_2 and H_2/CO.

Apparatus and methods

The apparatus employed to demonstrate gas separation via the $[Mn(PR_3)X_2]$ complexes is shown in Fig. 12. The figure shows H_2/O_2 separation, and this will now be fully described (*n.b.* it can be applied to any other gas separation system). In the process, quantitative uptake of the dioxygen in the mixture is followed via a gas burette. However, the gas burette and the tubing to the reaction flask contain only H_2.

The system works on the principle that if the ‘dead space’ above the solution is a H_2/O_2 mixture and the gas burette is filled with H_2/O_2, then as the uptake of O_2 progresses an O_2 concentration gradient would develop across the intervening tubing, and the remaining O_2 uptake would then

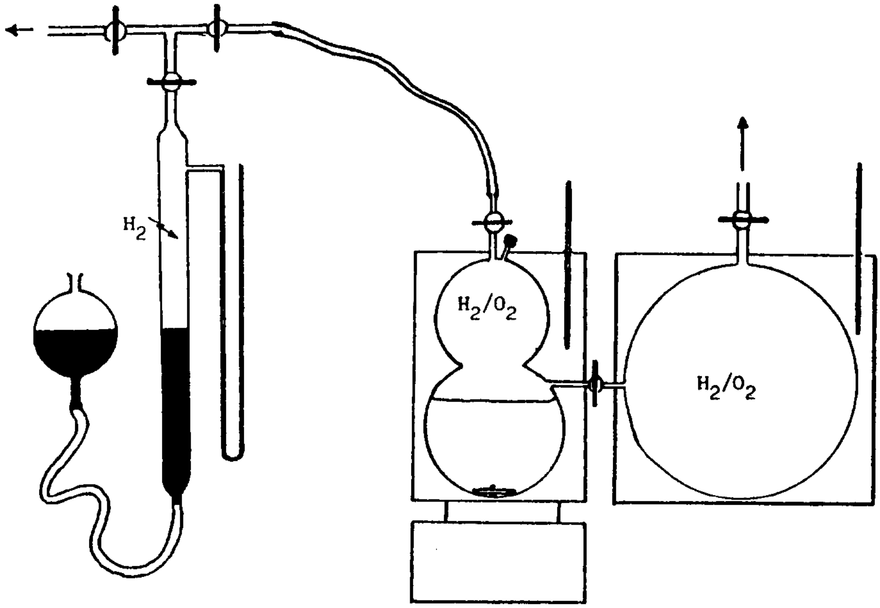


Fig. 12. Apparatus for separation of gas mixtures: H_2/O_2 separation shown.

become diffusion-controlled. To avoid this, all the O_2 to be absorbed is initially in the dead space above the solution. As the uptake of O_2 proceeds, the apparatus is maintained at atmospheric pressure via additions of H_2 from the gas burette. This in turn yields the quantitative uptake data.

To begin an uptake, the dead space volume above the solution is evacuated since the solution is normally stored under argon. This space is then filled with the pre-cooled gas mixture from the gas mixture reservoir. The whole apparatus is brought to atmospheric pressure via the gas burette using H_2. The initial volume of the gas burette is noted and the initial gas mixture sampled via the septum cap G, employing a gas-tight syringe. This is repeated at regular time intervals during the experiment.

The complex chosen for this study was $[Mn(PBu_3^n)I_2]$ in THF solution. There were a number of reasons for the choice of this particular complex; firstly, the complex is active only at −40 °C and, hence, is highly reversible when subjected to temperature and/or pressure swings. Secondly, the complex is, relatively, quite soluble and moderate uptakes of O_2 can therefore be accomplished on the uptake cycle. Thirdly, this complex is very robust to oxygenation/deoxygenation cycles and has been widely studied; its isotherm is shown in Fig. 13. Lastly, as can be seen in Fig. 13, the complex absorbs dioxygen at low partial pressures; hence, the final sample of gas remaining will contain very small amounts of dioxygen and be essentially pure hydrogen.

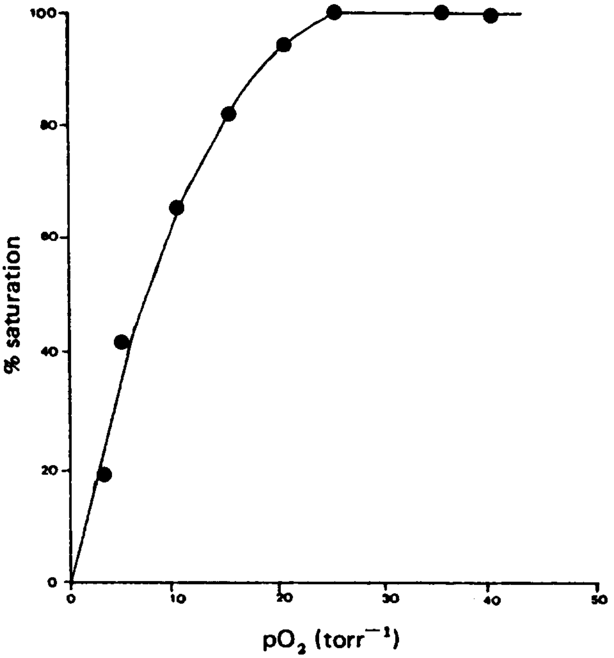


Fig. 13. The solution isotherm of $Mn(PBu_3^n)I_2$ at —40 °C in THF solution.

Calibration of recorder response

Before commencing any separation experiments, the recorder response was calibrated to dioxygen. To achieve this, five H_2/O_2 mixtures were prepared, Table 8, and the recorder response for each mixture noted. This was repeated five times to achieve a consistent reading for a given gas mixture. (It is not possible to use this method to follow the H_2 peak height in a linear fashion as with O_2.)

TABLE 8

Recorder calibration data

$p(O_2)$ (torr^{-1})	Recorder response (units)
159.6	71
80	43
40	18
20	12
10	7.5
0	5

TABLE 9

H_2/O_2 separation data for pure THF

Time (min^{-1})	Recorder response (units)	Volume absorbed (cm^3)	$p(O_2)$ ($torr^{-1}$)
0	58	—	128.0
5	45	13.1	106.5
10	37	24.5	87.5
15	34	30.3	80.0
20	30	35.2	70.0
25	28	39.1	64.5
30	25.2	42.5	58.5
35	25.2	42.5	58.5

Blank uptake of dioxygen from the H_2/O_2 mixture

Into the gas separation flask, 200 cm^3 of THF were freshly distilled and a 'blank' run performed on the pure solvent exactly as described in the previous section. These results are given in Table 9.

Separation of H_2/O_2 by $Mn(PBu_3^n)I_2$ in THF solution

Into the gas separation apparatus, Fig. 12, 200 cm^3 of a 1.59×10^{-2} molar solution of $[Mn(PBu_3^n)I_2]$ was introduced. Since the overall volume of the reaction flask was found to be 660 cm^3, we therefore have 460 cm^3 of the gas mixture above the solution. The partial pressure of dioxygen in this gas sample was found to be 128 torr. Hence we have 77.5 cm^3 of O_2 in this gas sample. Now 200 cm^3 of a 1.59×10^{-2} molar solution of $[Mn(PBu_3^n)I_2]$ in THF at −60 °C will absorb 113.2 cm^3 of O_2 (blank for 200 cm^3 THF = 42 cm^3 O_2), thus the $p(O_2)$ of the gas sample should fall to *ca.* 0. The results are given in Tables 10 and 11, and Figs. 14 and 15.

TABLE 10

Dioxygen partial pressure during separation

Time (min^{-1})	Recorder response (units)	$p(O_2)$ ($torr^{-1}$)
0	53	128
1	49	115
2	43.5	100
3	42	98
4	39	90
5	35.5	85
6	30.6	71
12	14.5	32.5
18	4.5	0
24	4.5	0

TABLE 11

Percentage composition of H_2 and O_2 during separation

Time (min)	$p(O_2)$ (torr)	Vol O_2 absorbed (cm^3)	Composition (%)	
			O_2	H_2
0	128	0	16.8	83.1
1	115	7.9	15.1	84.9
2	100	17.0	13.2	86.8
3	98	18.2	12.9	87.1
4	90	23.0	11.8	88.2
5	85	26.0	11.2	88.8
6	71	34.5	9.3	90.7
12	32.5	57.8	4.3	95.7
18	0	77.5	0	100
24	0	77.5	0	100

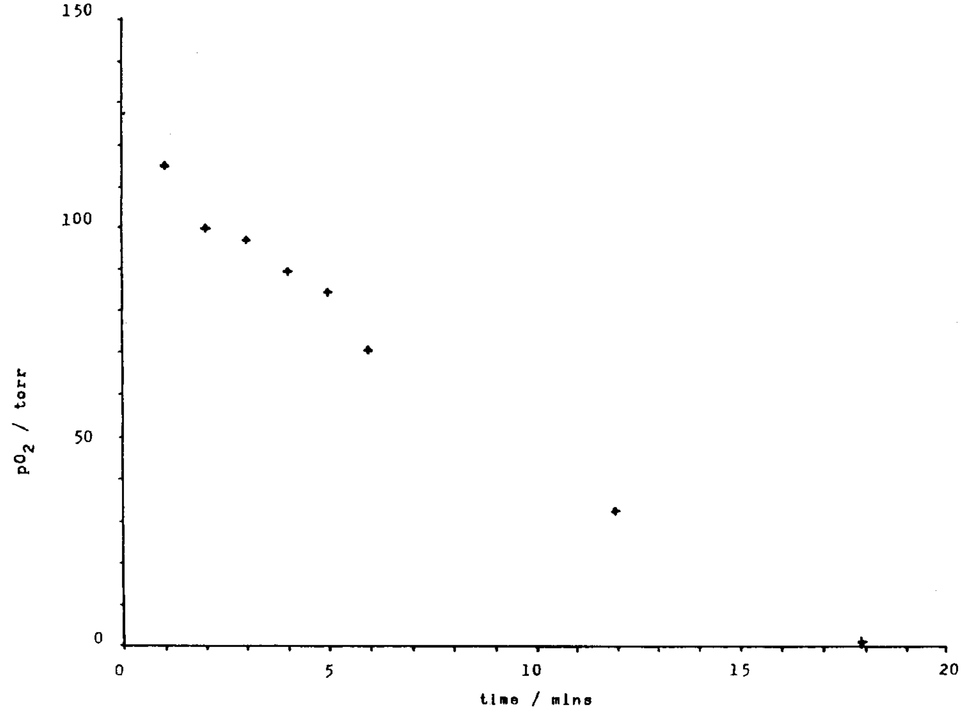


Fig. 14. $p(O_2)$ during gas separation experiment.

The results clearly show that, within the levels of detection, all the dioxygen is removed from the H_2/O_2 gas sample, yielding very pure H_2 above the solution and a solution of $[Mn(PBu_3^n)(O_2)I_2]$ in THF. The pure H_2 can be simply collected.

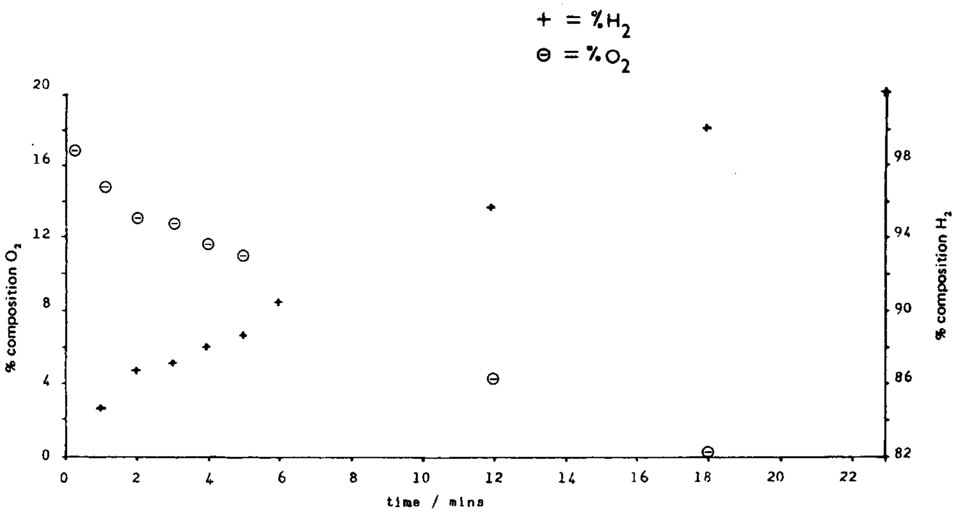


Fig. 15. Percent O_2 and H_2 during the gas separation experiment.

Separation of CO/H_2 by $Mn(PBu_3{}^n)I_2$ in THF

In a manner exactly analogous to that described above, the separation of CO/H_2 mixtures were investigated. The results are presented in Table 12 and Fig. 16.

These results show that in a manner similar to the H_2/O_2 separation described in the preceding section, the industrially important H_2/CO separation can also be achieved. In conclusion, then, we have demonstrated the

TABLE 12

Percentage composition of H_2 and CO during separation

Time (min^{-1})	p(CO) ($torr^{-1}$)	Vol CO absorbed (cm^3)	Composition (%)	
			CO	H_2
0	187.0	0	24.6	75.4
1	165.0	13.3	21.7	78.3
3	140.0	28.5	18.4	81.6
5	133.0	32.7	17.5	82.5
7	108.0	52.7	13.2	86.8
9	87.0	60.6	11.4	88.6
13	75.0	67.8	9.9	90.1
15	52.0	81.7	6.8	93.2
19	42.0	87.8	5.5	94.5
22	18.0	102.3	2.4	97.6
25	0	113.2	0	100
30	0	113.2	0	100

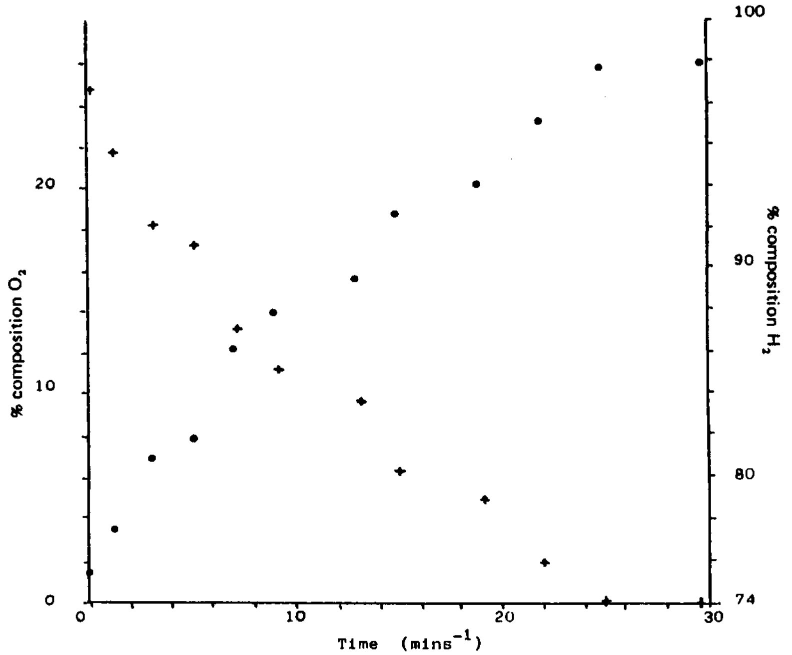


Fig. 16. Percent H_2 and CO during the gas separation experiment. ● = % H_2, + = % CO.

immense practical potential of this type of complex $Mn(PR_3)X_2$ to solve such gas separation problems.

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