Working Haem Analogues; Reversible Oxygenation of the Manganese–Tertiary Phosphine Complexes $MnLX_2$

By Charles A. McAuliffe,* Hussain Al-Khateeb, Martin H. Jones, William Levason, Karl Minten, and Francis P. McCullough

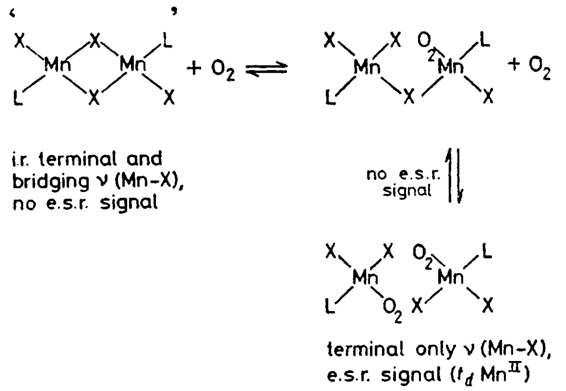
(*Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester* M60 1QD)

Summary The reversible oxygenation of the complexes $MnLX_2$ (L = tertiary phosphine, but not PPh_3, X = anion) has been investigated; these complexes resemble haemoglobin and myoglobin to a remarkable degree as reversible dioxygen carriers.

There is considerable current interest in mimicking the action of natural dioxygen carriers such as haemoglobin and myoglobin, and as well as several elegant steric approaches to the development of iron(II) porphyrins[1,2] there have been studies on cobalt(II) porphyrins.[3] Whilst these systems have significantly advanced our understanding of some of the factors which are important to the key concept of preventing iron-dimer formation and irreversible oxidation, their ability reversibly to co-ordinate dioxygen both rapidly and easily in the manner of the natural dioxygen transport and storage proteins is very poor.

We report preliminary data on some (> 200) compounds of formula $MnLX_2$ (L = tertiary phosphine but not PPh_3, X = anion) which we have prepared and characterised, the properties of which resemble to a remarkable degree the properties of both haemoglobin and myoglobin as dioxygen carriers.[4]

A very large number of tertiary phosphines co-ordinate to manganese(II) salts in a number of solvents leading to the isolation of complexes of empirical formula $MnLX_2$.† These complexes exhibit i.r. absorptions which are evidence of both terminal and bridging Mn–X linkages. Moreover, although their room temperature magnetic moments, μ_{eff} *ca.* 6·0 B.M., are equivalent to that expected for a high-spin $3d^5$ system, we do not observe e.s.r. signals for those complexes; it is well known that spin relaxation effects in M—X—M systems quench e.s.r. signals. These complexes in the solid state are certainly not monomers, and therefore we have indicated in the Scheme that they are at least dimeric, though a number of their reactions lead us to believe that they are tetrameric.[5] They may well have the well known cubane structure, $[MnLX_2]_4$.[6] These $MnLX_2$ complexes are pale in colour and react rapidly with molecular oxygen or with air to form deeply coloured red, blue, purple, or green complexes either in the solid state or in many non-hydroxylic solvents. In the solid state dioxygenation of the surface is complete in *ca.* 30—60 s, but full reaction to form $MnLX_2{\cdot}O_2$ can take up to 2—4 h depending on particle size. Our absorption–desorption measurements in the solid state were made on a vacuum microbalance. In tetrahydrofuran (THF) solution dioxygenation to form $MnLX_2{\cdot}O_2$ may be completed in *ca.* 3—5 min, this stoicheiometric absorption being followed by gas burette measurements and stoicheiometric desorption was followed by Toepler apparatus measurements together with gas chromatographic and mass spectral analysis of product gas. Repeated cycling without deterioration of the $MnLX_2$ species appears to depend on two factors: (i) $p(O_2)$ applied, and (ii) the temperature of the THF solution. The rate of absorption is dependent on $p(O_2)$ and the stability of the dioxygenated species is temperature dependent, *e.g.* for $Mn(PBu^n_3)Br_2$ at 0 °C we obtain >50% dioxygenation at $p(O_2) < 150$ Torr in 3 min, with no detectable decomposition of the dioxygenated species after 3 weeks. We have determined ΔH for the dioxygenation of $Mn(PPhMe_2)Br_2$ in the solid state and find it comparable to that for a number of myoglobin systems (Table 1).



SCHEME. Reactions of the complexes in the solid state or in toluene solution.

TABLE 1. ΔH for oxygenation.

Complex	ΔH/kcal mol^{-1}
Cobaltmyoglobin (whale)	−13·3
(Ferro)myoglobin ,,	−17·5
(Ferro)myoglobin (human)	−13·0
$Co(salen)(Me_2SO)^a$	−16·0
$Mn(Me_2PPh)Br_2$	−12·6

[a] $H_2salen = o\text{-}HOC_6H_4CH{=}NCH_2CH_2N{=}CHC_6H_4OH\text{-}o$.

In the solid state these $MnLX_2$ complexes appear to have almost indefinite stability to repeated oxygenation ⇌ deoxygenation cycles and this equilibrium is a function of partial pressure of dioxygen entirely analogous to that for the proteins haemoglobin and myoglobin.[7] The remarkable similarity of these compounds to the natural proteins in this respect is seen in Figure 1 which contains some solid state isotherms. The sigmoidal shape of these curves, evidence of 'co-operativity,' for $Mn(PBu^n_3)(NCS)_2$ and $Mn(PPhEt_2)Br_2$, and the hyperbolic curve for $Mn(PPhMe_2)Br_2$ indicates that the former pair are true analogues of haemoglobin and that the latter represents a true analogue of myoglobin. These complexes can undergo many thousands of oxygenation ⇌ deoxygenation cycles both in the solid state and in THF solution without apparent deterioration and complexes synthesised more than four years ago still exhibit activity. They may be stored in a dry atmosphere either as $MnLX_2$ or $MnLX_2{\cdot}O_2$.

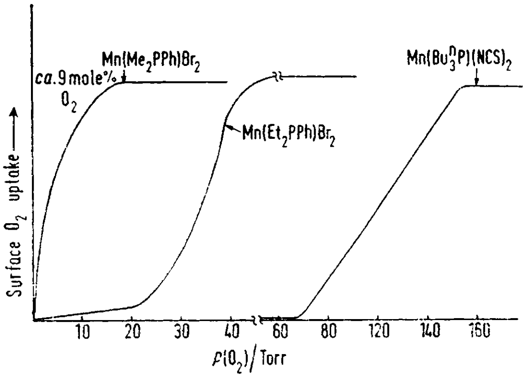


FIGURE 1. O_2 absorption isotherms. With finely divided solid samples *ca.* 9% of the calculated molar equivalent of O_2 is rapidly absorbed on the surface. In contrast, further uptake of O_2 is slow and can take *ca.* 2 h to reach the full stoicheiometric amount $Mn(PR_3)X_2{\cdot}O_2$.

---

† Some analytical data: found (calc.) $Mn(PPhMe_2)Br_2{\cdot}O_2$, C, 24·4 (24·9); H, 3·2 (2·9); P, 7·9 (8·1); Br, 42·0 (41·5); Mn, 14·4 (14·3); $Mn(PPhMe_2)I_2{\cdot}O_2$, C, 20·4 (20·1); H, 2·4 (2·3); P, 6·5 (6·5); I, 52·9 (53·0). Satisfactory analyses have also been obtained for the $MnLX_2$ species.

These compounds have practical potential. For example, $Mn(PBu^n_3)(NCS)_2$ binds O_2 at ambient partial pressure in air and begins to lose O_2 as the partial pressure drops below ambient (Figure 1). It could thus possibly be used in a pressure swing absorption (PSA) process for separating dioxygen from air and offers considerable potential savings over the energy-intensive cryogenic method of air separation currently used, and has considerable efficiency advantages over current PSA materials, such as carbon sieves, which cannot separate argon from the dioxygen produced; the resulting gas contains up to 4·5% argon and is thus not useful in steel cutting. $Mn(PPhMe_2)Br_2$ binds dioxygen at almost zero partial pressure (Figure 1) and thus is an excellent material for scavenging minute traces of dioxygen from inert gases; for example, we estimate that $Mn(PPhMe_2)Br_2$ is capable of removing O_2 in p.p.b. from N_2 streams. This may be applicable to O_2-sensitive chemical reactions and the manufacture of materials for the electronics industries.

The properties of the $MnLX_2$ complexes are extremely sensitive to changes in both L and X. For example, changing L = $PPhMe_2$ to L = $PPhEt_2$ in $MnLX_2$ not only shifts the isotherm (Figure 1) but also changes its shape from hyperbolic to sigmoidal.

The room temperature magnetic moments of the $[MnLX_2 \cdot O_2]$ complexes, μ_{eff} *ca.* 6·9 B.M., indicate a system containing six unpaired electrons. We have considered various possibilities to account for this. The most plausible is that there are two types of $MnLX_2 \cdot O_2$ complexes co-existing as 50:50 mixtures, *i.e.*, 50% exist as $Mn^{II}LX_2 \cdot (^3O_2)$ (and hence have a total of seven unpaired electrons) and 50% exist as $Mn^{II}LX_2 \cdot (^1O_2)$ (and hence have a total of five unpaired electrons), giving an average magnetic moment equivalent to six unpaired electrons. The following evidence is consistent with this theory: (i) the dioxygen is co-ordinated as neutral O_2 and not as superoxide or peroxide; the i.r. spectra clearly show bands at 1402—1430 cm^{-1} assignable to neutral O_2 [$^3O_2$ absorbs at 1556 cm^{-1}[8] and O_2 ($^1\Delta$) absorbs at 1483 cm^{-1}[9]] (Table 2); (ii) in surface dioxygenation of $MnLX_2$ the e.s.r. spectrum remains quenched until 50% of the dioxygen is added, and after this the e.s.r. signal grows as the remaining 50% is taken up (also the e.s.r. signal is typical of Mn^{II} and there is no evidence of a superoxide signal[10]); (iii) it is clear that in dioxygenation in THF solution the two visible absorption bands which develop (Figure 2) do so at vastly different rates, strong evidence for two species in solution.

TABLE 2. ν(O–O) for $MnLX_2 \cdot O_2$ complexes.

X	L	ν(O–O)/cm^{-1}[a]
Cl	$PPhMe_2$	1416
Br	,,	1409
Cl	PPr^n_3	1430
Br	,,	1409
I	,,	1402br
I	PBu^n_3	1403br

[a] Band disappears on deoxygenation of complex.

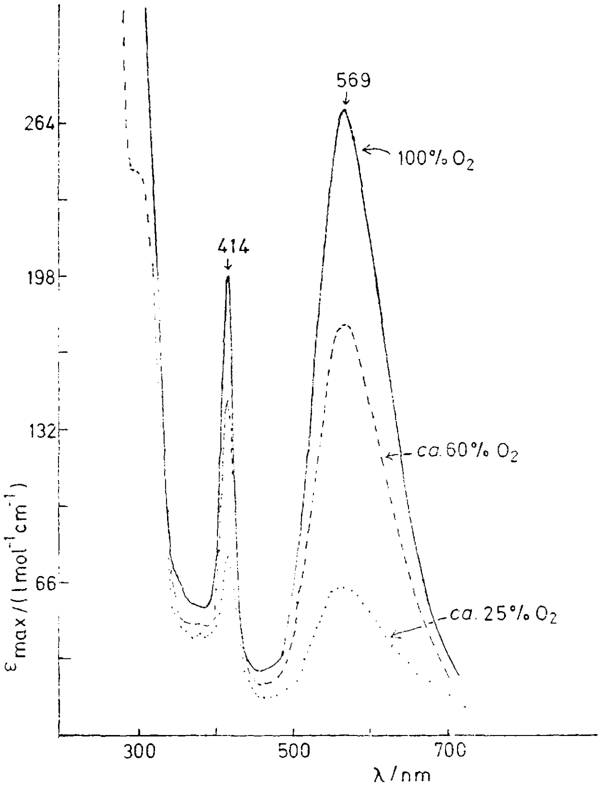


FIGURE 2. Electronic spectrum of $Mn(PBu^n_3)Br_2 + O_2$ in THF at 0 °C; $p(O_2)$ *ca.* 150 Torr.

A full account of this work[11] and the reactions of these complexes with other small molecules will be published shortly.[12]

We thank the S.R.C., The Burmah Oil Company, The British Oxygen Company, and The National Research Development Corporation for support, and Dr. R. D. Sedgwick and Mr. N. Royster for aid with gas analysis.

(*Received, 7th November* 1978;‡ *Com.* 1201.)

---

‡ Received in revised form 18th May 1979.

[1] J. E. Baldwin and J. Huff, *J. Amer. Chem. Soc.*, 1973, **95**, 5757; J. Almog, J. E. Baldwin, and J. Huff, *ibid.*, 1975, **97**, 227.

[2] J. P. Collman, R. R. Gagne, C. A. Reed, W. T. Robinson, and G. A. Rodley, *Proc. Nat. Acad. Sci. U.S.A.*, 1974, **71**, 1326; J. P. Collman, R. R. Gagne, C. A. Reed, and W. T. Robinson, *J. Amer. Chem. Soc.*, 1975, **97**, 1427.

[3] F. Basolo, B. M. Hoffman, and J. A. Ibers, *Accounts Chem. Res.*, 1975, **8**, 384.

[4] U.K. P. Appl. 8547/78, 8548/78.

[5] C. A. McAuliffe and M. H. Jones, manuscript in preparation.

[6] R. S. Nyholm, M. R. Truter, and C. W. Bradford, *Nature*, 1970, **228**, 648.

[7] A synopsis of the structure and dioxygen-binding mechanism of haemoglobin is given in F. A. Cotton and G. Wilkinson 'Basic Inorganic Chemistry,' Wiley, New York, 1976, p. 553.

[8] G. McLendon and A. E. Martell, *Co-ord. Chem. Rev.*, 1976, **19**, 1.

[9] L. Hertzberg and G. Hertzberg, *Astrophysics J.*, 1947, **105**, 133.

[10] B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 135.

[11] C. A. McAuliffe, H. Al-Khateeb, and F. P. McCullough, manuscript in preparation.

[12] C. A. McAuliffe, D. Edwards, K. Minten, and F. P. McCullough, manuscript in preparation.