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The Structure and Reactivity of Dioxygen Complexes of the Transition Metals

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This article gives a review of complexes in which a dioxygen ligand is bonded to a transition metal. Three aspects of these complexes are discussed in detail: the structure, the electronic structure, and the reactivity. The structural section summarises the recent X-ray crystal structure determinations, and the structural data obtained by other methods. The electronic structure is first considered in qualitative terms which allow the rationalisation of the different structures observed, and this qualitative model is compared with the results of calculations and with spectroscopic data. The reactivity of the complexes is discussed separately for each structural class in terms of the electronic structure. An attempt is made to compare the results obtained in historically different areas of research. Our objective is to give a clear summary of current knowledge of these compounds for workers interested in their application to catalysis and in their rôle in biochemical systems.

Structure and Bonding 55

A. Introduction

The study of dioxygen complexes of the transition metals is generally accepted to have begun with the report by Frémy in 1852 of the oxygenated ammoniacal salts of cobalt[1]. A satisfactory explanation of his results had however to await the development of a general theory of coordination compounds and the dioxygen bridged complexes of cobalt(III) figured among the many complexes studied by Werner at the turn of the century[2]. In the nineteen thirties the mechanism of the auto-oxidation of metal ions was studied and the first synthetic oxygen carriers discovered. In 1936, Pauling and Coryell proposed the first of many theoretical models to explain the iron dioxygen interaction in haemoglobin[3]. The increasing availability of physical methods allowing the ready characterisation of dioxygen complexes and the determination of their molecular structures, coupled with a better understanding of the electronic structures, has given considerable encouragement to the study of these compounds in recent years. The early work tended to concentrate on specific types of complex, and we may distinguish three basically different areas of research

(i) Complexes of cobalt with Schiff bases and nitrogen-containing ligands
(ii) Complexes of group VIII metals in low oxidation states.
(iii) Biological systems where transition metals (especially iron and copper) are known to be intimately involved in reactions with molecular oxygen. This field includes innumerable simpler "model" complexes, and covers systems which act as oxygen carriers as well as those acting as redox systems.

The distinctions between these topics have become somewhat blurred with the passing of time, and the increasing availability of good crystal structure data has brought to light many similarities between apparently different complexes. In 1976 Vaska[4] published an important paper classifying dioxygen complexes according to their molecular geometry, and showing that the complexes for which data were available fell into four closely related categories, and that the well known peroxo complexes of the early transition metals[5] were also structurally similar to many complexes of dioxygen.

From a practical point of view the study of the chemistry of dioxygen complexes has considerable interest Complexation of molecular oxygen by a transition metal has been widely adopted by biological systems as a means of reducing the considerable kinetic barrier to the reduction of O_2 Quite apart from the inherent interest of the biological systems, the transition metal complexes offer the possibility of efficient catalysis of auto-oxidation reactions, and have recently attracted interest as possible catalysts for the reduction of O_2 in fuel cells[6].

In this review we shall take Vaska's structural classification as the basis for the examination of the electronic structure and reactivity of dioxygen complexes. We wish to follow Vaska's unifying approach to the chemistry of these systems and to give as general a coverage as possible, and it is therefore impossible to discuss all the published work in a review of this length. Many reviews on the chemistry of these complexes have been published, dealing with general properties[4, 7, 8], complexes of cobalt with Schiff bases and nitrogen ligands[9, 10], complexes of group VIII metals[11, 12], catalysis by dioxygen complexes[13-16] and biological subjects[17, 18] including oxygen carriers[19-21] and redox systems[22-26] These reviews may be consulted for more detailed discussion of particular topics

B. Properties of Molecular Oxygen

For the purposes of this review we shall reserve the term molecular oxygen for free gaseous O_2; in cases where the O_2 entity is bound to other atoms we shall use the term dioxygen. This is a *structural* definition which requires only the continued existence of O-O bonding in the complex molecule, and gives no information on the bonding of the O_2 species.

The electronic structure of molecular oxygen in its ground state $^3\Sigma_g^-$ is well known (Fig. 1). The two lowest excited states of molecular oxygen, the $^1\Delta_g$ and $^1\Sigma_g^+$ are obtained by pairing the spins of the two electrons in the π_g^* orbital, and lie respectively at 94.2 and 156.9 kJ/mol above the ground state $^3\Sigma_g^-$ 27).

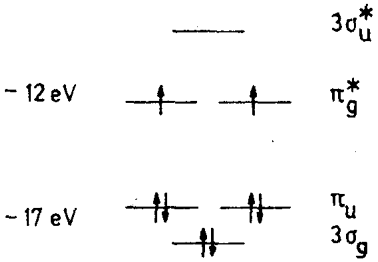


Fig. 1. The molecular orbitals of molecular oxygen

The triplet ground state of molecular oxygen provides a considerable kinetic barrier to the auto-oxidation of normally diamagnetic organic molecules where reactions involving change of spin are generally very slow, and where products formed in triplet states are unstable. This barrier may be circumvented in three ways:

(i) the formation of the lowest singlet state (by photochemical activation) where the spin conservation barrier is removed28);

(ii) reaction with radical species or the free electron in two distinct steps to give diamagnetic products;

(iii) reaction with a heavy element such as a transition metal where greater spin-orbit coupling considerably reduces the kinetic barrier to change of spin, and where the formation of a metal dioxygen complex may itself provide sufficient energy to pair the spins.

The ions arising from simple one electron reductions or oxidations of molecular oxygen are well characterised and their properties summarised in Table 1.

The possible importance of partially reduced dioxygen species in biochemical reactions has led to a reinvestigation of their equilibria in aqueous solutions45–47) and the values obtained are summarised in Table 2.

Several interesting points arise from these data. The potential for the first one electron reduction of molecular oxygen is unfavourable and gives the unstable superoxide anion. This and the other possible intermediates (H_2O_2 and HO) are notably more reactive than free molecular oxygen and most biological systems appear to have taken steps to eliminate them. O_2^- is eliminated by superoxide dismutase47–49) which catalyses the highly favourable reaction:

Table 1. Properties of some dioxygen species

Species	Bond order	Compound	O-O distance		$\nu_{O\text{-}O}$		Bond energy	
			Å	Ref.	cm^{-1}	Ref.	kJ/mol	Ref.
O_2^+	2.5	O_2AsF_6	1.123	30	1858	31	625	32
$O_2(^3\Sigma_g^-)$	2	O_2	1.207	30	1555	32	490	19
$O_2(^1\Delta_g)$	2	O_2	1.216	29	1484	33	396	32
O_2^-	1.5	NaO_2	1.33	34				
		KO_2	1.32–1.35	35	1146	37		
		$O_2^-(g)$	1.34	36				
O_2^{2-}	1	$H_2O_2(g)$	1.475	38				
			1.467	39				
		$H_2O_2(l)$			880	37		
		$H_2O_2(s)$	1.453	39				
		Na_2O_2	1.50	40	794	42	204	19
			1.49	41	738[a]			
		$Na_2O_2 \cdot 8H_2O$			842	42		
		BaO_2	1.49	43				
		CdO_2	1.49	44				

[a] There are two different peroxide ions in the unit cell

Table 2. Equilibria in aqueous solution

Reaction	Electrode potential (volts)	
	pH = 0	pH = 7
$O_2 + e^- \rightarrow O_2^-$	−0.33	−0.33
$O_2^- + 2H^+ + e^- \rightarrow H_2O_2$	+1.69	+0.87
$H_2O_2 + H^+ + e^- \rightarrow H_2O + HO$	+0.793	+0.38
$HO + H^+ + e^- \rightarrow H_2O$	+2.76	+2.33
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+1.23	+0.82

Values calculated for aqueous solutions at 25 °C with $P_{O_2} = 1$ atmosphere. $[O_2^-] = [H_2O_2] = [HO] = 1\,M$

$$2O_2^- + 2H^+ \rightarrow O_2 + H_2O_2$$

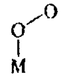
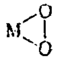
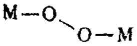
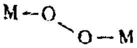
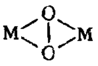
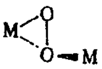
and ensures that the molecular oxygen liberated is exclusively in the less reactive $^3\Sigma_g^-$ state. H_2O_2 is eliminated by peroxidases. The OH radical, generally thought to be formed in acidic aqueous solutions of Fenton's reagent (hydrogen peroxide and a ferrous salt) is extremely reactive towards organic substrates[50, 51] and probably reacts in a non-specific way before it may be eliminated. The very reactivity of these intermediates justifies the use by biological systems of metal ion mediated pathways of molecular oxygen reduction.

Much of the experimental work on oxygen chemistry has been carried out in non-aqueous solvents and the thermodynamic data of Table 2 may not be applied to such systems. Molecular oxygen is appreciably more soluble in organic solvents than in water (the solubilities differ by a factor of ten between water and diethyl ether)[52]. Groves[51] has shown that Fenton's reagent in non-aqueous solutions does not produce OH radicals but rather a reactive Fe(IV) (ferryl) species. A change of solvent can thus have a considerable effect on the mechanism of oxygen reduction.

C. Structural Classification of Dioxygen Complexes

In his review[4], Vaska showed that every dioxygen complex whose structure was then known fell into one or other of 4 structural types. This structural classification has proved extremely useful in discussing the properties of dioxygen, and in this section we discuss the classification and review structural data published since 1976. Vaska's four structural types are the first four entries in Table 3; he grouped the four structures into the superoxo compounds (types I a and I b) where the O-O distance is roughly constant (~ 1.3 Å) and close to the value reported for the superoxide anion (Table 1), and the peroxo compounds (types II a and II b) where the O-O distance is close to the values reported for H_2O_2 and O_2^{2-} (~ 1.48 Å). The a or b classification distinguishes complexes where the dioxygen is bound to one metal atom (type a) or bridges two metal atoms (type b). In this review we shall use a "hapto" nomenclature in which the structures are classified by the number of atoms of dioxygen bound to the metal ion; although this does not distinguish explicitly between types I b and II b, it does avoid assigning a possibly misleading oxidation state to the dioxygen (see Sect. D) and may readily be applied to the structural types discovered since Vaska's review.

Table 3. Structural classification of dioxygen complexes

Structure type	Structural designation	Vaska classification	Example
	η^1dioxygen	Type I a (superoxo)	$[Co(CN)_5O_2]^{3-}$
	η^2dioxygen	Type II a (peroxo)	$(Ph_3P)_2PtO_2$
	$\eta^1:\eta^1$dioxygen	Type I b (superoxo)	$[(H_3N)_5CoO_2Co(NH_3)_5]^{5+}$
	$\eta^1:\eta^1$dioxygen	Type II b (peroxo)	$[(H_3N)_5CoO_2Co(NH_3)_5]^{4+}$
	$\eta^2:\eta^2$dioxygen	-	$[(UO_2Cl_3)_2O_2]^{4-}$
	$\eta^1:\eta^2$dioxygen	-	$[(Ph_3P)_2ClRh]_2O_2$

The $\eta^2:\eta^2$ structure with a "sideways" bound dioxygen bridging two metal atoms has been suggested for the complex $[\{Rh(diene)\}_2O_2]$[53] and a crystal structure showing this geometry has been reported for the uranium complex $[(UO_2Cl_3)_2O_2]^{4-}$[54] and a complex of La^{3+}[55]. The $\eta^1:\eta^2$ structure (Fig. 2) is known only for $[RhCl(O_2)(PPh_3)_2]_2$[56].

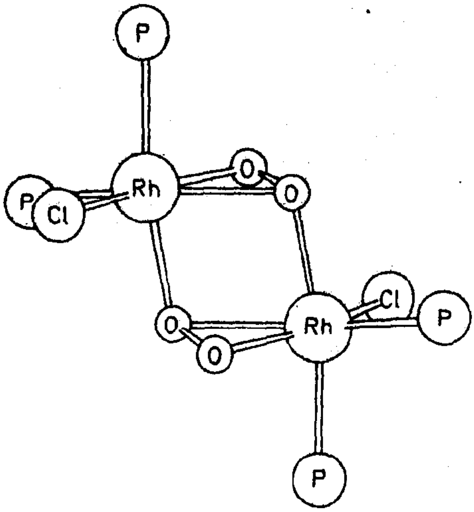
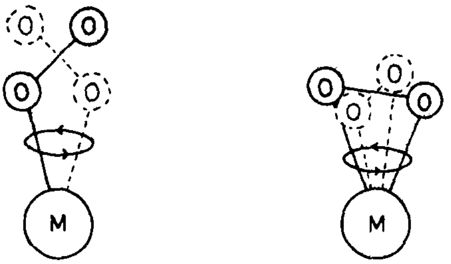


Fig. 2. The structure of $[(Ph_3P)_2RhCl(O_2)]_2$ (Ref. 56)

The only completely unambiguous method of structure determination has proved to be X-ray diffraction. Vaska noted however that the stretching frequencies attributed to the O-O vibration were closely related to the structural type[4]. Type I complexes show O-O stretching vibrations around 1125 cm^{-1} and type II around 860 cm^{-1}. This sharp difference enables the O-O stretching frequency as measured by infra-red or Raman spectroscopy to be used to assign the structure type, provided (as is usually the case) the formation of a dinuclear species can be confirmed or excluded by other means.

If X-ray diffraction gives an unambiguous description of the structure, it should nevertheless be noted that the accurate determination of bond lengths and angles for the coordinated dioxygen is not always easy. When the dioxygen is bonded closely to a very



(a) (b)

Fig. 3a, b. Disorder in dioxygen complexes heavy transition metal (for example Ta or Ir), precise location of the oxygen atoms is difficult, and independent determinations of the same structure do not always agree[57]. A second problem is the possible presence of disorder in the dioxygen bonding, especially in the non-bridging systems. In $[Co(CN)_5O_2]^{3-}$ the dioxygen was found to show rotational disorder as shown in Fig. 3 a[58], and a recent n.m.r. study of complexes of the type Ti(porphyrin)O_2 has shown a low barrier to rotation as shown in Fig. 3 b[59]. Bond angles and distances which deviate sharply from the average values should therefore be interpreted with prudence.

Tables 4–6 report the structural parameters of complexes studied by X-ray diffraction since the publication of Vaska's review, together with some of the more significant results published beforehand. Structural information obtained by other methods is discussed separately.

Structural investigations using methods other than X-ray diffraction have also provided much useful information, and in the remainder of this section we review some of the results obtained from such investigations.

Titanium Complexes

An η^1 dioxygen complex has been prepared as an intermediate in the auto-oxidation of Ti^{3+} complexes, and E.P.R. evidence for such a species has come from studies of the auto-oxidation of Ti(TPP)F trapped in a matrix of Ti(TPP)O[124], however, in contrast with the η^1 dioxygen complexes of cobalt, the spin density is only weakly localised on the dioxygen, and is quite high on the porphyrin ligand. E.P.R. spectroscopy has also been used to demonstrate an η^1 dioxygen species formed during the auto-oxidation of a Ti(III)

Table 4. Structural details of η^1dioxygen (Vaska type I a) complexes

Complex	O-O (Å)	M-O (Å)	M-O-O angle (deg.)	Ref.
$[Co(bzacen)pyO_2]$	1.26	1.86	126	60
$[Co(acacen)pyO_2]$		1.95		61
$[Co(salen\text{-}C_2H_4\text{-}py)(O_2)]$	1.1		136	58
$[Co(CN)_5O_2]^{3-}$	1.240	1.904	153	58
$[Co(t\text{-}Bu\text{-}saltmen)(BzIm)O_2]$	1.27^a	1.882	117.5	62
	1.26^b	1.974	118.5	62
$[Co(3F\text{-}saltmen)(MeIm)O_2]$	1.302^c	1.881	117.4	63
$[Co(saltmen)(BzIm)O_2]$	1.277	1.889	120.0	64
$[Co(3\text{-}t\text{-}Busalen)(py)O_2]$	1.35	1.87	116.5	248
oxycobaltmyoglobin	1.26	1.89	131	65
$[Fe(TpivPP)(MeIm)(O_2)]$	1.16	1.75	131	66
oxymyoglobin	1.25^d	1.83	115(5)	67
oxyerythrocruorin	1.25	1.8	170(30)	68
$[Fe(TpivPP)(2MeIm)(O_2)]$	1.22	1.898	129	69, 70
oxyhaemoglobin		1.67, 1.83	156(10)	71

^{a} at − 152 °C; ^{b} at room temperature; ^{c} at − 171 °C; ^{d} constrained to this value.
For ligand abbreviations, see Table 7.

Table 5. Structural details of $\eta^1:\eta^1$dioxygen complexes

Complex	O-O (Å)	M-O (Å)[a]	M-O-O (deg.)[a]	Dihedral angle (deg.)[b]	Ref.
(i) Vaska type Ib complexes					
$[(H_3N)_5Co(O_2)Co(NH_3)_5]^{5+\,c}$	1.31	1.89	118	175	72, 73
$[(H_3N)_5Co(O_2)Co(NH_3)_5]^{5+\,d}$	1.32	1.89	117.3	180	74
$[(en)_2Co(O_2;\,NH_2)Co(en)_2]^{4+}$	1.35	1.88	119	23.4	75, 76
$[(H_3N)_4Co(O_2;\,NH_2)Co(NH_3)_4]^{4+}$	1.320	1.867	120.9	0.0[e]	77
$[(en)_2Co(O_2;\,OH)Co(en)_2]^{4+}$	1.339	1.875	119.9	22.0	78
$[(NC)_5Co(O_2)Co(CN)_5]^{5-\,f}$	1.29	1.92	120.7	180	79
$[(NC)_5Co(O_2)Co(CN)_5]^{5-}$	1.24	1.94	121.2	165.9	79
(ii) Vaska type IIb complexes					
$[(H_3N)_5Co(O_2)Co(NH_3)_5]^{4+\,g}$	1.473	1.883	112.8	145.8	80
$[(H_3N)_5Co(O_2)Co(NH_3)_5]^{4+\,h}$	1.469	1.879	110.8	180	81
$[(H_3N)_5Co(O_2)Co(NH_3)_5]^{4+\,d}$	1.472	1.886	110.9	180	82
$[(dien)(en)Co(O_2)Co(en)(dien)]^{4+}$	1.488	1.896	110.0	180	83
$[(tren)(H_3N)Co(O_2)Co(NH_3)(tren)]^{4+}$	1.511	1.889	111.5	180	84
$[(O_2N)(en)_2Co(O_2)Co(en)_2(NO_2)]^{2+}$	1.529	1.887	110.0	180	85
$[(pydpt)Co(O_2)Co(pydpt)]^{4+}$	1.456	1.891	114.3	162	86
$[(pydien)Co(O_2)Co(pydien)]^{4+}$	1.489	1.876	112.5	180	87
$[(papd)Co(O_2)Co(papd)]^{4+}$	1.486	1.924	111.9	180	88
$[(NC)_5Co(O_2)Co(CN)_5]^{6-}$	1.447	1.938	111.8	180	89
$[(H_2O)(salen)Co(O_2)Co(salen)]_2$	1.31	1.97	118	122	90
$[(DMF)(salen)Co(O_2)Co(salen)(DMF)]$	1.339	1.910	120.3	110.1	91
$[(salptr)Co(O_2)Co(salptr)]$	1.45	1.93	118.5	149.3	92
$[(pip)(salen)Co(O_2)Co(salen)(pip)]$	1.383	1.912	120.1	121.9	93
$[(dmtad)Co(O_2;\,OH)Co(dmtad)]^{3+}$	1.43	1.89	108.6	68.0	435
$[(en)_2Co(O_2;\,OH)Co(en)_2]^{3+\,i}$	1.465	1.863	110.3	60.7	78
$[(en)_2Co(O_2;\,OH)Co(en)_2]^{3+\,j}$	1.460	1.873	109.3	64.5	94
$[(tren)Co(O_2;\,OH)Co(tren)]^{3+}$	1.462	1.863	110.8	60.7	95
$[(tren)Co(O_2;\,tren)Co(tren)]^{4+}$	1.49	1.90	115.8	19.8	436
$[(Ph_3P)_2Pt(O_2;\,OH)Pt(PPh_3)_2]^{+}$	1.55	2.01	102.8	79.0	96

[a] average of two values; [b] angle between two M-O-O planes; [c] acid sulphate; [d] nitrate; [e] the Co-N-O-O ring is nearly planar; [f] two independent ions in the unit cell; the first ion is centrosymmetric; [g] sulphate; [h] thiocyanate; [i] racemate; [j] *meso* form

tartrate complex[125)], and also in the auto-oxidation of Ti(III) bound to a pyridine-based polymer[126)]. An η^2 dioxygen complex with dioxygen bound to a TiN_4 square pyramidal fragment has been reported[127)].

Vanadium Complexes

Complexes formed by the action of hydrogen peroxide on vanadium compounds have been known for many years and have recently been studied by ^{51}V n.m.r. spectroscopy[129)]. A report of the reversible formation of a dioxygen complex by vanadium(IV) catecholates has been re-investigated recently and refuted[130)].

Table 6. Structural details of η^2dioxygen (Vaska type IIa) complexes

Complex	O-O (Å)	Ref.
$Ti(OEP)(O_2)$	1.458	97
	1.445	59
$Ti(dipic)(OH_2)O_2$	1.469^a	98
	1.477^b	98
	1.458^b	99
$[\{Ti(NTA)(O_2)\}_2O]^{4-}$	1.469	100
	1.481	98
$[Ti(pic)_2(HMPT)O_2]$	1.419	101
$[Nb(O_2)F_5]^{2-}$	1.47	102
$Nb(\eta^5\text{-}C_5H_5)(O_2)Cl$	1.47	103
$[Ta(O_2)F_5]^{2-}$ ^{c}	1.39	104
$[\{Ta(O_2)F_4\}_2O]^{4-}$ ^{c}	1.64	104
$[Ta(O_2)F_3(MepyO)]$	1.55	105
$[MoO(O_2)F(dipic)]$	1.46	106
$Mo(T(p\text{-}Me)PP)(O_2)_2$	1.40	107
$[MoO(O_2)_2(py2c)]$	1.462	108
	1.467	108
$MoO(O_2)(pycc)$	1.447	108
$[\{MoO(O_2)(pycc)\}_2F]$	1.43	109
$MoO(O_2)(PhCON(Ph)O)_2$^{d}	1.21	110
$MoO(O_2)_2((s)\text{-}MeCH(OH)CONMe_2)$	1.459	111
	1.451	111
$[WO(O_2)F_4]^{2-}$	1.20	102
$[Co(2{=}phos)_2(O_2)]^+$	1.42	112, 118
$L_3(NC)_2Co(\mu CN)Co(CN)L_2(O_2)$, $L{=}PPhMe_2$	1.44	113
$[Co(\mathbf{R},\mathbf{R}\text{-}C_{24}H_{38}As_4)(O_2)]^+$	1.424	114
$[Rh(PPhMe_2)_4(O_2)]^+$	1.43	115
$[RhCl(O_2)(PPh_3)_2]_2$^{e}	1.44	56
$RhCl(O_2)(PPh_3)_2$	1.413	116
$[Rh(O_2)(dppa)_2]^+$	1.419	117
$[Rh(2{=}phos)_2(O_2)]^+$	1.43	118
$[Rh(AsPhMe_2)_4(O_2)]^+$	1.46	119
$[Ir(2{=}phos)_2(O_2)]^+$	1.38	118
$[Ir(O_2)(dppe)_2]^+$	1.52	57
$[Ir(PPhMe_2)_4(O_2)]^+$	1.49	120
$[Ir(O_2)(dppm)_2]^+$	1.45–1.50	121
$IrCl(PPh_2Et)_2(CO)(O_2)$	1.47	122
$Pd(PPh(t\text{-}Bu)_2)_2O_2$	1.37	123
$Pt(PPh(t\text{-}Bu)_2)_2O_2$	1.43	123

[a] Triclinic form; [b] Orthorhombic form; [c] both ions found in $K_6Ta_3(O_2)_3OF_{13} \cdot H_2O$; [d] disorder in oxide and peroxide positions; [e] $\eta^1:\eta^2$ complex

Table 7. Abbreviations of ligands

Ligand	Ligand
acacen	N,N′-bis(acetylacetone)ethylenediamine
[14]ane N_4	see cyclam
bipy	2,2′-bipyridine
bzacacen	N,N′-bis(benzoylacetone)ethylenediamine
bzIm	benzimidazole
cyclam	1,4,8,11-tetra-aza-tetradecane
dien	diethylenetriamine
dipic	dianion of dipicolinic acid
DMF	N,N-dimethylformamide
dmtad	4,7-dimethyl-1,4,7,10-tetraazadecane
dppa	bis(diphenylphosphino)amine
dppe	1,2 bis(diphenylphosphine)ethane
dppm	bis(diphenylphosphino)methane
EDTA	ethylenediaminetetraacetate
en	ethylenediamine
F-salen	N,N′-bis(3-fluorosalicyldene)ethylenediamine
3 F-saltmen	N,N′-bis(3-fluorosalicyldene)tetramethylethylenediamine
HMPT	hexamethylphosphortriamide
IDA	dianion of iminodiacetic acid
Im	imidazole
J-en	N,N′-ethylenebis(2,2 diacetylethylideneamate)
L	any unspecified ligand
MeIm or 1-MeIm	N-methylimidazole
MepyO	2-methylpyridine-N-oxide
NTA	nitrilotriacetate
OEP	octaethylporphinate
papd	1,5,8,11,15-pentaazapentadecane
Pc	phthalocyanine
2=phos	*cis*-1,2-bis(diphenylphosphino)ethene
pic	picolinate
pip	piperidine
Porph	porphinate
py	pyridine
pycc	(=dipic) dipicolinate
py2c	picolinate
pydien	1,9-bis(2-pyridyl)-2,5,8-triazanonane
pydpt	1,11-bis(2-pyridyl)-2,6,10-triazaundecane
salen	N,N′-bis(salicylidene)ethylenediamine
S-salen	N,N′-bis(thiosalicylidene)ethylenediamine
salen-C_2H_4-py	N,N′-bis(salicylidene)-1-(ethyl-2-pyridine)ethylenediamine

Table 7 (continued)

Ligand	Ligand
salptr	N,N"-bis(salicylidene)dipropanetriamine
saltmen	N,N'-bis(salicylidene)tetramethylethylenediamine
S-Me$_2$en	N,N'-dimethylethylenediamine
t-Bu-saltmen	N,N'(3-tert-butylsalicylidene)tetramethylethylenediamine
TpivPP	*meso*-tetra($\alpha,\alpha,\alpha,\alpha$-o-pivalamidophenyl)porphinate (picket fence porphinate)
T(p-Me)PP	*meso*-tetra(p-methylphenyl)porphinate
TPP	*meso*-tetraphenylporphinate
tren	tris(2-aminoethyl)amine
trien	triethylenetetramine

Chromium, Molybdenum and Tungsten Complexes

The infra-red spectrum of Cr(TPP)py(O_2) obtained by the oxygenation of a chromium(II) porphyrin complex suggests the presence of an η^1 dioxygen species[131]. The photolysis of chromium complexes such as $[Cr_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ in the presence of O_2 gives paramagnetic complexes which may be studied by E.P.R.[132, 297]. The g-values lie close to 1.99 and isotopic labelling studies suggest that the two oxygen atoms are equivalent (implying an η^2 geometry) with the spin localised essentially on the metal atom. Photolysis of $Cr(CO)_6$ in an O_2-doped Ar matrix leads to the dioxo-compound $CrO_2(CO)_2$[133]. Cr^{2+} in a zeolite matrix has been reported to show reversible uptake of O_2[134].

An η^1 complex is reported to be formed by the reaction of MoO(TPP)(NCS) with superoxide anion to give MoO(TPP)(O_2)[135]; the complex has been studied by E.P.R. and U.V. – visible spectroscopies. The peroxide complexes $MO(O_2)_2 \cdot LL'$ (M = Mo, W; L = amine oxide, tertiary phosphine or arsine oxide; L' = L, OH_2) have been studied by infra-red spectroscopy. The O-O stretching frequency lies between 811 and 930 cm^{-1}, the arsine oxides generally give the lowest frequencies[136]. A similar study has recently been reported for $[MoO(O_2)_2(C_2O_4)]^{2-}$ [137]. The complex $[Mo_2Al(O\text{-}iPr)_4]_2(CH_3COO)_2$ which contains a quadruple Mo-Mo bond is reported to add dioxygen irreversibly, giving a product with $\nu_{O\text{-}O} = 840\ cm^{-1}$ [138].

Manganese Complexes

Although manganese-dioxygen complexes have been intensively studied there is very little definite structural information and no crystal structure is available. A review of the subject has appeared fairly recently[139], and we give below some of the more recent work in this field.

The phthalocyanine complexes of manganese have been studied for many years [140]. The most recent work has established the formation of an η^1 dioxygen complex on oxygenation of [Mn(Pc)] in N,N-dimethylacetamide solution[141], and a similar result has been obtained for a tetra-sulphonated phthalocyanine derivative[142]. The porphyrin complex Mn(TPP)O_2 was assigned an η^2 structure on the basis of E.P.R. data[143] and this assignment has recently been supported by infra-red data using $^{18}O_2$[144]. Schiff base complexes of Mn(II) were reported to form dinuclear $\eta^1 . \eta^1$ complexes on oxygenation in

1970[145], and similar complexes have been reported recently, either by oxygenation of Mn(II)[146] or by addition of superoxide ion to Mn(II) complexes[147, 148]. Addition of two equivalents of superoxide to Mn(TPP)Cl gives a product identified as Mn(II)(TPP)(O_2^-)[309].

There have been several other reports of manganese dioxygen complexes, but unambiguous spectroscopic evidence is lacking. The photolysis of $Mn_2(CO)_{10}$ and its derivatives in the presence of dioxygen gives complexes identified as $Mn(CO)_5O_2$. E.P.R. studies, including isotopic labelling, suggest this complex to have an η^1 structure[149]. There have been several studies on the interaction of Mn(II) catechol complexes with dioxygen[150, 151] but it is not clear whether oxygen attack occurs on the metal or the ligand as has been proposed for similar iron complexes[152]. The complexes $MnLX_2$ (L = tertiary phosphines) are reported to show reversible oxygenation[153] but little structural information is currently available, and the oxygenation reaction is the subject of some controversy[154].

Iron and Ruthenium Complexes

Most work published on iron-dioxygen complexes has been concerned with analogues of haemoglobin and myoglobin. Attention has been focussed on methods of preventing dimerisation of the dioxygen complexes formed by methods such as bonding the deoxygenated complex to a polymer[155, 156] or the construction of suitably hindered porphyrins or similar macrocycles[66, 69, 70, 157–159]. The dioxygen complexes are assumed to have η^1 structure, and, since many reviews on the subject are available[17, 19–21, 160] we will concentrate here on the other dioxygen complexes of iron. There is, however, one possible exception to this uniformity of structure since it has been reported that a capped porphyrin with *two* coordinated 1-methyl imidazole groups is also capable of binding dioxygen[161], thereby giving an apparently 7 coordinate species. A recent development in this field is the synthesis of η^1 complexes in which the axial ligand is a sulphur donor as is thought to be the case in cytochrome P450[162].

Less information is available for other types of dioxygen complex. ^1H n.m.r. was used to establish the formation of the $\eta^1:\eta^1$ dioxygen complex P-Fe-O_2-Fe-P (P = porphyrin) in toluene at low temperatures[163, 495]. This species, which appears to contain two high spin Fe(III) ions antiferromagnetically coupled through a peroxide bridge, deoxygenates reversibly at low temperatures, but decomposes on warming to an μ-oxo species. The $\eta^1:\eta^1$ dioxygen complex appears to be very unstable, and careful work has shown that a previous claim to have isolated an analogous complex with phthalocyanine replacing the porphyrin is unjustified[164]. More recently relatively stable $\eta^1:\eta^1$ species have been reported to be formed on oxygenation of ferrous complexes of a pentacoordinate nitrogen macrocycle[165] and of the N_2S_2 ligand S-salen[166]. In the biological oxygen carrier oxyhaemerythrin[167] a similar Fe(III)-(O_2^{2-})-Fe(III) structure is generally accepted. The two iron atoms are in slightly different environments and are thought to be bridged by a second ligand, possibly an oxo group[168]. A careful study of the electronic spectra supports this assignment[169].

A recent study of the interaction of superoxide anion with Fe(II) porphyrins in dimethyl sulphoxide or acetonitrile has suggested the formation of an η^2 complex (porphyrin)FeO_2, which is formulated on the basis of infra-red, U.V.-visible, n.m.r., and E.P.R. spectroscopic measurements as (porphyrin)-Fe^{3+}(high spin)-O_2^{2-} [170, 309]. The E.P.R. spectrum differs from that of other high spin ferric porphyrin complexes but is similar to that of rhombic high spin ferric complexes such as $[Fe(III)EDTA]^-$. The complex $Mn(porphyrin)O_2$ discussed earlier also shows a rhombic E.P.R. spectrum and is thought to have an η^2 structure. The formation of an unstable complex between $[Fe(III)EDTA]^-$ and H_2O_2 has previously been reported and is known to contain high spin Fe^{3+} 171,172). The resonance Raman spectrum of this complex shows an O-O stretch at 824 cm^{-1} in agreement with this assignment173).

In more unusual conditions, the η^1 complex $Fe(TPP)O_2$ has been prepared by condensation of Fe(TPP) in an O_2 doped argon matrix174) and the condensation of iron atoms in a similar matrix has also been studied175). The photolysis of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$ in the presence of oxygen is reported to give $[Fe(\eta^5\text{-}C_5H_5)(CO)_2O_2]$149,297).

Ruthenium dioxygen complexes are less popular and most published work has been concerned with dioxygen addition to Ru(O) complexes, although the formation of a dioxygen complex analogous to the dioxygen-ferrous porphyrins has been reported 176). Ru(O) complexes such as $Ru(NO)(PPh_3)_2Cl$177) and $Ru(CO)(CNR)(PPh_3)_2$178) add dioxygen to give η^2 dioxygen complexes similar to the adducts of Ir(I) complexes (see below). The crystal structure of $Ru(NO)(PPh_3)_2Cl(O_2)$ has been reported as similar to that of the dioxygen adduct of Vaska's compound179). A report of dioxygen complex formation by $RuCl_2(AsPh_3)_3$ has recently been shown to involve oxidation of the arsine rather than complex formation180).

Recently two reports of interaction of dioxygen with Ru^{3+} have appeared. The complex of Ru^{3+} with EDTA appears to form an $\eta^1 : \eta^1$ dioxygen complex with a bridging OH ligand similar to many Co(III) complexes181) and Ru^{3+} in a zeolite has been shown to react with dioxygen to give Ru^{4+} and superoxide182).

Cobalt Complexes

The many dioxygen complexes of cobalt represent by far the best structurally characterised family of dioxygen complexes and many references to crystal structure determinations are given in Tables 4–6. These complexes typically contain an octahedral cobalt atom with the dioxygen ligand bonded in an η^1 fashion and frequently acting as a bridging ligand to another cobalt atom. The other ligands around the cobalt are typically polydentate amines or Schiff bases, porphyrins or macrocycles, and recently polydentate ligands containing sulphur and oxygen donors as well as nitrogen donors have been used183–185). These complexes have been reviewed extensively9,10,19,186) and we will discuss here only those complexes of particular structural interest. The numerous spectroscopic studies on these complexes will be discussed at the end of Sect. D.

Dimerisation of monomeric η^1 complexes to give $\eta^1 : \eta^1$ complexes (types I b or II b) may be restricted by working in non-polar solvents, at low temperatures or by using ligands which sterically hinder the dimerisation such as the picketfence porphyrins mentioned for iron. This appears to be relatively easy for cobalt complexes, and simple methylation of the nitrogen atoms of ethylenediamine allows the monomeric η^1 complex $[Co(S\text{-}Me_2en)_2XO_2]^{n+}$ to be studied in solution187). Resonance Raman spectroscopy has been used to follow the dimerisation reaction188). A recent paper reports the formation of η^1 and $\eta^1 : \eta^1$ complexes in aqueous DMF solution on oxygenation of Co(II) complexes of a water soluble Schiff-base189). Cobalt(II) phosphine complexes add dioxygen readily, but phenyl groups on the phosphorus ligands prevent dimerisation: $Co(CN)_2(PPhMe_2)_3$ forms an η^1 dioxygen adduct detectable by E.P.R.190) which decomposes to the cyanide bridged η^2 complex $[Co(PPhMe_2)_3(CN)_2\text{-}\mu(CN)\text{-}Co(CN)(PPhMe_2)_2(O_2)]$113), while

$[Co(2{=}phos)_2]^{2+}$ adds dioxygen to give $[Co(2{=}phos)_2(O_2)]^{+}$[191], an η^2 complex where the phenyl groups of the phosphine prevent dimerisation[192]. This compound may also be formed by addition of O_2 to a Co(I) complex.

Some workers have deliberately synthesised ligands likely to favour the formation of an $\eta^1:\eta^1$ dimer by placing two multidentate ligands in proximity: two terdentate amino ligands joined by a xylene bridge form a template for the formation of an $\eta^1:\eta^1$ (type II b) complex[193] and two porphyrin groups held "face-to-face" by bridging side chains show the same effect[194]. In the second case the formation of the $\eta^1:\eta^1$ complex could be supressed by separating the two porphyrin rings sufficiently. Oxygenation of the dicobalt(II) complex of the dinuclear ligand 2,6bis[bis(2-pyridylmethyl)aminomethyl]-4-methylphenol is reported to give an $\eta^1:\eta^1$ complex[195].

Other studies have been concerned with trapping the Co-O_2 monomeric complex in an environment where dimerisation is impossible. Nakamoto and co-workers have published a series of papers on Co(II) complexes trapped in O_2-doped argon matrices[196–199], and a report has appeared of Co^{2+} complexed by a nitrogen macrocycle in a micellar phase[200]. Co^{2+} complexed by ethylenediamine in zeolite cages forms an η^1 mononuclear complex at low concentration but $\eta^1:\eta^1$ dinuclear complexes are observed at higher concentrations. There is some evidence for formation of free O_2^- ion[201]. Similar results were found for Co(II) ethylenediamine complexes absorbed on a cation exchange resin[202].

An early report of the formation of an η^1 dioxygen complex $Co(CO)_4O_2$ on sublimation of $Co_2(CO)_8$ in the presence of dioxygen[203] has been followed by studies with metal atom vapours[204] which support the existence of $Co(CO)_4O_2$ and also suggest the formation of $Co(CO)_nO_2$ (n = 1 to 3) in which the dioxygen appears from infra-red spectroscopy to form an η^2 complex.

Rhodium and Iridium Complexes

Most of the work in this field has been concerned with the η^2 complexes formed on addition of dioxygen to square planar M(I) complexes such as Vaska's compound, and a number of references to more recent work are given in Table 6. ^{31}P n.m.r. spectroscopy has been used recently to characterise the dioxygen adducts of a series of Rh(I)-chelating diphosphine complexes[205]. The NQR spectrum of the dioxygen adduct of Vaska's compound $[Ir(CO)Cl(PPh_3)_2O_2]$ shows the two oxygen atoms to be non-equivalent[206].

There has been relatively little effort made to synthesise rhodium and iridium analogues to the bridged cobalt dioxygen complexes although it has been known for some time that a μ-peroxo $\eta^1:\eta^1$ complex is formed on oxygenation of $[RhH(CN)_4(OH_2)]^{2-}$[207] and μ-peroxo and μ-superoxo $\eta^1:\eta^1$ complexes are formed on ozonolysis of solutions of $[Rhpy_4Cl_2]^{+}$[208]. More recently η^1 (mononuclear) and $\eta^1:\eta^1$ (binuclear) dioxygen complexes have been reported as having been formed after the photolysis in presence of oxygen of $[Rh(NH_3)_4H(OH_2)]^{2+}$[209] and $[Rh(en)_2(NO_2)_2]^{+}$ and similar compounds[210]. The dimeric Rh(II) porphyrin complex $[Rh(OEP)]_2$ reacts with dioxygen to give $Rh(OEP)O_2$ which later dimerises to $[Rh(OEP)]_2O_2$[211]. E.P.R. spectroscopy has been used to study the paramagnetic η^1 complexes. The only equivalent report for iridium concerns the unstable complex formed by dioxygen with the sterically hindered complex of Ir(II) with 3-methoxy-2-di-t-butylphosphinophenolate[212]. Condensation of rhodium atoms with Rh gives the complexes $Rh(O_2)$ and $Rh(O_2)_2$. Bimetallic species have also been found[218].

Finally we may recall that rhodium is at present the only transition metal known to form an $\eta^1:\eta^2$ complex[56] and that it also forms an $\eta^2:\eta^2$ complex[53].

Nickel, Palladium and Platinum Complexes

Most of the work involving the dioxygen complexes of these metals has been concerned with the planar η^2 $L_2M(O_2)$ complexes obtained by addition of dioxygen to M(O) species A recent crystal structure determination for L_2MO_2 (L = PPh(t-Bu)$_2$, M = Pd, Pt) shows that an opening of the L-M-L angle arising from the presence of the bulky phosphine destabilises the dioxygen adduct for Pd (L-M-L = 115 4°) in comparison with the Pt complex (L-M-L = 113 1°)[123] The complex $Pt(PPh_3)_2O_2$ may be protonated to give a μ-hydroxo-$\mu(\eta^1.\eta^1$dioxygen) species[213] and the crystal structure of this complex has been determined[96] Reaction of the di-μ-chloro complexes $[LL'PdCl]_2$ with superoxide is reported to form the $\eta^2:\eta^2$ dinuclear complex $[LL'Pd]_2O_2$[214] An EPR study of Ni(I) complexes fixed on substituted polymers and reacted with dioxygen reports the formation of Ni^{2+} O_2^--complexes[215] .

Ozin and co workers have reported infra-red spectra for Ni, Pd and Pt atoms condensed in an O_2/Ar[216] and an $O_2/N_2/Ar$ matrix[217] With dioxygen alone the complexes MO_2 and $M(O_2)_2$ were identified, whereas with nitrogen present $M(O_2)(N_2)$ and $M(O_2)(N_2)_2$ were found In all cases the dioxygen was bound in an η^2 mode

Copper, Silver and Gold Complexes

Copper resembles manganese in that it is known to play an important role in biological processes involving dioxygen, but there is very little reliable structural data available In recent reviews some of the properties of the bimetallic species haemocyanin and laccase were discussed[167, 219]. In the oxygen carrying protein oxyhaemocyanin EXAFS[220] and resonance Raman spectroscopy[221] suggest the formation of a doubly bridged species with an η^1 η^1 bridging dioxygen (Fig 4) but there is some disagreement as to the nature and disposition of the other ligands bound to copper. The oxidase and mono-oxygenase tyrosinase is thought to show a similar coordination of dioxygen[222] The enzyme superoxide dismutase is thought to use only one copper for binding O_2^- [223] An Fe-O-O-Cu bridging system has been suggested for cytochrome c oxidase by several authors, but no firm evidence is available.

Most of the recent preparative work has concentrated on trying to mimic the supposed coordination site[224-227] by careful design of ligands. Although reversible dioxygen binding has been observed in two cases[224 225] and in one case oxygenation of an aromatic residue of the ligand was observed[226], structural data is still lacking. The stoichiometry of dioxygen uptake indicates formation of a dinuclear complex. There is also abundant

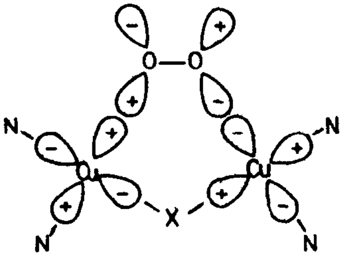


Fig. 4. The structure of oxyhaemocyanin (Ref 220)

evidence of formation of a 2 : 1 (Cu : O_2) complex from the kinetics of auto-oxidation and Cu catalysed oxidations[228]. A monomeric EPR silent complex has been observed to be formed on addition of O_2^- to a DMSO solution of a Cu^{2+} macrocycle complex[229].

The condensation of silver, gold and copper atoms with O_2 has been studied[331]. Copper gives the η^2 complexes CuO_2 and $Cu(O_2)_2$ and gold gives only $\eta^2 AuO_2$. Silver gives an apparently ionic compound $Ag^+O_2^-$ and a poorly characterised AgO_4 species.

Group IIB Metals, Lanthanides and Actinides

Zinc tetraphenylporphyrinate forms a weak complex with O_2^- in non-aqueous solutions. The bonding in this complex appears to be essentially ionic[230]. We have already mentioned crystal structure determinations of lanthanide[55] and actinide[54] compounds. There is every reason to suppose that these elements have a rich dioxygen complex chemistry[5], and this is confirmed by two recent papers[231, 232]. For reasons of space, however, we shall not discuss the dioxygen complex chemistry of these elements.

D. The Electronic Structure of Dioxygen Complexes

In the discussion of the electronic structure of dioxygen complexes we seek to understand how the dioxygen ligand binds to a transition metal and the factors determining the mode of coordination which is adopted. Any picture of the bonding in these complexes should enable us to rationalise the properties of the complexes, and we will be particularly interested in the spectroscopic properties which allow us to test the electronic model of the bonding, and in the chemical reactivity of the dioxygen ligand resulting from its binding to a transition metal. In this section we shall consider the various qualitative descriptions of binding in the complexes, the results of calculations and their agreement with the qualitative models, and the spectroscopic data relevant to the discussion of the bonding.

I. Qualitative Models of Dioxygen Binding

The tendency of early workers to concentrate on one type of dioxygen complex is also reflected in the earliest discussions of the bonding. In their original paper [3] Pauling and Coryell proposed a linear Fe-O-O structure for oxyhaemoglobin, but Pauling later changed his prediction[233] to the bent η^1 structure which has since been found experimentally. J. S. Griffith[234] concluded that a linear Fe-O-O group would be unstable in oxyhaemoglobin, but η^1 or η^2 geometries were possible. He favoured an η^2 structure in which the filled π_u bonding orbital acts as a donor to the metal rather than a non-bonding sp^2 hybrid. Following these two papers, the η^1 and η^2 structures have frequently been referred to as Pauling and Griffith structures respectively. In 1964 Weiss proposed that oxyhaemoglobin should be regarded as a $Fe^{3+}O_2^-$ complex[235].

The bonding in peroxychromates was initially discussed in completely different terms. Tuck and Walters considered the primary interaction to be that of the π_u bonding orbitals