Translated from *Uspekhi Khimii*, **44**, 214-235 (1975) U.D.C. 541.49 : 546.21 : 541.128 : 547.963.4

Activation of Molecular Oxygen on Interaction with Transition Metal Complexes

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The present state of research and ideas in the field of the activation of molecular oxygen by transition metal complexes and matrix systems is described.
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I. INTRODUCTION

One way of increasing the reactivity of oxygen is its "chemical" activation, in particular its fixation on transition metal complexes. It is suggested that, owing to the many possible valences in the complexes, the activated molecule can not only react under mild conditions but also exhibits a definite selectivity in relation to the substrate.

The formation of complexes by molecular oxygen can occur in many heterogeneous catalytic oxidation processes[1], in the autoxidation of complexes[2], and also in biochemical processes. The mechanism of action and the functions of oxygen carriers in such processes are usually elucidated with the aid of homogeneous models[3-5]. Transition metal complexes, which are capable of binding molecular oxygen, are normally employed as model systems.

Two approaches to the study of the mechanism of the activation of oxygen via its coordination have been devised.

In the first, analytical approach the aim is to select a theoretical quantum-chemical model which can describe satisfactorily the binding of molecular oxygen and can predict the possible reactivity of coordinated oxygen. This approach presupposes the existence of a definite relation between the geometry of the dioxygen complex, the nature of the binding of oxygen, and a definite type of reactivity of the coordinated oxygen molecule.

The second approach involves the creation of synthetic models of heterogeneous and biochemical systems in which molecular oxygen is fixed. The approach is based on matrix effects, i.e. the aim is to simulate the conditions for the fixation of oxygen in systems with polymeric structural elements.

A combination of these two approaches in the study of the mechanism of the activation of molecular oxygen is probably the most fruitful.

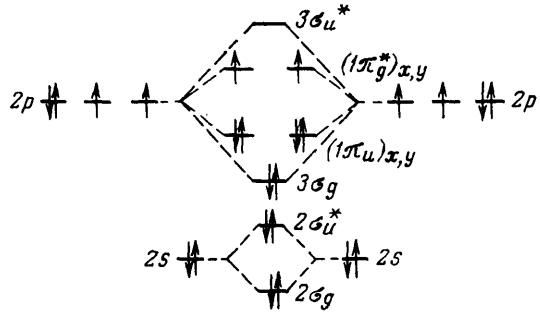
A number of reviews on this problem have been published in which the structure, binding, and reactivity of dioxygen complexes are discussed fairly extensively[6-11] and the general characteristics of the binding of oxygen are analysed[12,13].

Analogous processes have been dealt with in Soviet scientific literature: the activation of small molecules and new trends in the development of the chemistry of coordination compounds[14] and homogeneous catalytic oxidation of hydrocarbons[15]. However, one should note that the problem of activated binding and also the matrix principle of the fixation and activation of the oxygen molecule have not so far been adequately described.

In the present review an attempt is made to survey the latest results of studies of this kind.

II. THE STRUCTURE OF THE OXYGEN MOLECULE AND ITS ACTIVE FORMS

The structure of the oxygen molecule can be conveniently treated within the framework of molecular orbital method[16]. The two least strongly bound electrons are placed in doubly degenerate antibonding π orbitals and, according to the Hund rule, have parallel spins, i.e. the molecule has a triplet ground state $^3\Sigma_g$ (Fig. 1).



The bond between the atoms is due to the interaction of $2p$ electrons and consists of one two-electron σ bond $(3\sigma_g)^2$ and two three-electron π bonds $(1\pi_u)^2(1\pi_g^*)^1$. Each three-electron bond constitutes a combination of a pair of

bonding electrons and one antibonding electron in the same interaction plane. The bond order, defined as half the difference between the numbers of bonding and antibonding electrons, is two.

In chemical reactions of oxygen it is necessary to take into account the first excited state of the molecule $^1\Delta$(singlet) in which both π_g^* electrons occupy the same orbital and have antiparallel spins. The formal bond order is the same as in the ground state but the electron density is distributed less uniformly, since one π-interaction plane contains two electrons and the other contains four electrons. Therefore here one expects the appearance of an additional electrostatic repulsion, whose energy may contribute significantly to the energy of the $^3\Sigma \rightarrow {}^1\Delta$ excitation, which is 23 kcal mole^{-1}.[17]

The addition of electrons to the oxygen molecule leads to the population of antibonding orbitals, which entails a decrease of the O–O bond order. The observed changes in bond length and vibrational frequency confirm the existence of this tendency (Table 1).

Table 1. Characteristics of the O–O bond strengths.

Species	Calc. bond order	Bond length, Å	Stretching vibration frequency, cm^{-1}	References
O_2	2	1.21	1555	18,19
O_2^-	1.5	1.28 (KO_2)	1089	20,21
O_2^{2-}	1	1.49 (BaO_2)	880 (H_2O_2)	20,19

According to the results of *ab initio* MO SCF calculations, the $2\sigma_g$, $2\sigma_u^*$, and $3\sigma_g$ orbitals in different dioxygen species are mixed[22]. The directional character of hybrid orbitals in space is known[23] to be more marked compared with that of non-hybrid orbitals, which ensures a higher degree of overlapping on formation of σ bonds, in particular when the orbitals of both interacting species are hybridised. Furthermore, hybridisation leads to a decrease of the repulsion of the lone electron pairs. Therefore the ethylene-like reactive forms $O_2(^1\Delta)$, O_2^-, and O_2^{2-} with sp^2 hybridisation of the orbitals can play a definite role in complex formation.

III. THE NATURE OF ACTIVATING BINDING

The principle of the conservation of spin can impose limitations on the nature of the elementary processes in chemical reactions[8]. By virtue of spin conservation the interaction of the oxygen molecule in the triplet state with a molecule in the singlet state cannot lead to the formation of molecules in singlet states only. From this it follows that oxygen in the ground state is not a heterolytic (two- or four-electron) oxidant and reacts preferentially as a homolytic (one-electron) oxidant.

The main types of homolytic oxidation reactions occurring with conservation of spin are as follows:

(a) reaction with a molecule:

$$\overset{\uparrow\downarrow}{R}H + \overset{\uparrow\uparrow}{O_2} = \overset{\uparrow}{R} + \overset{\uparrow\uparrow}{HO_2} \quad ;$$

(b) reaction with a radical

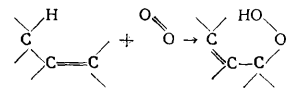
$$\overset{\downarrow}{R} + \overset{\uparrow\uparrow}{O_2} = \overset{\downarrow\uparrow\uparrow}{RO_2} \quad .$$

As a result of a termolecular homolytic reaction in which the oxygen molecule abstracts one hydrogen atom from each of two substrate molecules, the spin is also conserved[24,25]:

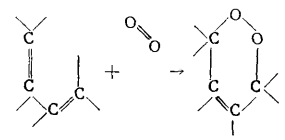
$$\overset{\uparrow\downarrow}{R}H + \overset{\uparrow\uparrow}{O_2} + \overset{\uparrow\downarrow}{R}H = \overset{\uparrow}{R} + \overset{\downarrow\uparrow\downarrow\uparrow}{HOOH} + \overset{\uparrow}{R} \quad .$$

The above homolytic reactions are difficult because they all occur with participation of free radicals, whose equilibrium concentration is as a rule very low under normal conditions.

In order to achieve the reaction without the involvement of free radicals, it is necessary to excite the oxygen molecule to the singlet state, for which, from the standpoint of spin conservation, it can react as a two-electron non-homolytic oxidant:



or



The formation of complexes by the oxygen molecule with transition metal compounds leads to a change in its spin state and in the nature of its reactivity. The activating effect of transition metal complexes is associated with the presence of closely spaced *d* levels of the metal ions, which are responsible for the ready formation of activated forms of different multiplicity.

When the oxygen molecule reacts with a doublet centre, a radical complex, capable of vigorous interaction not only with radicals but also with singlet molecules, can be formed:

$$\overset{\downarrow}{M} + \overset{\uparrow\uparrow}{O_2} = \overset{\downarrow}{M} \cdot \overset{\uparrow\uparrow}{O_2} \quad .$$

The interaction with a triplet centre can lead to the formation of a complex of singlet oxygen. It is assumed that a complex of triplet oxygen is formed in the first stage of the process. As a result of the change in molecular symmetry on complex formation, the energy degeneracy of the π_d^* orbitals is lifted, which facilitates the transition of the molecule to the singlet state:

$$\overset{\downarrow\downarrow}{M} + \overset{\uparrow\uparrow}{O_2} = \overset{\downarrow\downarrow}{M} \cdot \overset{\uparrow\uparrow}{O_2} = \overset{\downarrow\uparrow}{M} \cdot \overset{\downarrow\uparrow}{O_2} \quad .$$

The role of the triplet states of transition metal complexes in such processes is indicated by studies on the sensitised photoexcitation by molecular oxygen[26].

Coordination interaction alters the electronic structure of the molecule owing to the change in the population and disposition of its orbitals. The transition metal can withdraw electron density from certain bonding orbitals and shift it to certain antibonding orbitals, which is analogous to the electronic excitation of the free molecule. In terms of interatomic distances and valence angles, the coordinated molecule can resemble various activated forms of the free molecule[27]. A characteristic feature of this type of excitation is that it occurs solely due to the

coordination interaction with the metal atom without the external supply of energy. The heats of such complex formation processes are as a rule low, but the processes lead to considerable chemical changes in the coordinated ligand.

It is believed that the most significant factor in the activating complex formation between transition metal compounds and the oxygen molecule is its interaction with the metal atom, since in this case the specific role of the latter, associated with the presence of *d* valence states of different symmetry and spatial orientation, has the greatest effect. However, the nature of the ligand environment, whose influence extends via the metal atom to the coordinated molecule, is very important. Nor can one rule out the possibility of the activation of the oxygen molecule by its outer-sphere coordination[28].

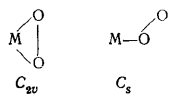
Evidently, apart from the electronic factor, the geometrical factor has an effect in the interaction between the dioxygen molecule and the activator, because definite steric hindrance to the binding of the oxygen molecule can probably lead to a definite strain in the bonds of the molecule and hence to a definite type of reactivity[29].

IV. THE STRUCTURE OF DIOXYGEN COMPLEXES

In the reaction with transition metal complexes the oxygen molecule behaves mainly as an electron acceptor, as shown by the results of studies using different methods (X-ray photoelectron spectroscopic[30,31], thermodynamic[32], and electrochemical[33]). The electron-donating capacity of the metal (the energy of the occupied *d* orbitals) can play a significant role in the binding of oxygen. Complexes with oxygen are usually formed by compounds of transition metals in the lowest oxidation state, which exhibit a sufficient electron-donating capacity to ensure charge transfer but not high enough to cause the dissociation of the O–O bond.

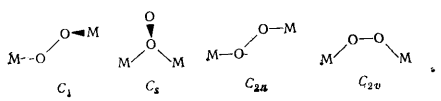
The nature of the binding of oxygen in the complex and the reactivity of the coordinated molecule are usually considered on the basis of the geometry of the oxygen adduct, since evidently the latter determines the state of oxygen in the complex and hence possibly also the type of reactivity of the bound oxygen.

Mononuclear complexes with different symmetries of the metal–dioxygen fragment—the closed (C_{2v}) and open (C_s) types—are known:



C_{2v} C_s

Furthermore, there are dinuclear complexes which can be regarded as structural derivatives of mononuclear complexes of the open type:



C_1 C_2 C_{2h} C_{2v}

In mononuclear complexes of the open type and in the corresponding dinuclear derivatives the MOO valence angles are close to 120°, i.e. these configurations are apparently based on the state of the oxygen atom with sp^2-hybridised orbitals.

No dioxygen complexes known to have a linear configuration of the metal–dioxygen fragment have yet been obtained; this distinguishes them from the complexes of molecular nitrogen in which linear coordination is most typical. Probably in this case the different populations of the antibonding orbitals and hence the different molecular symmetries have an effect. In the nitrogen molecule there are two vacant π orbitals, which accept two pairs of *d* electrons from the metal and this favours the formation of a linear structure[34]. In the oxygen molecule there can be only one vacant π orbital (in the $^1\Delta$ state) which can accept only one pair of *d* electrons and this rules out a linear coordination in this case.

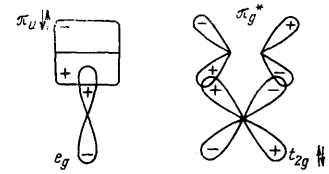


Figure 2. Griffith's model of a π-complex.

The formation of a dioxygen complex of the closed type may resemble the binding in olefin complexes[35], as pointed out by Griffith[36]. It is suggested that a σ bond is formed via an occupied π-bonding molecular orbital of oxygen and a vacant *d* orbital of the metal. Furthermore, there is a possibility of forming a π bond from the lone pair of *d* electrons of the metal atom and an antibonding orbital of the oxygen molecule (Fig. 2). Thus the energy splitting of the degenerate oxygen π^* orbitals in the ligand field of the complex is postulated.

Presumably when the degree of charge transfer from the metal to oxygen is fairly pronounced, the structure of the complex is best described by the model of a doubly coordinated σ complex, which may be important in the determination of the reaction mechanisms. The structural characteristics of a number of mononuclear complexes are presented in Table 2.

Table 2. Structural data for dioxygen complexes of the closed type (diamagnetic).

Compound	M–O bond length, Å	O–O bond length, Å	Type of addition	References
[Co $(Ph_2PCH{=}CHPPh_2)_2 \cdot O_2]BF_4 \cdot 2C_6H_6$	1.871; 1.902	1.420	irrev.	37
[Rh $(Ph_2PCH_2CH_2PPh_2)_2 \cdot O_2]PF_6$	2.026	1.418	rev.	38
[Ir $(Ph_2PCH_2CH_2PPh_2)_2 \cdot O_2]PF_6$	1.961; 1.990	1.625	irrev.	38
Ir $(PPh_3)_2$ Cl $(CO)O_2$	2.04; 2.09	1.30	rev.	39
Ir $(PPh_3)_2$Br (CO) O_2	—	1.36	rev.	37
Ir $(PPh_3)_2$I (CO) O_2	2.035; 2.082	1.509	irrev.	40
Ir $(PPh_2Et)_2$ Cl (CO) O_2	2.036; 2.084	1.461	rev.	41
Pt $(PPh_3)_2O_2 \cdot 1.5C_6H_6$	2.01	1.45	irrev.	42
Pt $(PPh_3)_2 \cdot O_2 \cdot 2CHCl_3$	2.006	1.505	irrev.	43

The influence of the metal can be estimated from experimental data for the structures of the cationic complexes of cobalt, rhodium, and iridium with bis(diphenylphosphinoethane) and bis(diphenylphosphinoethylene) ligands. The iridium atom is capable of forming a

stronger M–O bond than the rhodium atom and also of loosening the O–O bond (Table 2). This is attributed to the fact that the π-donor metal orbitals in the iridium complex must lie above those in the rhodium complex[38-44]. Neglecting the effect of the change of ligand, we may note that the observed sequence of changes in the $M-O_2$ bond lengths is consistent with the sequence of changes in the kinetic and activation parameters of the binding of oxygen by the bis(diphenylphosphinoethylene) complexes[44]. The difference between the energies of the *d* orbitals of the corresponding metal complexes probably plays a role here. The specificity of the bis(diphenylphosphinoethylene) ligand may be reflected in this series by the absence of a correlation between the M–O bond lengths on the one hand and the O–O bond lengths on the other.

It is noteworthy that the O–O bond length is very sensitive to changes in the ligand environment of the metal. As the auxiliary ligands become less electronegative (Cl > Br > I; PPh_3 > PPh_2Et), the O–O distance increases. A correlation is also observed between the O–O bond length and the degree of reversibility of the binding of oxygen. This can be explained by the fact that, with increase of the energy of *d* orbitals, the effect of the donation of π electrons to the antibonding molecular orbital is enhanced.

The O–O stretching vibration frequency in the spectra of complexes of the given type is greatly reduced compared with that for the free molecule, to a value of the order of 800–900 cm^{-1}.[45,46] The M–O stretching vibration frequency is in the range 450–600 cm^{-1}. A satisfactory correlation between these frequencies and the changes in the structural parameters of the compounds has not so far been obtained.

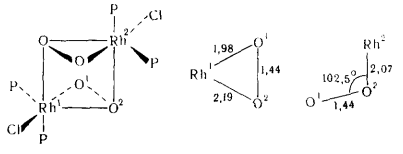


Figure 3. The structure of $[Rh(Ph_3P)_2ClO_2]_2$ (the bond lengths are given in Å).

The dinuclear diamagnetic complex $[Rh(PPh_3)_2ClO_2]_2$, in which two oxygen molecules are combined reversibly[47], is unusual (Fig. 3). Its unusual feature is that each oxygen molecule, which behaves as a bridging ligand, forms a coordinate bond of the closed type with one metal atom, behaving as an equatorial ligand, while the coordinate bond formed with the other metal atom is of the open type and oxygen behaves as an axial ligand. Each coordinated oxygen molecule forms two σ bonds: one via the occupied π_u orbital of oxygen and the vacant equatorial dsp^3 orbital of one metal atom and the other via the occupied nonbonding hybrid orbital of oxygen (*p* orbital with some *s* character) and the vacant axial dsp^3 orbital of the other metal atom. Furthermore, many-centre π bonding is postulated. This complex can be regarded as an intermediate structural type in relation to complexes of the open and closed types.

It is interesting that the coordinated oxygen molecule acquires the ability to form hydrogen bonds[43]. In the complex $Pt(PPh_3)_2O_2.2CHCl_3$ the hydrogen atoms of the solvate molecules are in the same plane as the Pt and O atoms, so that the PtOH angle is 180° and the O–H distance is 2.04 Å (Fig. 4). Compared with the benzene solvate, which shows no signs of the formation of hydrogen bonds, the O–O bond length is appreciably increased, while the M–O bond hardly changes (Table 2). It is so far not clear how the bond with the solvent species is formed: as a result of the excitation of the oxygen molecule or as a result of the excess negative charge on oxygen. The location of the hydrogen atoms in the same plane as the metal–dioxygen fragment suggests that the oxygen orbitals which form the $Pt-O_2$ bond are involved in hydrogen bonding, but the slight change in the Pt–O bond is not entirely consistent with this hypothesis.

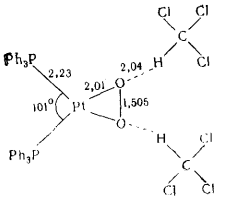


Figure 4. The formation of a hydrogen bond (the bond lengths are given in Å).

The complex $IrCl(PPh_3)_2(C_2H_4)O_2$, in which the simultaneous coordination of oxygen and ethylene has been demonstrated by infrared spectroscopy and NMR[48] (Fig. 5), can serve as a model of homogeneous catalytic oxidation.

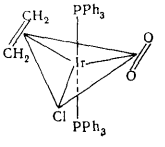
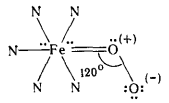


Figure 5. The proposed structure for $IrCl(PPh_3)_2(C_2H_4)O_2$.

The paramagnetic complex $Ru(AsPh_3)_2Cl_2O_2$ should probably be assigned to the same structural type in view of the appearance of the 880 cm^{-1} band in the infrared spectrum[49]. Another paramagnetic complex, $Cr[N(i\text{-}Pr)_2.]_3O_2$, has an effective magnetic moment of 2.03 Bohr magnetons (B.M.) and a vibrational frequency of 980 cm^{-1},[50] which indicates the possible characteristics of its structure.

Aleksandrov et al. recently demonstrated the possibility of the formation of oxygen complexes with organic derivatives of post-transition metals[51]: the "reversible" adduct $Et_2Cd.2O_2$, with an intense 790 cm^{-1} band in its infrared spectrum, was obtained. The transfer of the π_g electron pair of oxygen to the vacant 5*s* or 5*p* orbital of the metal and also the interaction via the occupied 4*d* orbitals of the metal and the vacant π_g orbital of oxygen can make a definite contribution to bond formation on complex formation.

The iron complex with porphyrin and histidine, having the configuration of a tetragonal pyramid, is the active centre for the binding of oxygen in haemoglobin and myoglobin[52]. The planar porphyrin ligand is located at the base of the pyramid, the bivalent iron ion coordinated to four nitrogen atoms being in the centre. The apex of the pyramid is occupied by the tertiary nitrogen atom of histidine and the oxygen molecule adds to the base of the pyramid. The orientation of the dioxygen group relative to the iron atom has not so far been determined experimentally. According to Pauling[53], the structure of the coordination centre of oxyhaemoglobin can be represented as follows:



It is believed that the tervalent oxonium ion with sp^2-hybridised orbital is involved in the formation of a bond. From the standpoint of the molecular orbital method, this structure can be regarded as a π-bonded complex of the open type.

According to Griffith, the oxygen in oxyhaemoglobin is coordinated as in a complex of the open type[36]. Since in this case the iron ion must have a coordination number of seven, one may expect the occurrence of steric hindrance[54]. So far no model compound with a similar configuration has been obtained.

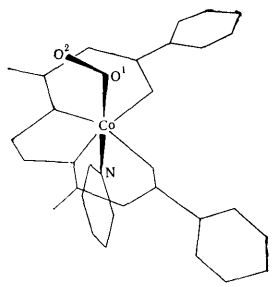


Figure 6. The structure of Co(bzacen)(pyridine)O_2.

The orientation of the coordinated molecule relative to the metal atom proposed by Pauling has been demonstrated for the tetraphenylporphyrin complex of cobalt with NO,[55] which is isoelectronic with the porphyrin complex of iron with oxygen. A similar orientation of the dioxygen group was established for Co(bzacen)(pyridine)O_2,[56] where bzacen is *NN'*-ethylenebis(benzoylacetoniminide) (Fig. 6). One should note that in these molecular structures the projection of the coordinated molecule onto the plane of the equatorial ligand lies between the adjacent bonds of the metal in the equatorial plane. The staggered conformation probably corresponds to minimum repulsion of the non-bonded atoms. However, this disposition of the dioxygen group should decrease the effectiveness of π-bonding since the maximum overlap of the oxygen p orbital with one of the metal t_{2g} orbitals may be expected for the eclipsed conformation[12,57]. The unusual conformation of oxygen can be one of the factors determining the possibility of the reversible binding of oxygen to haemoglobin.

Three types of dioxygen compounds of cobalt, in which the coordinated oxygen molecule forms an obtuse CoOO angle, are distinguished: mononuclear paramagnetic, dinuclear diamagnetic, and dinuclear paramagnetic (Table 3).

Mononuclear complexes are formed on direct interaction between certain bivalent cobalt compounds and oxygen. Their magnetic moments are 1.85 ± 0.35 B.M., which is evidence for the presence of one unpaired electron in the complex[65,66]. According to ESR studies[67-71], the unpaired electron is located in an orbital having 10–20% of metallic character, i.e. is localised preferentially at the dioxygen group. X-Ray photoelectron spectroscopic[31] and thermodynamic studies[32] suggest that the charge state of the metal corresponds more closely to cobalt(III) than to cobalt(II). The bond with the oxygen molecule can arise as a result of spin pairing and electron transfer from the metal atom to oxygen. The coordinated molecule has the character of the molecular ion O_2^-, forming a donor–acceptor bond with the tervalent cobalt atom via the sp^2-hybridised lone electron pair with some delocalisation of the unpaired electron over the metal[65,66,72]. In mononuclear complexes of this type the O–O interatomic distance (1.26 Å)[56] and the O–O stretching vibration frequency (1120–1140 cm^{-1})[66] correspond to the structural parameters of the O_2^- ion (Table 1).

The presence of an additional electron in the mononuclear cobalt analogues of oxyhaemoglobin can be responsible for some of its structural characteristics. Since the iron atom in oxyhaemoglobin has a stable 18-electron inert gas shell, the additional electron must be located in an oxygen orbital. Owing to the high energy of the vacant $3\sigma_g$ orbital, the electron interacts with the π_g orbital, displacing the electron pair involved in the dative π interaction on the metal side. Thus a considerable weakening of the π-bonding component may be expected in cobalt analogues of oxyhaemoglobin as compared with oxyhaemoglobin itself.

Apart from the mononuclear complexes, fairly numerous dinuclear oxygen complexes of cobalt are known. Assuming the formation of covalent bonds between cobalt ions and the oxygen molecule, it is believed that the latter undergoes a two-electron reduction[13]. The resulting dinuclear complex can be regarded as a coordination compound of the peroxide type: $Co^{III} \leftarrow O_2^{2-} \rightarrow Co^{III}$.

The dinuclear coordination of the peroxide anion can be achieved in two ways: by the addition to each oxygen atom of one metal atom (C_1) or by the addition of both metal atoms to one oxygen atom (C_S).

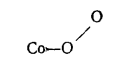
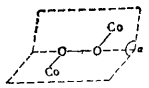
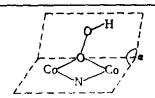
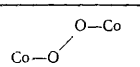
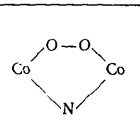
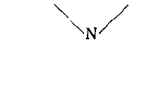
The one-electron oxidation of the diamagnetic complexes leads to the corresponding paramagnetic compounds. As for the mononuclear complexes, there is a tendency towards the retention by the metal of the stable 18-electron shell, i.e. an electron must be removed from the dioxygen group:

$$Co^{II} \leftarrow O_2^{2-} \rightarrow Co^{III}\!-\!\bar{e}\!=\!Co^{III} \leftarrow \dot{O}_2^- \rightarrow Co^{III} \quad .$$

ESR spectra confirm the preferential location of the unpaired electron in the dioxygen group[73]. In contrast to the diamagnetic complexes, the metal–dioxygen fragment in the dinuclear paramagnetic complexes has a planar structure (C_{2h}), in accordance with its superoxide character.

The data presented in Table 3 show that, as the π-bonding electron pair is transferred towards the dioxygen group, the strength of the M–O bond increases and that of the O–O bond falls. The changes in the valence angles

Table 3. Structural data for dioxygen complexes of cobalt.

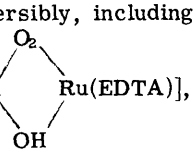
Structural type	Configuration of the metal-dioxygen group	Compound	Co-O bond length, Å	O-O bond length, Å	Angles		Type of addition	References
					CoOO	others		
$Co^{III} \leftarrow \dot{O}_2^-$ (paramagnetic)		Co(bzacen)(pyridine)O_2*	1.88	1.26	126	—	rev.	56
$Co^{III} \leftarrow O_2^{2-} \rightarrow Co^{III}$ (diamagnetic)		(H_2O) (3F— Salen) CoO_2Co(3F—Salen)** $+ 2CHCl_3 + C_6H_{11}$	2.000 1.931	1.308	119 117	$\alpha = 122$	rev.	58
		(DMF)(Salen)CoO_2Co(Salen)(DMF)***	1.910	1.338	120	$\alpha = 110$	rev.	59
		$[(NH_3)_5CoO_2Co(NH_3)_5](SO_4)_2$	1.882	1.47	112	$\alpha = 146$	irrev.	60
			1.92	1.42	<129	CoOCo= =102 $\alpha < 180$	irrev.	61
$Co^{III} \leftarrow \dot{O}_2^- \rightarrow Co^{III}$ (paramagnetic)		$[(NH_3)_5CoO_2Co(NH_3)_5] \cdot SO_4(HSO_4)_3$	1.894	1.312	117	—	irrev.	62
		$[(NH_3)_5CoO_2Co(NH_3)_5] \cdot (NO_3)_5$	1.895	1.317	117	—	irrev.	63
			1.867	1.320	121	—	irrev.	64
			1.88	1.36	119	—	irrev.	61

* bzacen = *NN'*-ethylenebis(benzoylacetoniminide) (Ed. of Translation).
** 3F-Salen = bis-(3-fluorosalicylidene)ethylenediamine (Ed. of Translation).
*** Salen = bis-salicylidene-ethylenediamine (Ed. of Translation).

of the $Co-O_2-Co$ groups can be accounted for by a change in the character of the orbitals involved in the binding of the oxygen molecule.

X-Ray diffraction studies have established that the orientation of the dioxygen group relative to the equatorial ligand is the same as for the mononuclear complexes.

Dinuclear compounds of other transition metals are known, in which the oxygen is bound reversibly, including



the diamagnetic complex $K_2Na[(EDTA)Ru(O_2)Ru(EDTA)(OH)]$, obtained by Ezerskaya and Solovykh[74,75], where EDTA is the tetrabasic residue of ethylenediaminetetra-acetic acid, and the paramagnetic complex [Mn(Salen†)]$_2O_2$, whose effective magnetic moment is 2.79 B.M.[76]

The role of the specific ligand environment of the metal in biological oxygen carriers is manifested by a change in the thermodynamic parameters of the oxygenation process[77-85].

The differences between the stabilities of the oxygen complexes of cobalt with different equatorial ligands (for example TMPP and Salen, Table 4) are probably due to the differences between the π-acceptor capacities of these equatorial ligands. π-Conjugated macrocyclic systems do not as a rule promote strong binding of oxygen. For certain complexes with the same type of ligand environment, ΔG° may be correlated with pK_a for the axial ligand. A decrease in the stability of the mononuclear oxygen complex with sterically hindered axial ligands (2,6-lutidine, 2,4,6-collidine, and quinoline) has been noted. The sterically hindered groups in the ligand prevent its effective approach to the metal, weakening the stabilising *trans*-influence on the metal–oxygen bond. As a result of the distortion of the configuration, the stability of the dinuclear compound may be reduced[84]. For a rigidly bound equatorial ligand of the type of porphyrin, the importance of steric hindrance of the coordination of the axial ligand increases[81].

† See Table 4 (Ed. of Translation).

Table 4. Thermodynamic characteristics of the reversible binding of oxygen in solution by cobalt complexes ($CoII + O_2 = CoO_2$).[82,83]

Ligand		Standard state	ΔG°, kcal mole^{-1}	ΔH°, kcal mole^{-1}	ΔS°, e.u.
equatorial	axial				
Dibasic residue of tetra-4-methoxyphenylporphyrin (TMPP)	Pyridine	$P_{O_2} = 1$ atm	−0.50	−9.3	−42
	4-Picoline	$T = 208°$	−0.75	−8.8	−39
	2,4,6-Collidine		−0.09	−8.5	−45
Dibasic residue of bis-salicylidene-ethylenediamine (Salen)	Pyridine	$P_{O_2} = 1$ atm	−0.80	−16.7	−54
	4-Picoline	$T = 298°$	−0.87	−17.0	−54
	2,6-Lutidine		−0.67	−18.3	−59
	Quinoline		+0.03	−15.2	−51

V. MATRIX FIXATION OF OXYGEN

The stabilisation of the oxygen-fixing centre of haemoglobin is probably promoted by the matrix effect. The basic unit of haemoglobin is the planar tetracoordinate complex of iron(II) and protoporphin. The haemoglobin

molecule contains four haem groups, which are linked by peptide chains via histidine to the protein moiety. Each of the four protein chains forms a fairly complex three-dimensional structure around the haem in such a way that the latter is located in a fold of the protein chain (matrix) within which oxygen may be bound.

In accordance with Pauling's hypothesis[53], it is believed that the terminal atom of the coordinated oxygen molecule, which carried an excess negative charge, is oriented towards the NH group of distal histidine, forming a hydrogen bond. Thus a two-point fixation of the molecule is achieved by a cooperative interaction with the metal complex and with the histidine group of the protein (Fig. 7).

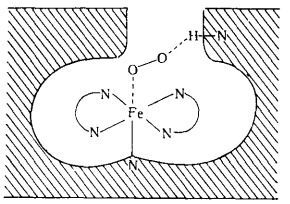


Figure 7. A model of the matrix fixation of oxygen by haemoglobin.

Presumably the matrix effect plays a dual role: firstly it prevents the irreversible interaction of molecular oxygen with the active component of haemoglobin and secondly it rules out the possible oxidation of labile substrates.

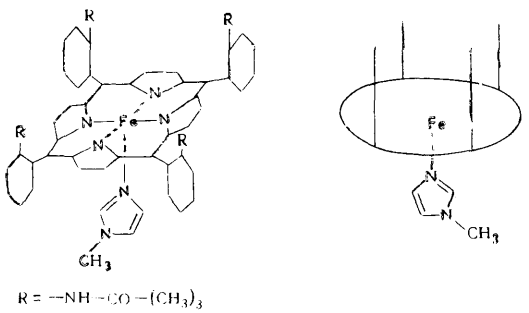


Figure 8. The unit of a matrix with artificial steric hindrance and a schematic representation of the element.

Definite information about the occurrence of the matrix principle in the fixation of molecular oxygen can be provided by a study of the binding of oxygen in synthetic models. A number of approaches to the creation of models based on the matrix principle may be noted. In the first case the model is formed by the incorporation of an analogue of the active centre in the polymer being formed. A cavity should be created over the active centre. The cavity is usually produced by incorporating in the polymer a model compound in which a small molecule, particularly CO, is reversibly combined. After the formation of the polymer, the small molecule is removed (by flushing with an inert gas).[29,86]

The second approach involves the creation of artificial steric hindrance around the active centre[87] (Fig. 8).

Apart from the creation of artificial steric hindrance, the elements of matrix systems can be formed by employing the conformations of the ligand environment[88] (Fig. 9). According to certain observations[88], the steric hindrance influences the stability of the adduct of molecular oxygen with the metal complex.

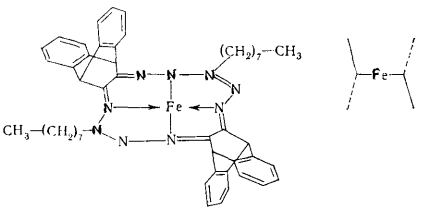


Figure 9. A model of the matrix formed as a result of the conformation of the ligand environment and a schematic representation of the model.

However, the matrix effect can be shown under certain conditions even in the absence of steric hindrance, when one employs a model in which there is an appreciable cooperative interaction with the ligand environment[89,90] (Fig. 10). The cooperative interaction in matrix systems has a definite advantage over simple complexes which are haemoglobin analogues. According to the results of Cheng and Traylor[86], there is a very significant difference between the degrees of binding of molecular oxygen to the iron(II) complex in which the *trans*-ligand (pyridine) is coordinated to the iron ion only and the analogous complex in which pyridine is additionally linked to the equatorial ligand (Fig. 10).

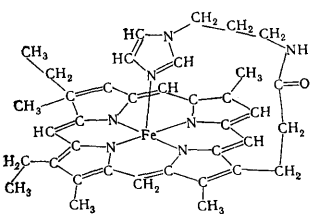


Figure 10. A model of the matrix with an independent linkage between the axial and equatorial ligands.

Together with a change in reactivity, one can also expect a change in selectivity when the *trans*-ligand is replaced; this has been confirmed by studies on the binding of carbon monoxide and molecular oxygen. In particular, these results show that, when imidazole in the *trans*-position is replaced by pyridine, the system loses its ability to bind oxygen[86].

Furthermore, the results of studies involving similar systems lead to the conclusion that the coordinated oxygen molecule is additionally stabilised when there is a possibility of the formation of a hydrogen bond with fragments of the system (two-point fixation)[86].

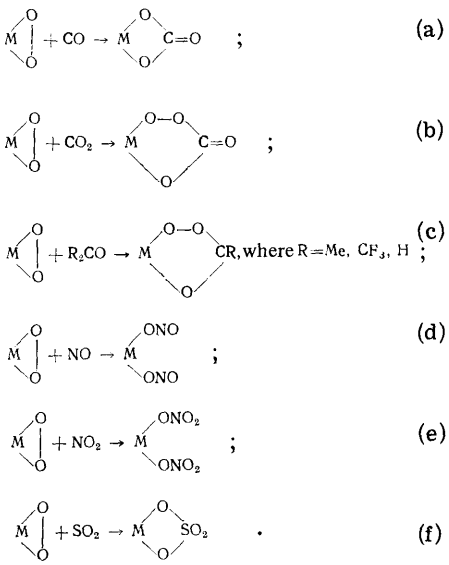
Coboglobins apparently occupy a special place among matrix systems[91,92], since the protein moiety is fully retained in their structure. Consequently the study of the binding of oxygen by coboglobins can elucidate the role of the protein moiety in this process.

Furthermore, the employment of such systems as haemoglobin analogues makes it possible to elucidate certain characteristics of the influence of the metal on the effects accompanying the addition of the oxygen molecule (the phosphate effect, the Bohr effect, and *gem*–*gem* interaction). In particular, a definite difference has been observed[92] between the *gem*–*gem* interactions in coboglobin and haemoglobin during the binding of oxygen.

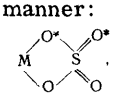
VI. REACTIVITY OF THE COORDINATED MOLECULE

Two main types of reactions of the complexes are distinguished: the inner-sphere interactions with preliminary coordination of the substrate in the inner sphere and the outer-sphere interactions where there is no inner-sphere coordination of the substrate. Evidently in the first case both oxygen and the substrate are activated, while in the second case only oxygen is activated.

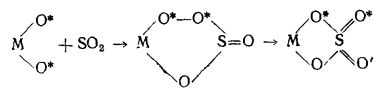
The reactions can be stoichiometric or catalytic. The addition of small molecules to the dioxygen complexes of Group VIII metals must be classified as stoichiometric oxidation reactions[93–99]:



All the reactions with coordination-unsaturated platinum complexes take place readily and probably involve an inner-sphere mechanism[100]. The coordination-saturated rhodium and iridium compounds react only with NO_2 and SO_2, i.e. molecules in which the aprotic acid properties are most pronounced. In these cases one might postulate a mechanism involving a simple outer-sphere addition. However, studies with isotopically labelled oxygen in the complex have shown that the label is distributed in the product in the following manner:



i.e. the dissociation of the O–O bond is accompanied by the dissociation of the M–O bond[101]. The electrophilic attack by SO_2 is probably directed to the negatively charged oxygen atom, facilitating the heterolytic dissociation of the M–O bond with subsequent insertion of the SO_2 molecule in this bond and a further rearrangement of the resulting peroxide complex:

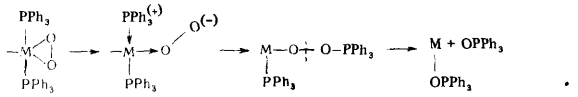


Oxygen π complexes of the closed type catalyse the oxidation of tertiary phosphines to the corresponding oxides[91,102–104] and also of isocyanides to isocyanates[45]. Since the substrates undergoing oxidation can function as specific π-acceptor ligands, presumably the reactions have an inner-sphere mechanism. According to the results of kinetic studies, all the intermediate complexes contain substrate molecules and have an 18-electron coordination sphere (Table 5), which is specific to inner-sphere catalysis according to Halpern's hypothesis[105].

Table 5. Characteristics of the intermediate complexes.

Composition	No. of coordinated ligands	No. of electrons in valence shell of metal	References
$Ru(O_2)(SCN)(NO)(PPh_3)_3$	6	18	104
$Ir(O_2)(I)(CO)(PPh_3)_2$	5	18	38
$Pt(O_2)(PPh_3)_3$	4	18	95

A remarkable reaction is catalysed by a ruthenium complex. According to infrared spectroscopic data[104], the coordination of the oxygen molecule in the initial 16-electron compound $Ru(O_2)(SCN)(NO)(PPh_3)_3$ is of the closed π-complex type, i.e. the coordination number is probably six. The addition of the PPh_3 molecule leads to the formation of a sterically strained configuration with a coordination number of seven, which can promote the inner-sphere *cis*-migration of the ligand with a change in the orientation of the dioxygen group relative to the metal atom:



In the general case there is also a possibility of an inner-sphere mechanism with a simultaneous transfer of two ligands.

The electronic factor can determine the possibility of the inner-sphere oxidation reaction for a specific geometry of the complex. The latter should probably also ensure both definite relative positions of the oxygen and reacting ligand molecules and a definite stoichiometry (in particular for concerted reactions).

The lack of data precludes an adequately detailed discussion of the interesting reaction involving the catalytic hydrogenolysis of molecular oxygen in the presence of a number of complexes[106]. However, it is known that oxygen-fixing complexes can accelerate the autoxidation of

hydrocarbons[107-111]. Reactions of this type can proceed via an outer-sphere mechanism, since they have certain features of radical-chain processes, in particular they are retarded in the presence of specific inhibitors. It is also possible that in some cases the initiating effect of the metal complexes is not associated with the activation of molecular oxygen but with the acceleration of the decomposition of the hydroperoxides arising in the oxidation of the substrate[71-111]. However, the sensitisation of molecular oxygen by the complex appears to be more probable in many cases[109]. It has been noted[110] that complexes in which oxygen is least strongly bound exhibit the highest activity in the autoxidation of styrene. It is suggested that the sensitising species in such reactions may be a mononuclear complex of the superoxide type[11]:

$$M^{n+} + O_2 \rightarrow M^{(n+1)} + \dot{O}_2^- \xrightarrow{RH} M^{(n+1)} + OOH^- + R\cdot \ ;$$

$$M^{(n+1)} + OOH^- \rightarrow M^{n+} + HOO.$$

Mononuclear cobalt complexes of the superoxide type have been used as model compounds for the investigation of the mechanism of outer-sphere oxidation reactions. The ESR signal of the oxygen complex of corrinoid [Co^{II}(vitamin B_{12})] in the presence of small amounts of one-electron reducing agents (hydroquinone, *p*-phenylenediamine, ascorbic acid, and thiols) is replaced by the signal of the radical of the oxidised substrate, i.e. a one-electron oxidation–reduction reaction takes place between the oxygen complex and the substrate[71]. In the presence of excess reducing agent cobalt(II) is regenerated and the corresponding catalytic reaction occurs.

Table 6. Polarographic reduction of oxygen complexes[33].

Compound	Half-wave potential, V	Medium, reference electrode
(DMF) (*o*-Phenylenesalen)Co(O_2)	−0.300	DMF, Ag|AgCl, KCl
(DMF) (3-CH_3O-Salen)Co(O_2)	−0.324	Ditto
(DMF) (*Salen*)Co(O_2)	−0.420	"
(DMF) (acacen)Co(O_2)	−0.520	"
(Pyridine) (*o*-Phenylenesalen)Co(O_2)	−0.656	Pyridine, sat. cal.e-de
(Pyridine) (3-CH_3O-Salen)Co(O_2)	−0.660	Ditto
(Pyridine) (Salen)Co(O_2)	−0.660	"
O_2	−0.810	DMF, Ag|AgCl, KCl
O_2	−0.836	Pyridine, sat. cal.e-de

* *o*-Phenylenesalen = *o*-phenylenebis-salicylidene-ethylenediamine (Ed. of Translation).
** Salen = bis-salicylidene-ethylenediamine (Ed. of Translation).
*** acacen = *NN'*-ethylenebis(acetylacetoniminide) (Ed. of Translation).

It follows from the results of polarographic studies[33] that paramagnetic cobalt complexes of oxygen are more powerful one-electron oxidants than free oxygen or the initial non-oxygenated cobalt(II) species. The half-wave potential corresponding to the reversible one-electron reduction of the oxygen complex decreases as the electron-donating effect of the ligand environment of this metal becomes enhanced. Both the equatorial and the axial ligand then have an effect. For a more basic *trans*-ligand (pyridine), the electron-donating effect of the equatorial ligand is not differentiated (Table 6).

It follows from the data in Table 6 that the transfer of the negative charge from the metal atom to oxygen decreases the oxidising capacity of the oxygen complex, which can be readily understood within the framework of a simplified model postulating the location of the unpaired electron at the dioxygen group. Since the metal atom has a filled 18-electron shell and the oxygen has an accessible half-filled orbital, the reducing electron must occupy the latter. Evidently the energy of this orbital depends on the effective charge of the dioxygen group. Therefore the addition of the electron will be hindered by energy factors when the dioxygen group has an excess negative charge. In this case the most labile oxygen complexes, in which the M–O_2 bond is largely covalent, should exhibit the greatest oxidising capacity.

The results show that the labile mononuclear complex (PPh_3)(Salen)Co(O_2) can give rise to non-chain catalytic oxidation of aliphatic alcohols under mild conditions[112].

Thus two extreme types of active structures are characteristic of mononuclear oxygen complexes. They differ in the nature of the relative orientation of the oxygen molecule and the metal atom, in the degree of π-bonding, and in the spin state: they are diamagnetic π-complexes of the closed type and paramagnetic σ-complexes of the open type. The coordinated oxygen molecule in the diamagnetic complex bears some similarity to the oxygen molecule in the singlet state, which can account for its involvement in inner-sphere reactions of the non-radical type. In the paramagnetic complex the coordinated molecule resembles the active superoxide radical, and this is the reason for the occurrence of outer-sphere reactions of the radical type. Apart from these extreme structures, definite information about the nature of the activation of the molecule can be provided by structures of intermediate type.

It has been shown[49] that the high-spin complex $Ru(AsPh_3)_2Cl_2O_2$ readily combines with an SO_2 molecule, forming the corresponding sulphate, like a low-spin π-complex. The unpaired electrons are in this case probably located at the metal and the coordinated dioxygen group is spin-paired, i.e. the reactivity of the complex is determined by the state of the coordinated molecule and not of the metal atom.

There is so far no information about the nature of the reactivity of diamagnetic complexes of the open type. Presumably the coordinated oxygen molecule can exhibit a hydride acceptor activity.

It is known that dinuclear cobalt complexes are capable of oxidative combination with SO_2 and NO_2 molecules[113,114], but the mechanisms of these interesting reactions have not been elucidated.

The problem of creating an artificial matrix catalyst, an analogue of an oxidase-type enzyme, is extremely urgent. It was established recently[115] that the polymeric ligand poly-4-vinylpyridine causes a sharp increase of the catalytic activity of copper ions in the autoxidation of ascorbic acid. Although the interpretation of this effect is at present difficult, studies of this kind appear promising. The problem of the synthesis of the catalytic matrix can be solved on the basis of the specific sorption effect by obtaining "imprints" of the surface of the solid with the given orientation of the substrate molecule relative to the active centre[116].

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Studies on the activation of molecular oxygen have been recently carried out mainly using biological models for the fixation of molecular oxygen. They have yielded many

new data. Calculation by the Hückel molecular orbital method[117] on the fragment M–O_2–M, where M is an element of the first transition series ranging from titanium to nickel (there is an analogy with dinuclear dioxygen complexes), yielded some information about the specific role of the metal and also about the nature of the binding of the dioxygen group. The calculation demonstrated that the population of the M–O_2 bond is a maximum in the middle of the series of 3*d* complexes. This variation is determined by the fact that the overlap integrals of the d_{yz} and p_y orbitals decrease on passing from titanium to nickel and the coefficient defining the contribution of the d_{yz} orbital to the bonding molecular orbital increases in the same direction.

It has been suggested on the basis of calculations that σ-bonding, responsible for the strengthening of the M–O_2 bond, is more important in non-dissociable compounds, while the population of the O–O bond in such compounds is smaller than in dissociable compounds, which is consistent with the concept of a greater weakening of the O–O bond in non-dissociable compounds.

The results of ultraviolet spectroscopic studies on the interaction of catalytically active 'onium compounds of the type M_nAX, where A = S, P, Se, or Te and X = Cl, Br, I, BF_4, or ClO_4, with molecular oxygen were used to carry out a semiquantitative calculation by the SCF method[118], from which it follows that (1) not only fully populated *d* orbitals but also only partly populated orbitals can be involved in the activation of molecular oxygen, (2) the electron density of *d* orbitals can serve as a measure of the activation of molecular oxygen, and (3) the *d* orbitals of the catalytic centre can interact with the molecular orbitals located above the $1\pi_g$ orbital.

An X-ray diffraction analysis of an iron complex which is a matrix model of myoglobin has been carried out for the first time[119] (Fig. 8). It showed that the Fe–O–O plane is bisected by the angle between the two adjacent Fe–N bonds in the equatorial plane, which is probably a common feature of both iron and cobalt complexes (Fig. 6).

Resolution of the structure of the Fe–O–O fragment demonstrates the possibility of two statistically equally probable positions of the dioxygen group in mutually perpendicular planes.

Depending on the position of the Fe–O–O plane, the *trans*-ligand plane can be either parallel to the former or at right angles to it. The authors note that a difference between the two extreme positions of the *trans*-ligand plane is possible in principle, but the effect caused by this difference has not so far been discovered. A calculation yielded the following results: d_{O-O} = 1.23 ± 0.08 and 1.26 ± 0.08 Å, the angle Fe–O–O = 135° ± 4° and 137° ± 4°, and d_{Fe-O} = 1.75 ± 0.02 Å. The reduced Fe–O bond length is comparable with the Co–O bond length, which is usually in the range of 1.90 Å.

Among the new dioxygen complexes (matrix models of myoglobin), mention should be made of the paramagnetic complex Fe(αααα-TpivPP)$(THF)_2O_2$ (μ = 2.4 B.M.)[120] where αααα-H_2TpivPP = *meso*-tetra-(αααα-*o*-pivalamidophenyl)porphyrin and THF = tetrahydrofuran. This complex is capable of many repetitions of the deoxygenation–oxygenation cycle in the solid state with concomitant changes in magnetic susceptibility.

The structure of the mononuclear complex $(Et_4N)_3[Co(CN)_5O_2].5H_2O$,[121] in which the Co–O–O angle is 175° ± 2° according to structural studies, i.e. the Co–O–O fragment is nearly linear, is of considerable interest. Unfortunately the authors note that the accuracy of the observed Fe–O–O angles and O–O bond lengths is greatly influenced by the thermal motion of the O_2 group.

The high-spin complex[122] $[Bu_4N][Co(PFP)(HPFP)O_2]$, where Bu_4N is tetrabutylammonium and PFP and HPFP are the dibasic and monobasic residues of perfluoropinacol $[(CF_3)_2C(OH)C(OH)(CF_3)_2]$ occupies a special place. Its magnetic moment is 3.64 ± 0.04 B.M. Studies of its electronic spectra led to the hypothesis that a Co–O_2 bond is formed in this complex without charge transfer.

A copper complex of a polymeric ligand[123], capable of reversible interaction with molecular oxygen and carbon monoxide, was obtained for the first time quite recently[123]. A polyoxime, obtained from an alternant copolymer of ethylene and carbon monoxide, was used as a ligand. Its

unit is described by the formula $\{[CH_2-CH_2]_{1.2}[C]\}$ and its molecular weight is 4000. It is believed that copper is in the monovalent state.

The latest electrochemical studies on dioxygen complexes of cobalt[124] showed that the redox potential of the Co^{II}/Co^{III} system reflects the overall effect of the σ- and π-interactions and steric factors, in conformity with the specific ligand environment.

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