

I,⁴¹⁻⁴³ SR,⁴⁴ TeR,⁴⁵ PR₂,^{5,39,46} AsR₂,^{5,6,47}), which for the bromine-bridged derivative was characterized both by X-ray diffraction⁴⁸ and by detailed infrared spectral studies⁴³ to possess D_{2h} symmetry.

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It is hoped that a neutron diffraction study of this compound can be undertaken in the near future in order to verify our proposed configuration.

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Structure of IrO₂Cl(CO)(P(C₆H₅)₃)₂, the Oxygen Adduct of a Synthetic Reversible Molecular Oxygen Carrier¹

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The structure of IrO₂Cl(CO)(P(C₆H₅)₃)₂, which is the oxygen adduct of the synthetic molecular oxygen carrier IrCl(CO)(P(C₆H₅)₃)₂, has been determined from three-dimensional X-ray data collected from a single crystal. The material crystallizes in space group C₂^h-P1̄ of the triclinic system with two molecules in a cell of dimensions $a = 19.02$, $b = 9.83$, $c = 9.93$ Å.; $\alpha = 94.0$, $\beta = 64.9$, $\gamma = 93.2^\circ$; $V = 1676$ Å.³. The crystal structure consists of the packing of discrete, monomeric molecules. The molecular structure surmised by Vaska from spectroscopic data has been confirmed, and, in addition, details of the attachment of molecular oxygen to iridium have been obtained. The iridium may be described as either five- or six-coordinated: the iridium, the two oxygen atoms, the carbonyl group, and the chlorine atom lie in the basal plane, with phosphorus atoms above and below this plane. The two oxygen atoms are equidistant from the iridium atom, with an average Ir-O distance of 2.07 Å. The O-O bond length of 1.30 ± 0.03 Å. is intermediate between those characteristic of O₂ (1.21 Å.) and O₂⁻² (1.49 Å.) and corresponds closely to O₂⁻ (1.28 Å.).

Introduction

Knowledge of the manner in which oxygen is attached in natural molecular oxygen carriers, such as hemoglobin and hemocyanin, is obviously of great importance to our understanding of the molecular bases for such properties as reversibility of oxygen uptake and oxygen transport. No direct information on the mode of attachment is available at present, and the prospects for a direct determination by diffraction methods, though not altogether bleak, are at least not immediate. On the basis of indirect spectroscopic and magnetic measurements, several models for the mode of attachment of molecular oxygen to the iron in hemoglobin have been put forward.²⁻⁵ These run the gamut from a

linear bonding arrangement² through a bent configuration^{3,4} to the triangular, or π -bonding, arrangement⁵ in which both oxygens are equidistant from the iron. There has also been recent speculation and discussion concerning the disposition of the electrons in the bonding scheme.^{4,6-8}

The synthetic molecular oxygen carriers offer advantages over the natural ones in simplicity and variety. It is evident that by studying the physical and structural properties of synthetic carriers and their oxygen adducts one should be able to increase the understanding of the molecular bases for such phenomena as reversibility. Yet very few studies of a definitive nature have been carried out on these synthetic carriers or their oxygen adducts, probably because most of them are unstable or poorly characterized.⁹ Vaska's discovery¹⁰ of the 1:1 reversible molecular oxygen carrier IrCl(CO)(P(C₆H₅)₃)₂ is thus of great importance, for the oxygen adduct IrO₂Cl(CO)(P(C₆H₅)₃)₂ may be crystallized and is extremely stable and well characterized in comparison with previously known oxygen adducts. In a preliminary report¹¹ we gave some details of our study of the molecular structure of this remarkable compound. In this paper we present our results in full.

Collection and Reduction of the X-Ray Data

Excellent light orange crystals of IrO₂Cl(CO)(P(C₆H₅)₃)₂ were very kindly supplied by L. Vaska. These crystals were stable in air during the X-ray photography,

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(3) L. Pauling, "Hemoglobin, Sir Joseph Barcroft Memorial Symposium," Butterworth and Co. (Publishers) Ltd., London, 1949, p. 57.

(4) L. Pauling, *Nature*, **203**, 182 (1964).

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(6) J. J. Weiss, *Nature*, **202**, 83 (1964).

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(8) R. O. Viale, G. M. Maggiora, and L. L. Ingraham, *ibid.*, **203**, 183 (1964).

(9) See L. H. Vogt, H. M. Faigenbaum, and S. E. Wiberley, *Chem. Rev.*, **63**, 269 (1963), for a review of synthetic carriers.

(10) L. Vaska, *Science*, **140**, 809 (1963).

(11) J. A. Ibers and S. J. La Placa, *ibid.*, **145**, 920 (1964).

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

and although they did darken gradually, no detectable changes in X-ray intensities resulted. The crystals were assigned to the triclinic system as a result of an optical examination and preliminary X-ray photography. A Delaunay reduction failed to suggest the presence of hidden symmetry. The cell chosen is a primitive one of dimensions $a = 19.02 \pm 0.03$, $b = 9.83 \pm 0.02$, $c = 9.93 \pm 0.02$ Å., $\alpha = 94.0 \pm 0.1$, $\beta = 64.9 \pm 0.1$, $\gamma = 93.2 \pm 0.1^\circ$. The unit cell volume is 1676 Å.³ and the calculated density is 1.61 g./cm.³ for two molecules in this cell. A very sensitive test for a piezoelectric effect was kindly performed for us by F. Holtzberg; no effect was found. Accordingly the space group $C_1^2-P\bar{1}$ was assumed in this work, and this assumption seems justified in view of the excellent agreement obtained between observed and calculated structure amplitudes. Since there are two molecules in $P\bar{1}$, no crystallographic symmetry conditions need be imposed on the molecules.

Integrated intensity data were collected at room temperature by the equi-inclination Weissenberg technique. Zirconium-filtered Mo $K\alpha$ radiation was employed. The layers $h0l$ through $h6l$ were photographed. The intensities of 1128 independent reflections within the limiting sphere $\theta_{Mo} \leq 18^\circ$ were estimated visually. (About 60% of the accessible reflections were sufficiently strong to be estimated reliably.) The usual Lorentz polarization factor was applied to these intensities to yield F_o^2 values (where F_o is the observed structure amplitude), and these were then corrected for absorption. In order to carry out the absorption correction, the eight faces on the crystal used in the X-ray photography were identified by optical goniometry and their dimensions were carefully determined. The volume of the crystal used is approximately 0.0021 mm.³ and has a calculated weight of only 3.2 μ g. Yet because the crystal is not of equant habit, but has linear dimensions of approximately $0.31 \times 0.09 \times 0.08$ mm., the absorption corrections are important. Using a linear absorption coefficient of 44.3 cm.⁻¹, we find the transmission coefficients vary from 0.50 to 0.75.¹² The F_o values were subsequently brought to an approximate common scale through a modification of Wilson's procedure.

Solution and Refinement of the Structure

The positions of the Ir and P atoms were evident from inspection of the three-dimensional Patterson function. The positions of the two oxygen atoms and of the ring carbon atoms were easily found in a subsequent difference Fourier synthesis, based on structure factors phased by the Ir and P contributions. The two most prominent peaks on this map corresponded to reasonable positions for the Cl and CO, but they were similar in shape and height and in neither were the C and O of the CO group resolved. A disordered arrangement of CO and Cl was suspected and was confirmed in later calculations.

The structure was refined by the least-squares method. The function minimized was $\sum w(F_o - F_c)^2$, where the weights w were assigned in the following way: I (the raw intensity) ≤ 16 , $w = (I/32F)^2$; $I > 16$, $w = (2F)^{-2}$. The atomic scattering factors for the neutral

(12) In addition to a variety of local programs for the IBM 7090, the following were employed in the calculations: local modifications of Burnham's GNABS absorption program, Zalkin's FORDAP Fourier program, and the Busing-Levy ORFLS least-squares program.

atoms tabulated by Ibers¹³ were used. The anomalous parts of the Ir, Cl, and P scattering factors were obtained from Templeton's tabulation¹⁴ and were included in the calculated structure factors.¹⁵

The refinement was carried out using the group procedure discussed more fully elsewhere.^{16,17} In this manner the phenyl rings were constrained to their well-known geometry (D_{6h} symmetry, C-C = 1.392 Å., C-H = 1.08 Å.) with consequent increase in convergence rate and decrease in the number of parameters and in computing time. This procedure permits the introduction of physically reasonable information, namely the phenyl ring geometry, into the refinement and this is particularly important since this geometry is known more accurately than it could be deduced from a structure determination of this sort. The variable parameters for each phenyl ring are a single, isotropic thermal parameter and six positional parameters. These are the fractional coordinates of the ring center, x_c , y_c , and z_c , and three angles, δ , ϵ , and η , which are successive counterclockwise rotations about the \mathbf{a}_2' , \mathbf{a}_1' , and \mathbf{a}_3' orthogonal internal axes that bring about alignment, except for translation, of this coordinate system with an orthogonal, external coordinate system \mathbf{A} . The origin of the internal coordinate system is taken at the ring center, and \mathbf{a}_3' is normal to the plane of the ring while \mathbf{a}_1' intersects a vertex. The orthogonal, external coordinate system \mathbf{A} is formed from the triclinic coordinate system \mathbf{a} in the following way: \mathbf{A}_2 is parallel to \mathbf{a}_2 ; \mathbf{A}_1 is parallel to $\mathbf{a}_2 \times \mathbf{a}_3$; \mathbf{A}_3 is parallel to $\mathbf{A}_1 \times \mathbf{A}_2$.

In the initial refinement, Cl scattering factors were assigned to each of the Cl-CO peaks, and each of the heavy atoms was assigned a single, variable isotropic thermal parameter. This refinement of 70 individual and group positional and thermal parameters converged rapidly to a conventional R factor ($R = \sum |F_o| - |F_c| / \sum |F_o|$) of 0.085 and to a weighted R factor R' ($R' = (\sum w(F_o - F_c)^2 / \sum w F_o^2)^{1/2}$) of 0.100. A difference Fourier synthesis based on this refinement provided no indication of an incorrect treatment of the Cl-CO peaks, but did suggest that the Ir atom is vibrating anisotropically.

In a final round of calculations the Ir was assigned anisotropic thermal parameters, the Cl-CO positions were again approximated by a Cl scattering factor, and this time the hydrogen atom contributions on the phenyl rings were included in the calculations. This refinement of 75 positional and thermal parameters converged to values of R of 0.071 and of R' of 0.074 and led to the final parameter values given in Table I. The standard deviations of these parameters, as estimated from the inverse matrix, are also listed in Table I. (Table II lists the fractional coordinates for the ring carbon atoms that can be derived from the data of Table I.) A final difference Fourier based on this refinement had density no higher than 0.9 electron/Å.³, about 30% of the height of a phenyl carbon atom in this structure. The only obvious feature on this difference Fourier relates to the vibration of the phenyl rings:

(13) J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, Table 3.3.1.

(14) D. H. Templeton, ref. 13, Table 3.3.2C.

(15) J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, 17, 781 (1964).

(16) S. J. La Placa and J. A. Ibers, *J. Am. Chem. Soc.*, 85, 3501 (1963).

(17) S. J. La Placa and J. A. Ibers, *Acta Cryst.*, 18, 511 (1965).

Table I. Positional, Thermal, and Group Parameters for $\text{IrO}_2\text{Cl}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å. ²
Ir	0.2342(1) ^a	0.2100(2)	0.0068(2)	<i>b</i>
P ₁	0.1335(6)	0.3207(13)	0.2136(11)	3.9(3)
P ₂	0.3430(7)	0.1266(15)	-0.2024(13)	6.0(4)
X ₁ ^c	0.2873(9)	0.1153(18)	0.1618(16)	11.0(4)
X ₂	0.1467(10)	0.0293(21)	0.0019(19)	13.6(5)
O ₁	0.224(1)	0.366(3)	-0.117(2)	4.9(7)
O ₂	0.279(2)	0.397(3)	-0.073(3)	8.4(1.0)

Group	<i>x</i> _c ^d	<i>y</i> _c	<i>z</i> _c	δ	ε	η	<i>B</i> , Å. ²
P ₁ R ₁ ^e	-0.033(1)	0.313(2)	0.195(2)	4.97(4)	5.22(2)	4.97(4)	5.6(6)
P ₁ R ₂	0.098(1)	0.203(2)	0.528(2)	3.04(2)	5.81(2)	1.69(2)	5.2(5)
P ₁ R ₃	0.181(1)	0.635(2)	0.250(1)	1.21(2)	5.86(1)	2.91(2)	5.2(5)
P ₂ R ₁	0.375(1)	0.279(2)	-0.494(2)	4.86(2)	0.29(2)	5.20(2)	6.3(5)
P ₂ R ₂	0.496(1)	0.152(2)	-0.146(2)	0.30(2)	0.33(2)	2.46(2)	7.2(6)
P ₂ R ₃	0.330(1)	-0.192(2)	-0.281(2)	5.34(5)	5.10(2)	3.85(5)	6.3(5)

^a Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits. ^b Ir was refined anisotropically. The thermal ellipsoid had the form $\exp(-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$ and the values obtained are $\beta_{11} = 0.00205(6)$; $\beta_{22} = 0.0088(2)$; $\beta_{33} = 0.0085(2)$; $\beta_{12} = 0.00082(9)$; $\beta_{13} = -0.0025(1)$; $\beta_{23} = 0.0020(2)$. ^c X₁ and X₂ refer to disordered Cl-CO positions. ^d *x*_c, *y*_c, and *z*_c are the fractional coordinates of the ring centers. The angles δ, ε, η (in radians) are defined in the text. ^e P₁R₁ is phosphorus 1, ring 1, etc.

Table II. Derived Parameters for Group Carbon Atoms

Group atom ^a	<i>x</i>	<i>y</i>	<i>z</i>
P ₁ R ₁ C ₁	0.039(1)	0.317(3)	0.203(4)
P ₁ R ₁ C ₂	0.036(1)	0.325(3)	0.066(3)
P ₁ R ₁ C ₃	-0.036(2)	0.321(3)	0.058(2)
P ₁ R ₁ C ₄	-0.104(1)	0.309(4)	0.188(4)
P ₁ R ₁ C ₅	-0.101(1)	0.302(3)	0.324(3)
P ₁ R ₁ C ₆	-0.030(2)	0.306(3)	0.332(2)
P ₁ R ₂ C ₁	0.111(1)	0.257(3)	0.394(2)
P ₁ R ₂ C ₂	0.098(1)	0.118(3)	0.410(3)
P ₁ R ₂ C ₃	0.085(1)	0.063(2)	0.545(3)
P ₁ R ₂ C ₄	0.085(1)	0.148(3)	0.663(2)
P ₁ R ₂ C ₅	0.098(1)	0.288(3)	0.646(3)
P ₁ R ₂ C ₆	0.111(1)	0.342(2)	0.512(3)
P ₁ R ₃ C ₁	0.160(2)	0.499(2)	0.238(3)
P ₁ R ₃ C ₂	0.111(1)	0.601(4)	0.243(3)
P ₁ R ₃ C ₃	0.132(2)	0.737(3)	0.256(3)
P ₁ R ₃ C ₄	0.202(2)	0.772(2)	0.263(3)
P ₁ R ₃ C ₅	0.251(1)	0.670(4)	0.258(3)
P ₁ R ₃ C ₆	0.230(2)	0.534(3)	0.245(3)
P ₂ R ₁ C ₁	0.361(2)	0.217(3)	-0.363(3)
P ₂ R ₁ C ₂	0.435(2)	0.271(3)	-0.448(3)
P ₂ R ₁ C ₃	0.449(1)	0.334(3)	-0.579(3)
P ₂ R ₁ C ₄	0.390(2)	0.342(3)	-0.625(3)
P ₂ R ₁ C ₅	0.316(2)	0.288(3)	-0.540(3)
P ₂ R ₁ C ₆	0.302(1)	0.225(3)	-0.409(3)
P ₂ R ₂ C ₁	0.431(2)	0.138(4)	-0.178(3)
P ₂ R ₂ C ₂	0.444(2)	0.257(3)	-0.107(3)
P ₂ R ₂ C ₃	0.509(2)	0.271(3)	-0.075(3)
P ₂ R ₂ C ₄	0.561(1)	0.166(4)	-0.114(3)
P ₂ R ₂ C ₅	0.548(2)	0.046(3)	-0.185(3)
P ₂ R ₂ C ₆	0.483(2)	0.033(3)	-0.216(3)
P ₂ R ₃ C ₁	0.333(2)	-0.052(2)	-0.250(4)
P ₂ R ₃ C ₂	0.352(1)	-0.102(3)	-0.396(3)
P ₂ R ₃ C ₃	0.349(2)	-0.241(4)	-0.427(2)
P ₂ R ₃ C ₄	0.326(2)	-0.331(2)	-0.313(4)
P ₂ R ₃ C ₅	0.307(1)	-0.282(3)	-0.167(3)
P ₂ R ₃ C ₆	0.310(2)	-0.142(3)	-0.136(2)

^a C₁ is attached to P; other C atoms are numbered in succession so that C₄ is *para* to C₁. The standard deviations are derived from estimated standard deviations in the group parameters and are meant to be used in error analyses on inter-ring distances. Intra-ring distances, of course, are fixed (C-C = 1.392 Å.).

there is a clear indication that the carbon atoms nearest to phosphorus are vibrating less than those farther

away. The differences in thermal parameters were not derived. Even in this difference Fourier there was no indication that the treatment of the disorder was improper. Although a more elaborate treatment might be desirable, it does not seem possible, since the Ir-Cl and Ir-C distances and the thermal parameters of Cl, C, and O would have to be known in advance, and could not be refined, if one were to use a model consisting of 1/2 Cl and 1/2 CO at each position. Undoubtedly the high thermal parameters for "atoms" X₁ and X₂ (where X designates a Cl-CO composite position) are a reflection of the fact that the peak is broadened both by the composite C-O peak and also because the C-O peak center and the Cl peak center do not necessarily coincide. Both for this reason and because of the excellent agreement achieved with the present model, the parameters of Table I are taken as final parameters for this structure. In Table III the values of *F*_o and *F*_c (in electrons) are given for the 1128 observed reflections. The *F*_c values for unobserved reflections are omitted from Table III, since none of the intensities calculated for unobserved but accessible reflections exceeds our estimate of a minimum observable intensity value.

The anisotropic thermal parameters of Ir lead to principal root-mean-square amplitudes of vibration of 0.125 ± 0.004 , 0.192 ± 0.002 , and 0.220 ± 0.003 Å.

Description of the Structure

The crystal structure described by the space group, the parameters of Table I, and the cell parameters consists of the packing of individual, monomeric molecules (shortest Ir-Ir distance >9 Å.). A perspective drawing of a monomer molecule is shown in Figure 1; the molecular structure is essentially that deduced by Vaska¹⁰ from spectroscopic and magnetic data. The Ir, O₁, O₂, X₁, and X₂ atoms are coplanar: the best least-squares plane¹⁸ through these five atoms has the equation $8.331x - 3.931y - 5.312z = 1.089$ (triclinic coordinates). The distances of these atoms from this plane are given in Table IV. Figure 2 shows part of the difference electron density in this plane.

(18) W. C. Hamilton, *Acta Cryst.*, **14**, 185 (1961).

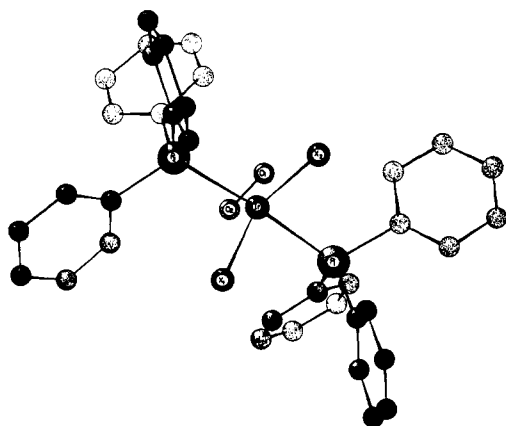


Figure 1. A perspective drawing of the $\text{IrO}_2\text{Cl}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$ molecule. X_1 and X_2 are the disordered Cl-CO positions; phenyl hydrogen atoms are not shown.

This difference Fourier is based on F_c values that do not include contributions from O_1 , O_2 , X_1 , or X_2 and displays the electron density at these positions. Figure 2 illustrates rather well the near equivalence of the X_1 and X_2 peaks and the fact that while the O_1 - O_2 peaks are readily resolved, there is no indication of CO resolution. This total disorder of the Cl and CO positions may be rationalized in the following way. Presumably the compound results from the attack above or below the square-planar $\text{IrCl}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$ molecule by O_2 in benzene solution, for the method of preparation¹⁰ is essentially the reaction of O_2 with a benzene solution of $\text{IrCl}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$. Since the triphenylphosphine ligands are equivalent in solution,¹⁰ only one isomer is formed, and if the relative positions of Cl and CO do not affect the crystallization process, then total disorder would be expected. This is not unreasonable, for the packing is determined almost entirely by the triphenylphosphine groups: the volume per triphenylphosphine in this structure is only 15% greater than in triphenylphosphine¹⁹ itself.

Table IV. Distances of Atoms from Best Least-Squares Plane

Atom	Distance, Å.
Ir	0.0008(19)
X_1	-0.007(15)
X_2	0.008(18)
O_1	-0.039(21)
O_2	0.063(28)

Principal intramolecular distances and angles are given in Table V. (All intermolecular contacts appear to be normal and are therefore not listed.) The intramolecular distances seem normal. The average Ir-P distance of 2.37 Å. may be compared with the basal Ru-P distances of 2.39 Å. in $\text{RuCl}_2(\text{P}(\text{C}_6\text{H}_5)_3)_2$,²⁰ and with Rh-P distances of 2.32 Å. in $\text{RhH}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_3$.¹⁶ There is no comparable Ir- O_2 geometry described in the literature. However, the Cr-O distances in K_3CrO_8 average 1.89 Å.,²¹ and since the Cr- O_2 bonding seems to be similar to the Ir- O_2 bonding found here and since

(19) J. J. Daly, *J. Chem. Soc.*, 3799 (1964).

(20) S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, **4**, 778 (1965).

(21) J. D. Swalen and J. A. Ibers, *J. Chem. Phys.*, **37**, 17 (1962).

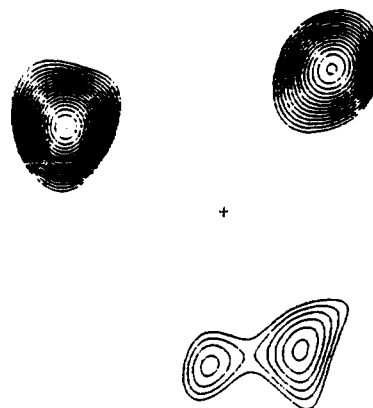


Figure 2. Electron density at the X_1 , X_2 , O_1 , and O_2 positions in the best least-squares plane containing these positions and the Ir. The Ir position is marked with a cross. The contour interval is 0.26 electron/Å.³ and contours from 1.31 to 5.24 electrons/Å.³ are shown.

the Cr radius is about 0.1 Å. less than the Ir radius, the average Ir-O distance of 2.07 Å. does not seem unreasonable. The triphenylphosphine geometry is similar to that found recently in other compounds,^{16,20} with the C-P-C angles being somewhat larger.

Table V. Selected Intramolecular Distances and Angles

Intramolecular distance, Å.		Angle, deg.	
Ir-P ₁	2.38(1)	P ₁ -Ir-P ₂	172.8(5)
Ir-P ₂	2.36(1)	P ₁ -Ir-X ₁	93.0(5)
Ir-X ₁	2.42(2)	P ₁ -Ir-X ₂	90.9(5)
Ir-X ₂	2.38(2)	P ₁ -Ir-O ₁	85.4(7)
Ir-O ₁	2.09(3)	P ₁ -Ir-O ₂	89.2(9)
Ir-O ₂	2.04(3)	P ₂ -Ir-X ₁	87.7(5)
P ₁ -P ₂	4.73(2)	P ₂ -Ir-X ₂	96.0(6)
P ₁ -X ₁	3.48(2)	P ₂ -Ir-O ₁	90.6(7)
P ₁ -X ₂	3.39(2)	P ₂ -Ir-O ₂	84.1(9)
P ₁ -O ₁	3.04(2)	X ₁ -Ir-X ₂	100.1(6)
P ₁ -O ₂	3.11(3)	X ₁ -Ir-O ₁	152.4(8)
P ₂ -X ₁	3.32(2)	X ₁ -Ir-O ₂	115.9(1.0)
P ₂ -X ₂	3.52(2)	X ₂ -Ir-O ₁	107.4(9)
P ₂ -O ₁	3.17(3)	X ₂ -Ir-O ₂	144.0(1.1)
P ₂ -O ₂	2.96(3)	O ₁ -Ir-O ₂	36.7(9)
X ₁ -X ₂	3.68(2)	C ₁ -P-C ₁ '	105(1)
X ₁ -O ₁	4.39(3)	(av. of six)	
X ₁ -O ₂	3.79(4)		
X ₂ -O ₁	3.61(3)		
X ₂ -O ₂	4.21(4)		
O ₁ -O ₂	1.30(3)		
P-C ₁	1.81(1)		
(av. of six)			

The significant facts with regard to oxygen attachment are that the two oxygen atoms are equidistant from the Ir (difference in Ir-O bond lengths is 0.051 ± 0.045 Å.) and the O-O distance of 1.30 ± 0.03 Å., while longer than that in molecular oxygen (1.21 Å.), is significantly less than that in a typical peroxide (1.49 Å.).²² This equivalence of the oxygen atoms is consistent with Griffith's⁵ model of the π -bonding of molecular oxygen to iron in hemoglobin (also a 1:1 oxygen carrier). The facts that oxygen uptake is reversible and that the O-O bond length is significantly shorter

(22) As a result of thermal motion, this bond distance of 1.30 Å. is shorter than the equilibrium distance; however, we estimate that it is within 0.04 Å. of the equilibrium distance.

than that in a typical peroxide are consistent with the views of Martell and Calvin²³ that reversibility probably depends upon some electron transfer from metal to oxygen, but not sufficient transfer to bring about irreversible oxidation of the metal. In the present case this transfer amounts to approximately one electron, since the O—O distance corresponds closely to O₂⁻ (1.28 Å.); thus the formal oxidation state is Ir(II) and yet the compound is diamagnetic. Of course, in compounds of this type the concept of a formal oxidation state is not particularly useful. A less qualitative and possibly more useful description of the bonding might result from a molecular orbital calculation, although this would be more meaningful if the structures of a series of analogous compounds were known. Even the question of whether Ir is five- or six-coordinated in this structure has been tacitly ignored. (The Ir could be thought of as five-coordinated if the O₂ molecule were counted as a single ligand, as is, for example, the ethylene molecule in Zeiss's salt.) An analogous compound with SO₂ in place of O₂ has been prepared by Vaska²⁴ and its structure is now under investigation.²⁵ The differences between the stereochemistry of the SO₂ and O₂ com-

(23) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1952, p. 352.

(24) L. Vaska, unpublished results.

(25) NOTE ADDED IN PROOF. The SO₂ complex is five-coordinated, with an Ir—S bond. However, the coordination geometry is tetragonal

pounds should provide additional insight into the bonding in each.

It is particularly interesting that the combination Fe³⁺·O₂⁻ has been proposed very recently by Weiss^{6,7} as the structure of oxyhemoglobin and that a preliminary molecular orbital calculation⁸ appears to support such a structure. It may be that the analogy between the oxyhemoglobin system and the synthetic iridium system studied here is a very good one. Nevertheless, it is obviously dangerous to extrapolate from this one structure determination and conclude that in both natural and synthetic molecular oxygen carriers π -bonding of the oxygen to the metal is the rule and that the O—O distance approaching that of O₂⁻ is necessary for reversibility of oxygen uptake. Clearly additional experiments are needed to discover new, synthetic oxygen carriers of sufficient stability so that additional molecular structures of their oxygen adducts can be determined.

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pyramidal with S at the apex, rather than the trigonal bipyramidal geometry which may be assigned to the O₂ complex.