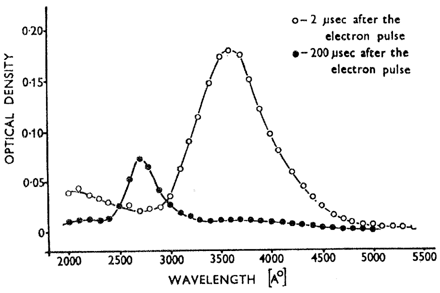

Fig. 1. Transient spectra of aerated $10^{-2}M$ potassium bromide at *p*H 2.1 subjected to pulse radiolysis (pulse of 2-μsec duration). The absorption maximum at 3600 Å is due to the dibromide ion-radical, Br_2^-; the long-lived absorption at 2700 Å is due to the tribromide ion, Br_3^-.

This new transient was stable over a period of at least 2 minutes. By comparison with the data of Grossweiner and Matheson (*3*), and Dorfman *et al.* (*4*), we assign the absorption at 3600 Å to the dibromide ion-radical, Br_2^-. The spectrum of the long-lived species resembled that of a solution prepared by the addition of bromine to $10^{-2}M$ potassium bromide at *p*H 2, and we attribute it to the tribromide ion Br_3^-. We found in a separate experiment that Br_3^- reacts surprisingly slowly with hydrogen peroxide; the optical density due to Br_3^- in a solution of $10^{-2}M$ KBr, $1.5 \times 10^{-5}M$ H_2O_2, and $4 \times 10^{-6}M$ Br_2 at *p*H 2 being decreased only by 47 percent in 4.5 hours. Despite its expected long half-life and its high molar extinction coefficient of 36.000 ± 3.6000 mole^{-1} cm^{-1} we were unable to see absorption due to Br_3^- in γ-radiolysis at a dose rate of 9.2 rad sec^{-1}. Therefore, we attribute the formation of Br_3^- under pulse radiolysis conditions to the high dose-rates used, leading to concentrations of HO_2 radicals such that HO_2 reacts with Br_2^- to yield ultimately H_2O_2 and Br_3^-. We found $G(H_2O_2)$ to be 2.8 ± 0.15. Estimations of the sum of $G(Br_2)$ plus $G(Br_3^-)$ gave 1.5. The rate constant for the reaction of HO_2 with Br_2^- was found to be $(6.4 \pm 0.3) \times 10^9$ mole^{-1} sec^{-1}.

In de-aerated acid potassium bromide ($10^{-2}M$) solutions the Br_3^- absorption was not seen (*3*).

In view of our results, the mechanism for the pulse radiolysis of potassium bromide solutions must be more complex than the mechanism proposed by Allen and Holroyd (*5*) and Sworski (*6*) for radiolysis at low intensities (*7*).

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References and Notes

1. J. P. Keene, *Nature* **188**, 843 (1960); *J. Sci. Instr.*, in press.
2. C. J. Hochanadel, *J. Phys. Chem.* **56**, 587 (1952).
3. L. I. Grossweiner and M. S. Matheson, *J. Chem. Phys.* **23**, 2444 (1955); *J. Phys. Chem.* **61**, 1089 (1957).
4. L. M. Dorfman, I. A. Taub, R. E. Buhler, *J. Chem. Phys.* **36**, 3051 (1962).
5. A. O. Allen and R. A. Holroyd, *J. Am. Chem. Soc.* **77**, 5852 (1955).
6. T. J. Sworski, *Radiation Res.* **2**, 26 (1955); *J. Amer. Chem. Soc.* **76**, 4687 (1954).
7. Full details of the pulse radiolysis studies of aerated and de-aerated potassium bromide solutions will be published elsewhere.
8. We thank H. C. Sutton for invaluable comments.

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12 June 1964

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Molecular Structure of the Synthetic Molecular Oxygen Carrier $O_2IrCl(CO)(P[C_6H_5]_3)_2$

Abstract. *The synthetic molecular oxygen carrier* $O_2IrCl(CO)(P[C_6H_5]_3)_2$, *discovered by Vaska, has been characterized in a complete molecular structure determination. The structure surmised by Vaska from spectroscopic data has been confirmed and, in addition, definitive details on the attachment of molecular oxygen to iridium in this 1 : 1 reversible oxygen carrier have been obtained. The two oxygen atoms are equidistant from the metal atom, as in Griffith's model of the oxygen atoms in oxyhemoglobin. The O-O bond length of 1.30 ± 0.03 Å is intermediate between those characteristic of* O_2 *(1.20 Å) and* O_2^{-2} *(1.48 Å), and corresponds closely to* O_2^- *(1.28 Å).*

Metal chelate oxygen carriers are of interest both because of the kinetics of oxygen exchange and because of the possible analogy of such carriers to biological oxygen carriers, such as hemoglobin. It is clear from the recent review of Vogt, Faigenbaum, and Wiberley (*1*) that there is little information on how the oxygen molecule is attached to the metal atom in synthetic oxygen carriers. There is some information on the 1:2 complexes, in which one molecule of oxygen is shared between two metal atoms (*2*), but such compounds are not analogous to the oxyhemoglobin system, in which there is one molecule of oxygen for each iron atom. The best characterized of the previously reported 1:1 complexes are the type II *bis*-salicylaldehyde-imine cobalt oxygen carriers (*3*), but in these compounds nothing definitive is known about the bonding which is discussed in terms of the oxygen filling "holes" in the crystal lattice. Moreover these compounds apparently exist in several crystalline modifications, not all of which are active carriers. Recently Vaska (*4*) discovered the 1:1 reversible oxygen carrier $O_2IrCl(CO)(P[C_6H_5]_3)_2$, and this discovery is of great importance since the compound can not only be isolated, but is stable. In this report we summarize our study, by diffraction techniques, of this compound, and we present the first definitive evidence on the mode of attachment of molecular oxygen to the metal atom in a 1:1 synthetic metal-chelate oxygen carrier.

L. Vaska very kindly supplied excellent single crystals of $O_2IrCl(CO)(P[C_6H_5]_3)_2$. These crystals were stable in air during x-ray photography, although they did gradually darken from light orange to orange-brown, without detectable change in the x-ray intensities. The material crystallizes with two molecules in a primitive triclinic cell of dimensions

$$a = 19.02 \pm 0.03, \quad \alpha = 94.0 \pm 0.1,$$
$$b = 9.83 \pm 0.02, \quad \beta = 64.9 \pm 0.1,$$
$$c = 9.93 \pm 0.02 \text{ Å}, \quad \gamma = 93.2 \pm 0.1°,$$

a, b, and *c* being the axial lengths and α, β, and γ being the interaxial angles. The unit cell volume is 1678 Å^3 and the calculated density 1.61 g/cm^3. A sensitive test for a piezoelectric effect was negative (*5*) and a reasonable structure has been determined on the assumption that the structure is centrosymmetric, space group $P\bar{1}$. The crystal chosen for the x-ray photography had approximate linear dimensions of 0.31 by 0.09 by 0.08 mm and a calculated weight of 3.2 μg. Data were collected at room temperature with MoKα radiation by the equi-inclination Weissenberg technique on a Nonius integrating camera. The intensities were estimated visually against a calibrated strip and were reduced to structure amplitudes F_o in the usual way after a reliable correction for absorption.

The positions of the Ir and P atoms were evident from inspection of the three-dimensional Patterson function.

Table 1. Principal interatomic distances and angles.

Distance	Å	Angle	Deg.
Ir–P_1	2.38(1)*	P_1–Ir–P_2	173(1)
Ir–P_2	2.36(1)	X_1–Ir–X_2	100(1)
Ir–X_1	2.42(2)	X_2–Ir–O_1	107(1)
Ir–X_2	2.38(2)	O_1–Ir–O_2	37(1)
Ir–O_1	2.09(3)	O_2–Ir–X_1	116(1)
Ir–O_2	2.04(3)	P_1–Ir–X_1	93(1)
O_1–O_2	1.30(3)	P_1–Ir–X_2	91(1)
		P_1–Ir–O_1	85(1)
		P_1–Ir–O_2	89(1)
		P_2–Ir–X_1	88(1)
		P_2–Ir–X_2	96(1)
		P_2–Ir–O_1	91(1)
		P_2–Ir–O_2	84(1)

* The number in parentheses is the estimated error in the least significant figure.

The positions of the two oxygen atoms and the ring carbon atoms were easily found in subsequent difference Fourier syntheses. In addition two strong peaks, corresponding to Cl and CO, were found on these maps, but they were similar in shape and height, and in neither was the C and O of the carbonyl resolved. This trial structure was refined by successive least-squares calculations, using the group refinement of the phenyl rings described previously (*6*). From this refinement and subsequent difference Fourier syntheses it was evident that the CO and Cl positions in the structure are disordered in the sense that the two electron-density peaks in question are made up of both CO and Cl contributions. A final refinement was carried out in which a Cl scattering factor was assigned to the composite peaks. In this refinement the Ir was allowed to vibrate anisotropically and the other heavy atoms were constrained to vibrate isotropically, while each phenyl ring (including the hydrogen contributions) was assigned an individual overall isotropic thermal parameter. This refinement converged rapidly to an overall agreement factor

$$R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$$

of 0.071 for the 1128 observed reflections.

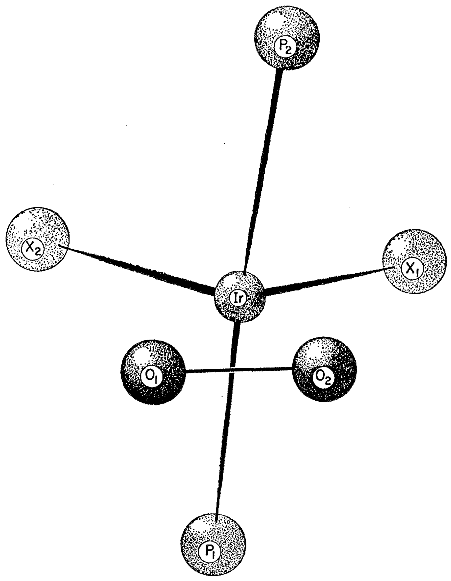

Fig. 1. A perspective drawing of the $O_2IrCl(CO)(P[C_6H_5]_3)_2$ molecule. Phenyl rings are not shown. X_1 and X_2 refer to the disordered positions of CO and Cl.

The structure is shown in Fig. 1 and it closely resembles the one surmised by Vaska (*4*) on the basis of less direct information. The Ir may be described as six-coordinated: in the basal plane there are the Ir, the C (of the CO) and the Cl atoms (denoted by *X* in Fig. 1), and the two O atoms of the O_2 molecule; above and below this basal plane are the two P atoms of the $P(C_6H_5)_3$ groups. The P-Ir-P direction is essentially normal to the basal plane. Principal interatomic distances and angles, together with their estimated standard deviations, are given in Table 1. The disordering of the Cl and CO positions can be rationalized in the following way. The compound results from the attack above or below the square-planar $IrCl(CO)(P[C_6H_5]_3)_2$ by O_2. In solution, because the $P(C_6H_5)_3$ are equivalent (*4*), only one isomer is formed, and if these $P(C_6H_5)_3$ groups remain equivalent throughout the crystallization process (that is, if the relative positions of Cl and CO have no effect on this process), total disorder of the Cl and CO positions should result. Apparently this is the case, and the packing is determined almost entirely by the phenyl rings. (The volume per triphenylphosphine group is only 10 percent greater than in triphenylphosphine itself.)

The significant results relating to the oxygen attachment to the iridium are (i) the two oxygen atoms are equidistant from the iridium atom and are thus equivalent; (ii) the O–O distance, while longer than in molecular oxygen (1.20 Å), is significantly less than in a typical peroxide (1.48 Å). The equivalence of the oxygen atoms is consistent with Griffith's (*7*) picture of the π-bonding of molecular oxygen to the iron in oxyhemoglobin, which differs from Pauling's (*8*) earlier ideas on the subject. The fact that the O–O distance is intermediate to O_2 and O_2^{-2} is in striking agreement with the qualitative principles of reversible oxygen uptake suggested by Vogt, Faigenbaum, and Wiberley (*1*). That the O–O distance corresponds very nearly to that for O_2^- is perhaps misleading, for then the Ir is formally Ir(II) and yet the compound is diamagnetic. Of course in molecular complexes the concept of formal charge on the metal ion is of limited utility and validity. A less qualitative description of the bonding depends upon a molecular orbital calculation for the complex, and this in turn depends among other things upon the existence of reliable wave functions for iridium. These are as yet unavailable. At present one must be satisfied with the experimental results that the oxygens are equivalent and that the O–O bond length is intermediate to those in O_2 and in O_2^{-2}.

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References and Notes

1. L. H. Vogt, H. M. Faigenbaum, S. E. Wiberley, *Chem. Rev.* **63,** 269 (1963).
2. N. Vannerberg and C. Brosset, *Acta Cryst.* **16,** 247 (1963).
3. A. E. Martell and M. Calvin, *Chemistry of the Metal Chelate Compounds* (Prentice-Hall, New York, 1952), especially section 8.2.
4. L. Vaska, *Science* **140,** 809 (1963).
5. We thank F. Holtzberg for performing this measurement for us.
6. S. J. La Placa and J. A. Ibers, *J. Am. Chem. Soc.* **85,** 3501 (1963); *Acta Cryst.,* in press.
7. J. S. Griffith, *Proc. Roy. Soc. Ser. A* **235,** 23 (1956).
8. L. Pauling and C. D. Coryell, *Proc. Natl. Acad. Sci. U.S.* **22,** 210 (1936); L. Pauling, *Hemoglobin, Sir Joseph Barcroft Memorial Symposium* (Butterworth, London, 1949), p. 57.
9. We thank L. Vaska for the sample and for several helpful discussions of the chemistry. Research performed under the auspices of the U.S. Atomic Energy Commission.

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Location of an Aircraft Impact from Gravity Waves

Abstract. *The energy released upon impact of an airliner that crashed into Lake Pontchartrain, Louisiana, on 25 February 1964 caused changes in water levels of sufficient duration and amplitude to be recorded by tide gages situated within the lake. Analysis of the recorded arrival times made it possible to locate the point of impact within an irregular area approximately 1500 feet (500 meters) in radius.*

On 25 February 1964, a four-engine jet airliner, enroute from New Orleans to Chicago, crashed in Lake Pontchartrain, Louisiana. After the disaster in-