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The Preparation and Crystal Structure of the Dioxygen Adduct of Bis(Diphenylethylphosphine)Chlorocarbonyl Iridium(I)

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The synthesis of the titled compound has been accomplished, its infrared vibrational spectra measured and the crystal structure determined. The O–O, C–O, and Ir–Cl stretching frequencies were found to be 848, 1997 and 293 cm^{-1}, respectively. The O–O distance was found from the crystal structure analysis to be 1.469(10) Å. These data are in agreement with quadrupole resonance data that indicate this compound and those closely related must be viewed as peroxo–metal species and not molecular oxygen bound to metal.

The crystal structure consists of isolated $O_2IrCOCl[P(C_6H_5)_2C_2H_5]_2$ molecules separated by ordinary van der Waals distances. The molecule is most simply described as a trigonal bipyramid with the O_2-center, CO and Cl moieties defining the equatorial plane. As expected, the O_2^{2-} is bound to the Ir side on. The metal–oxygen(2), metal–phosphorous(2), metal–chlorine and metal–carbon distances are: 2.033(7), 2.083(7), 2.363(3), 2.363(3), 2.356(3) and 1.900(12) Å, respectively. The O–O distance is 1.469(10) Å. Crystallographic Data: Monoclinic $P2_1/a$; $a = 14.772(2)$, $b = 19.604(4)$, $c = 9.929(1)$ Å and $\beta = 101.02(4)°$; $Z = 4$; $D_{obs} = D_{calc} = 1.67$ gcm^{-3}; 3306 non-zero hkl reflections were corrected for absorption and decay and used to solve and refine the structure by full matrix least-squares to a final R of 0.0431.

Introduction

Molecular oxygen adducts of the transition metals are interesting for a variety of reasons and have commanded attention for some time. They are of importance to commercial oxidation processes [1], are intermediates in the oxidation of the parent metal complex [2] and are, in fact, viewed as oxidative addition reactions of low valent transition metal complexes. This metal–dioxygen interaction is also of importance in catalytic processes [3]. Numerous reviews have been written on the subject and on the nature of the metal–oxygen and oxygen–oxygen bond in these adducts; the most recent are those of Vaska [4], McLendon and Martell [5], Lever and Gray [6], Jones, Summerville and Basolo [7] and Drago and Corden [8]. Furthermore, the metal–dioxygen species is well documented in biological compounds, particularly those with iron and copper [9a,b].

Martell and Calvin synthesized a number of reversible Co(II)–dioxygen complexes in the 1930s [10]. The first reversible d^8 metal–dioxygen [dioxygen – bis(triphenylphosphine) chlororocarbonyliridium(II)] complex was reported by Vaska [11] (for further references and more up-to-date interpretations of data, see ref. 4), and its crystal structure was later determined by LaPlaca and Ibers [12]. This crystal structure determination along with that of the iodide derivative [13] led to a correlation of O–O distance with reversibility [Cl derivative $d_{O-O} = 1.30(3)$ Å, rev.; I derivative $d_{O-O} = 1.509(26)$ Å. irr.]. In a preliminary report on the titled compound [14], we showed that with a relatively minor change on the phosphine (one phenyl replaced by an ethyl group), the O–O distance was found to be 1.461(10) Å. Since that time Nolte, *et al.* [15–18] have shown that for $[O_2ML_4]X$ where M = Rh, Ir; L = PMe_2Ph, X = BPh_4^-; M = Ir, L_2 = bis(diphenylphosphinomethane) X = PF_6^-, ClO_4^-, as well as our results with Co(I) [19] and Rh(I) [20], the O–O distance is in the range 1.41–1.52 Å regardless of metal or ligand in these d^8 systems. We wish to present here the details of the synthesis, IR data, and correlation with other physical measurements, as well as details of the structure determination of $O_2 \cdot IrCOCl(PPh_2Et)_2$.

Experimental

The unoxygenated solid material of $IrCOCl(PPh_2Et)_2$ was synthesized by refluxing a mixture of $IrCl_3$

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and diphenylethylphosphine in DMF for 12 hours [21, 22]. Twice the volume of methanol was added and the solution was cooled to 0 °C. The unoxygenated solid material, which precipitated, was collected, dried, dissolved in benzene and oxygenated by bubbling O_2 into the solution. Methanol was added to the solution and the mixture cooled to 5 °C. After one week, brown, approximately parallelepiped-shaped crystals of the oxygenated material appeared.

The infrared spectra were measured on a Perkin-Elmer Model 283 spectrophotometer. The O–O stretching frequency was found at 846 cm^{-1} in KBr pellets as was the Ir–Cl and C–O stretching frequency at 293 and 1997 cm^{-1}, respectively. The Ir–Cl band was also observed in Nujol mull at 305 cm^{-1}.

Air-sensitive crystals used for data collection were placed in thin-walled capillary tubes and sealed. Preliminary Weissenberg and precession film data showed the following extinctions: for h0*l*, h = 2n + 1; for 0k0, k = 2n + 1; indicating the space group $P2_1/a$ [23]. Two crystals of approximate dimensions, 0.08 × 0.19 × 0.40 mm (#1) and 0.09 × 0.20 × 0.45 (#2) were mounted along the [001] direction and aligned on a full circle Picker FACS-1 automated diffractometer by a local variation of well known methods [24]. Initially, the data crystals were optically aligned from the prominent faces to limit unnecessary exposure to x-rays. Axial reflections were then found by proper positioning of these faces. The cell constants were obtained by a least-squares refinement of the χ, ϕ and 2θ angles for nine well-centered general hk*l* reflections at room temperature. The cell constants obtained were $a = 14.772(2)$, $b = 19.604(4)$, $c = 9.929(1)$ Å and $\beta = 101.02(4)°$, $\lambda = 0.710683$ Å. With four molecules per unit cell, the calculated density was 1.67 g cm^{-3} and the observed density measured by flotation in a solution of 1,2-dibromoethylene and benzene was 1.67(2) g cm^{-3}.

A total of 7509 reflections on one crystal and 3924 reflcetions on a second crystal were collected with MoKα radiation using graphite monochromated MoKα radiation, $\lambda = 0.71068$ Å. Data were collected on the second crystal for that part of the reciprocal lattice where the standard peak had lost 25% or more in intensity for the first crystal.

The data was collected in two octants, hk*l* and hk$\bar{l}$ to 2θ max of 60° for the first crystal and from 22° to 60° for the second crystal. Backgrounds were measured at ±0.85° on 2θ from the peak maximum for 20 seconds, and the peaks were scanned for 50.5 seconds (1.7°, 2θ) by the usual θ–2θ scan technique. A standard reflection (hk*l* = 5,6,3) was measured every ten reflections to monitor the stability of the operation and crystal decomposition. In addition, three general reflections were measured twice daily to check for uniform decomposition. The decay of these three reflections did not differ significantly from 5,6,$\bar{3}$. A 2θ and ω scan were taken of the standard peak and the half-width spread at half-peak height was measured to establish the mosaic spread of the crystal. The spread was no more than 0.25° which indicated that the entire peak was canned for each reflection. The total variation in the standard reflection from one standard to another was no more than two percent of the total scan intensity. From the beginning to the end of the data collection the standard peak of the first crystal showed a total loss in intensity from decomposition of approximately 45 percent. The source-to-crystal distance was 18 cm, while the crystal-to-counter distance was 23.0 cm. The take-off angle was 3.7° and the counter aperture was 6 mm × 8 mm (high). The incident beam and receiving collimators were both 1.5 mm in diameter.

Reduction of Data

The net integrated intensity was calculated, assuming a linear variation in background from the function $I(net) = I(scan) - 1.2625\ (B_1 + B_2)$ where B_1 and B_2 are the background counts. The standard reflection was used to scale the data for each section of ten reflections. The variation of the standard from one measurement to the next was well within the counting statistics, $\sigma I(net) = [I(scan) + (1.2625)^2(B_1 + B_2)]^{1/2}$. Reflections were considered absent if I(net) was less than $2.0[1.2625(B_1 + B_2)]^{1/2}$. With a linear absorption coefficient, μ, of 52.4 cm^{-1} the maximum and minimum transmission coefficients [25] were found to be 0.679 and 0.430 for crystal #1 and 0.611 and 0.381 for crystal #2 for all hk*l* reflections. The crystals were bound by planes of the {100}, {010} and {001} forms. The data from the two crystals were merged after absorption corrections and scaled relative to the standard reflections. The agreement between data from crystal #1 showing 25% or more decomposition with data from crystal #2 were surprisingly good, generally within 10% of I_{hkl}. After merging, 3305 non-zero independent hk*l* intensities remained.

Solution and Refinement of Structure

The structure was solved by standard heavy atom techniques [24]. The structure was refined by full matrix least-squares with anisotropic temperature factors to a final R, weighted R and standard error of 0.0431, 0.0424 and 1.533, respectively. Parameter shifts of the final cycle were all less than 0.1 standard deviation. The function minimized was $\Sigma w(F_o - F_c)^2$ where the weights were determined from counting statistics [26]. The effects of anomalous dispersion were included for Ir, Cl and P. A final difference electron density map was qualitatively featureless. Final atom positional and thermal parameters are listed in Table I. Interatomic distances, angles and esds are listed in Table II. Observed and calculated structure factors are available from the editor or the authors.

TABLE I. The Preparation and Crystal Structure of the Dioxygen Adduct of Bis(Diphenylethylphosphine)Chlorocarbonyl Iridium(I). Positional Parameters and their Estimated Standard Deviations.

Atom	*X*	*Y*	*Z*	*B* Equiv.
Ir	0.25230(3)	0.36590(2)	0.17880(4)	4.38(7)
P(1)	0.2966(2)	0.2580(1)	0.1073(3)	4.9(3)
P(2)	0.2098(2)	0.4694(1)	0.2718(3)	4.8(3)
Cl	0.1077(2)	0.3589(2)	0.0304(3)	7.5(4)
O(1)	0.2382(7)	0.3165(4)	0.3537(7)	8.2(7)
O(2)	0.3302(5)	0.3477(4)	0.3735(7)	5.3(7)
C(5)	0.3161(9)	0.4120(6)	0.057(1)	5.8(7)
O(5)	0.3510(7)	0.4373(5)	−0.013(1)	9.(1)
C(1)	0.3962(7)	0.2234(6)	0.228(1)	6.(1)
C(2)	0.4833(8)	0.2693(6)	0.239(1)	7.(1)
C(3)	0.1178(7)	0.5184(5)	0.160(1)	5.5(7)
C(4)	0.1476(8)	0.5404(6)	0.024(1)	6.4(7)
C(11)	0.2112(7)	0.1911(5)	0.103(1)	5.0(7)
C(12)	0.2045(9)	0.1577(6)	0.230(1)	7.(1)
C(13)	0.1400(9)	0.1060(7)	0.229(2)	8.(1)
C(14)	0.0834(9)	0.0846(6)	0.109(1)	7.(1)
C(15)	0.0888(9)	0.1184(7)	−0.012(1)	8.(1)
C(16)	0.1531(9)	0.1728(6)	−0.017(1)	7.(1)
C(21)	0.3227(8)	0.2576(5)	−0.066(1)	5.6(7)
C(22)	0.4009(8)	0.2215(6)	−0.091(1)	7.(1)
C(23)	0.4221(9)	0.2238(6)	−0.224(1)	7.(1)
C(24)	0.364(1)	0.2587(6)	−0.330(1)	8.(1)
C(25)	0.287(1)	0.2952(6)	−0.305(1)	8.(1)
C(26)	0.2657(8)	0.2944(5)	−0.170(1)	6.3(7)
C(31)	0.3034(8)	0.5288(6)	0.3233(9)	5.6(7)
C(32)	0.3941(8)	0.5060(7)	0.330(1)	6.6(7)
C(33)	0.470(1)	0.5533(8)	0.368(1)	9.(1)
C(34)	0.448(1)	0.6207(8)	0.405(1)	10.(1)
C(35)	0.358(1)	0.6432(7)	0.397(1)	9.(1)
C(36)	0.2843(9)	0.5960(7)	0.355(1)	7.(1)
C(41)	0.1622(8)	0.4545(6)	0.426(1)	6.(1)
C(42)	0.2094(9)	0.4765(7)	0.552(1)	7.6(7)
C(43)	0.169(1)	0.4618(8)	0.669(1)	9.(1)
C(44)	0.085(1)	0.4273(8)	0.654(2)	8.(1)
C(45)	0.040(1)	0.4059(8)	0.527(2)	10.(1)
C(46)	0.079(1)	0.4189(7)	0.407(1)	8.(1)

Discussion

The structure consists of discrete molecules of $O_2 \cdot IrClCO(PPh_2Et)_2$ separated by ordinary van der Waals distances, Fig. 1. The discrete molecules may be described as a trigonal bipyramidal Ir(I) with Cl, CO and the center of the O_2 molecule defining the equatorial plane and the phosphine groups in the axial positions, Fig. 2. However, an alternative description of the structure could be as a very distorted octahedral Ir(III) with O_2^{2-} [5] (*vide infra*). The general features of the molecule are not significantly different from that of $O_2IrClCO(PPh_3)_2$ as determined by LaPlaca and Ibers [12].

TABLE II. Important Intramolecular Bond Distances (A) and Angles (degrees).[a]

Bonded Distances		Interatomic Angles	
Ir–P(1)	2.363(3)	P(1)–Ir–P(2)	174.5(1)
Ir–P(2)	2.363(3)	P(1)–Ir–Cl	91.7(1)
Ir–Cl	2.356(3)	P(1)–Ir–O(1)	84.8(2)
Ir–O(1)	2.033(7)	P(1)–Ir–O(2)	89.4(2)
Ir–O(2)	2.083(7)	P(1)–Ir–C(5)	92.0(3)
O(1)–O(2)	1.469(10)	P(2)–Ir–Cl	91.0(1)
Ir–C(5)	1.900(12)	P(2)–Ir–O(1)	89.8(2)
C(5)–O(5)	1.07(1)	P(2)–Ir–O(2)	85.7(2)
		P(2)–Ir–C(5)	92.4(3)
		Ir–P(2)–C(3)	115.6(3)
		Ir–P(2)–C(3,1)	114.7(3)
		Ir–P(2)–C(4,1)	111.3(4)
		O(2)–Ir–C(5)	114.8(4)
		Cl–Ir–O(1)	106.2(3)
		Cl–Ir–C(5)	97.4(4)
		O(1)–Ir–O(2)	41.8(4)
		Ir–P(1)–C(1)	111.6(4)
		Ir–P(1)–C(1,1)	114.9(3)
		Ir–P(1)–C(2,1)	113.9(4)

[a] More routine bond distances and angles are available from the editor or the authors.

The least-squares plane containing Ir, Cl, C(5), O(1) and O(2) is essentially planar although O(1) and O(2) deviate from the plane by 0.069(6) Å and −0.082(5), respectively; *i.e.*, a slight twist of the O–O molecule. The Ir–P, Ir–Cl, Ir–C and P–C are the expected distances. The C–C distances of the phenyl rings are not significantly different from one another nor are they expected to be. The interatomic angles are also the expected values. The striking feature is the O–O distance of 1.469(10) Å which is long compared to the 1.30(3) Å of $O_2IrCOCl(PPh_3)_2$ [12] but in the middle of the range of 1.41–1.52 Å found for O–O distances in a wide variety of oxygen adducts to Ir(I), Rh(I), Co(I) [14–20]. It is most unlikely that the replacement of one phenyl group by an ethyl group on each phosphine could bring about a change in O–O distance of 0.16 Å. Furthermore, the O–O vibrational frequency in this oxygen adduct is found to be at 848 cm^{-1}, again in the middle range for metal peroxo complexes regardless of whether they are of type IIa or IIb [4]. In addition, Lumpkin *et al.* [27] have shown that the ^{17}O nuclear quadrupole resonance in the oxygen adduct of Vaska's compound is very much like that of hydrogen peroxide. Therefore, there is little doubt that the O–O distance in the oxygen adduct of Vaska's compound should be also in the range 1.41–1.52 Å. In addition, the O–O distances quoted in ref. 4 from our structural studies of $O_2IrCOBr(PPh_3)_2$ at 1.36(2) Å and of $O_2Ir(Ph_4P_2C_2H_2)_2$ at 1.37(2) Å should be viewed with caution. The former of these has the same disorder problems that exist in $O_2IrCOCl(PPh_3)_2$ and

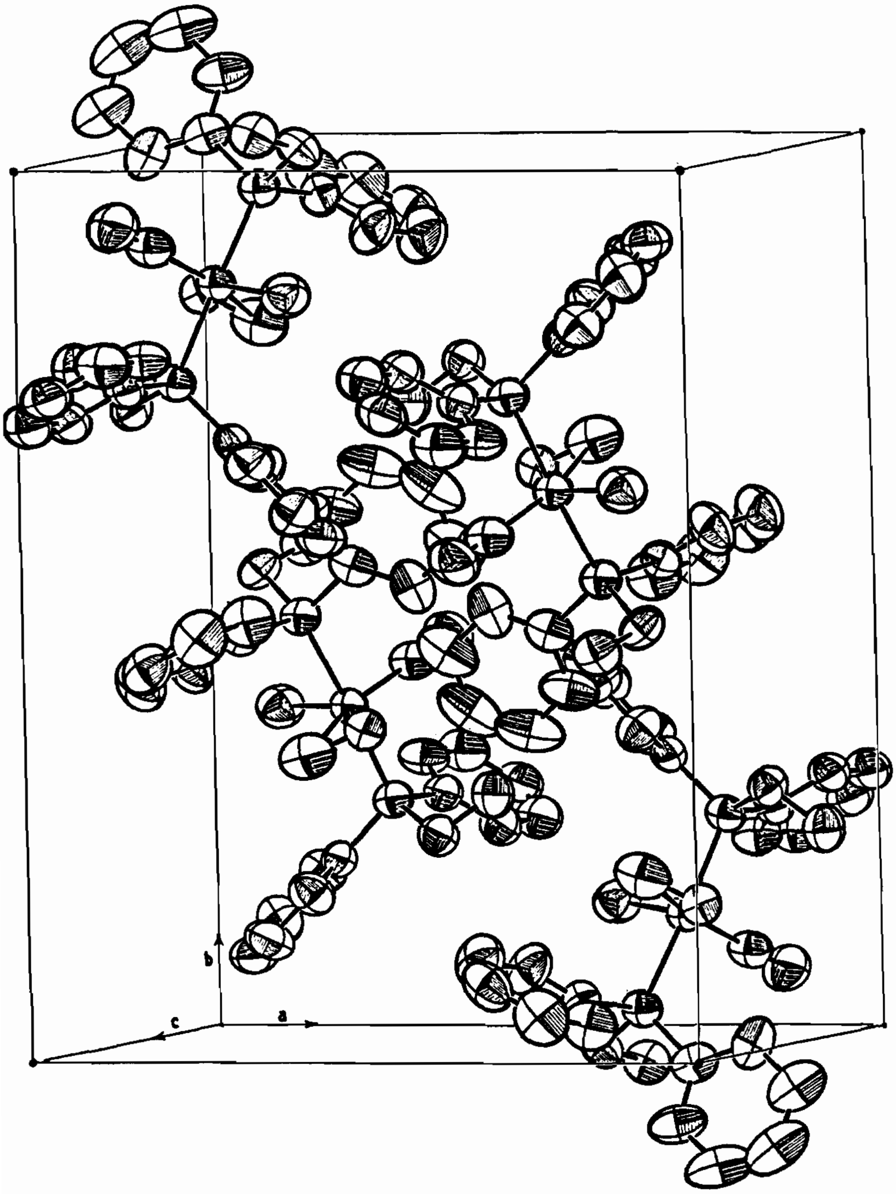

Fig. 1. An ORTEP drawing of the contents of the unit cell of $O_2 \cdot IrCOCl(PPh_2Et)_2$. The axial system and origin of the unit cell are shown in the lower left hand corner. The relationship between the ethyl groups and the phenyl groups on adjacent molecules is to be noted and, after the fact, it is clear how disorder is avoided in this packing arrangement. The thermal ellipsoids are drawn at the 50% probability level.

the latter is plagued with other diffraction problems. However, our Ir–O distances of 2.033(7) and 2.083(7) Å compare favorably with the triphenylphosphine analog distances of 2.04(3) and 2.09(3) Å.

Vaska [4] has made the suggestion that $O_2Ir(I)COCl(PR_3)_2$ species, because the O–O distances are usually more nearly like the 1.49 Å distance of the peroxide ion, would be more appropriately described as $O_2^{2-}Ir(III)COCl(PR_3)_2$ with a very distorted octahedral environment about the metal. The present results and their implications strongly support this interpretation.

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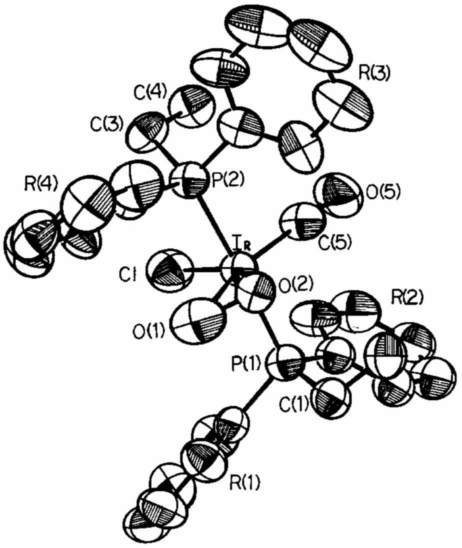

Fig. 2. An ORTEP drawing of the isolated molecule with notation consistent with text and Table II. Individual phenyl ring atoms are not denoted for reasons of simplicity, but *e.g.* C(2,1) of Table II refers to a carbon of ring (R)2. The thermal ellipsoids are drawn at the 50% probability level.

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