# Structure of the Cation Bis[bis(diphenylphosphino)methane]dioxygen-iridium(I) in Two Different Environments: Comparison of the Crystal Structures of the Hexafluorophosphate and Perchlorate Salts

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The crystal structures of the $PF_6$ and $ClO_4$ salts of $[IrO_2(dppm)_2]$ [dppm = bis(diphenylphosphino)methane] have been determined by *X*-ray diffraction methods from counter data. Crystals of both compounds are monoclinic, space group $P2_1/c$, with $Z = 4$. $[PF_6]^-$ salt (I): $a = 11.40(1)$, $b = 19.26(1)$, $c = 22.06(4)$ Å, $\beta = 101.2(1)°$. $[ClO_4]^-$ salt (II): $a = 11.87(1)$, $b = 11.12(1)$, $c = 34.6(3)$ Å, $\beta = 96.1(1)°$. The structures have been solved by the heavy-atom method and refined by least squares to *R* 0.06 for *ca.* 3 400 observed reflections in both cases. The O–O distances [1.45(2) (I) and 1.49 (1) Å (II)] are identical within the precision of the analyses. Although the packing in the two compounds differs greatly, the geometry of the cation remains the same in each and is trigonal bipyramidal, with the dioxygen ligand occupying one equatorial site. The cation is chiral and mean bond lengths and angles are: Ir–P(ax) 2.36, Ir–P(eq) 2.31, Ir–O 2.02, O–O 1.47 Å; P(ax)–Ir–P(ax) 170, P(ax)–Ir–P(eq) 70° (*within the chelate ring*).

THE results of crystallographic determinations [1-3] of the structures of the neutral complexes $[M(CO)XO_2(PPh_3)_2]$ and the cations $[MO_2(dppe)_2]^+$ [M = Rh or Ir; X = Cl or I; dppe = 1,2-bis(diphenylphosphino)ethane] led [3] to the following inferences: a short O–O bond (1.30—1.42 Å) corresponds to reversible oxygen uptake; a long O–O bond (1.50—1.625 Å) corresponds to irreversible oxygen uptake; increasing the donor strength of the ligand favours longer O–O bonds and increased ' uptake properties,' and the O–O bond length in the rhodium complex is shorter than that in the iridium analogue. However, the recent structure determination [4] of $[Ir(CO)ClO_2(PEtPh_2)_2]$ showed an anomaly: although the dioxygen ligand is reversibly taken up, the O–O length of 1.46 Å falls close to the value supposedly typical of irreversible oxygen uptake.

If the trends derived [3] from the limited data were meaningful, then in the systems $[MO_2(L\text{–}L)_2]X$ (irreversible oxygen uptake) changing the ligand L–L from dppe to either $2AsMe_2Ph$ or $2PMe_2Ph$ should cause an increase in O–O bond length for both the rhodium and iridium complexes. The values obtained for $[MO_2L_4]^+$ (M = Rh, L = $PMe_2Ph$ or $AsMe_2Ph$; M = Ir, L = $PMe_2Ph$) were 1.43,[5] 1.46,[6] and 1.49 Å.[7] Furthermore, in these three cations no variation in M–O bond lengths was observed. Thus it seemed that there were some inconsistencies in the trends previously reported.[3] To try to rationalise these apparent anomalies, we have determined the structures of the salts $[IrO_2(dppm)_2]X$ [dppm = bis(diphenylphosphino)methane; X = $PF_6$ or $ClO_4$] in order to measure the effect on O–O and M–O bonding parameters of changing the geometry of the chelating ligand from dppe to dppm, the reproducibility of bond lengths and angles of a supposedly identical cation, and the effect of changing the anion on the molecular arrangement inside the unit cell, the unit-cell dimensions, and packing forces.

## EXPERIMENTAL

*Preparation.*—Bis(diphenylphosphino)methane (0.97 g) was added to a suspension of di-μ-chloro-bis(cyclo-octadiene)di-iridium(I) (0.4 g) in ethanol (20 $cm^3$). The solution was filtered and oxygen then bubbled through until the red solution became yellow-orange (*ca.* 5—10 min). The solution was then divided into two portions: to one was added a filtered solution of $[NH_4][PF_6]$ and to the other a filtered solution of $Li[ClO_4]$, both in ethanol. The resulting yellow-orange precipitates were recrystallised from dichloromethane–ethanol. Crystal data are shown in Table 1.

TABLE 1

Crystal data for $[IrO_2(Ph_2P{\cdot}CH_2{\cdot}PPh_2)_2][PF_6]$, (I), and $[IrO_2(Ph_2P{\cdot}CH_2{\cdot}PPh_2)_2][ClO_4]$, (II)

| | (I) | (II) |
|---|---|---|
| *M* | 1 137.98 | 1 092.46 |
| Space group | $P2_1/c$ | $P2_1/c$ |
| *a*/Å | 11.40(1) | 11.87(1) |
| *b*/Å | 19.26(1) | 11.12(1) |
| *c*/Å | 22.06(4) | 34.61(3) |
| β/° | 101.2(1) | 96.1(1) |
| $D_m/g\ cm^{-3}$ | 1.60 | 1.59 |
| $D_c/g\ cm^{-3}$ | 1.59 | 1.60 |
| $U/Å^3$ | 4 752 | 4 541 |
| *Z* | 4 | 4 |
| μ(Mo-$K_\alpha$)/$cm^{-1}$ | 32.06 | 33.61 |

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Orange single crystals suitable for $X$-ray work were obtained as needles (I) and prisms (II), and specimens of dimensions 0.13 × 0.12 × 0.40 (I) and 0.14 × 0.16 × 0.32 mm (II) were mounted parallel to the largest dimension. Intensity data were collected with a Philips PW 1100 four-circle single-crystal diffractometer for the diffraction range $\theta$ 3—20°, by use of graphite-monochromated Mo-$K_\alpha$ radiation in the $\omega$–$2\theta$ scan mode for (I) and the $\omega$ scan mode for (II). Each reflection was scanned for 20 (I) and 30 s (II) and the same times were taken to accumulate the background counts. Three standard reflections were monitored for each complex during data collection. The intensities of 4 416 (I) and 4 223 (II) reflections were measured of which 3 371 (I) and 3 495 (II) having $I > 2\sigma(I)$ were considered observed. No corrections were made for crystal decomposition. Background and Lorentz-polarisation corrections were applied, but corrections for extinction were considered unnecessary. Transmission coefficients varied from 0.68 to 0.75 (I) and from 0.60 to 0.69 (II). Absorption corrections were calculated by

TABLE 2

Positional parameters (× $10^4$) with estimated standard deviations in parentheses

(*a*) For (1)

| | | | |
|---|---|---|---|
| Ir | 707(1) | 2 864(1) | 4 550(1) |
| P(1) | −1 293(4) | 2 622(2) | 4 620(2) |
| P(2) | −494(4) | 2 897(2) | 3 578(2) |
| P(3) | 2 670(4) | 2 958(2) | 4 353(2) |
| P(4) | 1 478(4) | 1 774(2) | 4 459(2) |
| O(1) | 810(10) | 3 780(6) | 4 991(5) |
| O(2) | 1 155(10) | 3 210(6) | 5 420(5) |
| C(12) | −1 742(14) | 2 386(8) | 3 798(7) |
| C(34) | 2 687(13) | 2 067(8) | 4 059(7) |
| C(111) | −2 148(14) | 3 366(8) | 4 767(7) |
| C(112) | −3 203(13) | 3 572(10) | 4 380(9) |
| C(113) | −3 788(16) | 4 163(16) | 4 529(9) |
| C(114) | −3 362(18) | 4 555(11) | 5 067(11) |
| C(115) | −2 303(22) | 4 338(11) | 5 447(12) |
| C(116) | −1 677(18) | 3 729(10) | 5 304(9) |
| C(121) | −1 693(13) | 1 946(8) | 5 103(7) |
| C(122) | −2 688(15) | 1 529(8) | 4 896(7) |
| C(123) | −3 014(18) | 1 035(10) | 5 301(10) |
| C(124) | −2 368(21) | 979(10) | 5 902(11) |
| C(125) | −1 367(20) | 1 391(11) | 6 103(9) |
| C(126) | −1 004(17) | 1 882(10) | 5 707(8) |
| C(211) | −223(15) | 2 485(9) | 2 877(7) |
| C(212) | −972(17) | 1 990(11) | 2 566(7) |
| C(213) | −706(20) | 1 676(11) | 2 031(9) |
| C(214) | 380(19) | 1 837(10) | 1 831(9) |
| C(215) | 1 094(16) | 2 346(11) | 2 131(8) |
| C(216) | 818(14) | 2 707(10) | 2 655(7) |
| C(221) | −1 121(14) | 3 755(9) | 3 353(8) |
| C(222) | −812(16) | 4 306(9) | 3 764(9) |
| C(223) | −1 369(17) | 4 961(10) | 3 623(10) |
| C(224) | −2 220(18) | 5 034(11) | 3 085(10) |
| C(225) | −2 552(19) | 4 484(11) | 2 675(10) |
| C(226) | −1 981(16) | 3 808(11) | 2 811(9) |
| C(311) | 3 041(14) | 3 529(8) | 3 761(7) |
| C(312) | 3 918(14) | 3 296(10) | 3 421(7) |
| C(313) | 4 187(18) | 3 773(12) | 2 983(9) |
| C(314) | 3 663(21) | 4 407(11) | 2 904(9) |
| C(315) | 2 789(23) | 4 613(11) | 3 230(10) |
| C(316) | 2 450(20) | 4 164(9) | 3 669(9) |
| C(321) | 3 813(13) | 3 060(9) | 5 037(7) |
| C(322) | 4 796(15) | 2 621(10) | 5 176(8) |
| C(323) | 5 642(16) | 2 714(12) | 5 726(9) |
| C(324) | 5 461(19) | 3 264(13) | 6 132(10) |
| C(325) | 4 477(19) | 3 709(12) | 5 964(9) |
| C(326) | 3 647(15) | 3 623(10) | 5 417(8) |
| C(411) | 705(13) | 1 052(8) | 4 033(7) |
| C(412) | −155(14) | 697(9) | 4 300(8) |
| C(413) | −825(18) | 173(10) | 3 978(10) |
| C(414) | −658(18) | −10(11) | 3 388(10) |
| C(415) | 237(19) | 316(10) | 3 143(9) |
| C(416) | 890(16) | 852(8) | 3 462(7) |
| C(421) | 2 312(14) | 1 393(9) | 5 164(7) |
| C(422) | 2 971(15) | 792(9) | 5 134(9) |
| C(423) | 3 738(16) | 539(10) | 5 667(9) |
| C(424) | 3 806(17) | 894(11) | 6 227(8) |
| C(425) | 3 169(19) | 1 503(12) | 6 258(9) |
| C(426) | 2 401(15) | 1 749(10) | 5 718(8) |
| P(5) | 5 112(5) | 1 240(3) | 3 091(3) |
| F(1) | 5 276(11) | 1 766(9) | 3 629(7) |
| F(2) | 6 366(11) | 941(7) | 3 368(7) |
| F(3) | 5 683(16) | 1 795(12) | 2 760(9) |
| F(4) | 4 958(15) | 805(11) | 2 518(9) |
| F(5) | 3 853(11) | 1 534(8) | 2 857(6) |
| F(6) | 4 596(16) | 712(11) | 3 427(12) |

TABLE 2 (*Continued*)

(*b*) For (II)

| | | | |
|---|---|---|---|
| Ir | 1 051(1) | 1 442(1) | 1 234(1) |
| P(1) | 2 556(3) | 1 476(3) | 836(1) |
| P(2) | 2 545(3) | 2 524(3) | 1 551(1) |
| P(3) | −317(3) | 1 777(3) | 1 660(1) |
| P(4) | −29(3) | 3 100(3) | 1 031(1) |
| O(1) | 1 149(7) | −368(8) | 1 357(2) |
| O(2) | 353(7) | −121(8) | 1 005(2) |
| C(12) | 3 349(12) | 2 661(12) | 1 124(4) |
| C(34) | −598(10) | 3 340(11) | 1 502(3) |
| C(111) | 2 320(12) | 1 995(12) | 334(4) |
| C(112) | 3 027(13) | 2 840(13) | 182(5) |
| C(113) | 2 837(15) | 3 162(15) | −216(5) |
| C(114) | 1 963(16) | 2 593(17) | −447(5) |
| C(115) | 1 283(15) | 1 734(15) | −311(5) |
| C(116) | 1 429(11) | 1 419(14) | 88(4) |
| C(121) | 3 517(9) | 205(12) | 815(4) |
| C(122) | 4 547(12) | 413(13) | 681(4) |
| C(123) | 5 299(12) | −539(15) | 642(4) |
| C(124) | 4 993(12) | −1 706(14) | 746(4) |
| C(125) | 3 940(12) | −1 895(12) | 872(4) |
| C(126) | 3 191(11) | −933(11) | 908(4) |
| C(211) | 2 500(10) | 4 024(11) | 1 761(3) |
| C(212) | 3 006(11) | 5 001(11) | 1 604(4) |
| C(213) | 2 958(12) | 6 121(13) | 1 783(4) |
| C(214) | 2 440(12) | 6 256(14) | 2 118(5) |
| C(215) | 1 995(13) | 5 256(14) | 2 289(5) |
| C(216) | 2 010(11) | 4 136(13) | 2 111(4) |
| C(221) | 3 392(10) | 1 651(12) | 1 923(3) |
| C(222) | 3 349(11) | 398(12) | 1 900(4) |
| C(223) | 3 958(12) | −300(14) | 2 202(4) |
| C(224) | 4 496(12) | 280(14) | 2 539(4) |
| C(225) | 4 511(13) | 1 507(16) | 2 556(4) |
| C(226) | 3 994(12) | 2 213(15) | 2 257(4) |
| C(311) | −1 652(10) | 957(12) | 1 605(4) |
| C(312) | −2 654(11) | 1 541(14) | 1 681(4) |
| C(313) | −3 623(12) | 846(16) | 1 691(4) |
| C(314) | −3 634(12) | −355(15) | 1 610(4) |
| C(315) | −2 643(13) | −927(14) | 1 521(5) |
| C(316) | −1 649(12) | −273(12) | 1 509(4) |
| C(321) | 114(11) | 1 800(11) | 2 178(3) |
| C(322) | 912(10) | 949(12) | 2 328(4) |
| C(323) | 1 292(11) | 964(14) | 2 733(4) |
| C(324) | 875(13) | 1 795(15) | 2 978(4) |
| C(325) | 89(13) | 2 640(15) | 2 825(4) |
| C(326) | −298(11) | 2 650(13) | 2 428(4) |
| C(411) | 455(10) | 4 558(11) | 877(4) |
| C(412) | 444(10) | 5 562(11) | 1 095(3) |
| C(413) | 819(14) | 6 674(13) | 980(4) |
| C(414) | 1 211(12) | 6 731(12) | 606(4) |
| C(415) | 1 221(12) | 5 714(14) | 371(4) |
| C(416) | 834(10) | 4 605(12) | 501(3) |
| C(421) | −1 274(11) | 2 764(11) | 697(3) |
| C(422) | −2 145(11) | 3 615(13) | 639(4) |
| C(423) | −3 134(12) | 3 351(15) | 402(4) |
| C(424) | −3 268(12) | 2 247(14) | 210(4) |
| C(425) | −2 393(12) | 1 427(15) | 248(4) |
| C(426) | −1 382(12) | 1 654(13) | 494(4) |
| Cl | 3 878(4) | 343(4) | 3 675(1) |
| O(11) | 2 797(12) | 742(16) | 3 755(5) |
| O(12) | 4 379(10) | 1 255(12) | 3 474(3) |
| O(13) | 4 549(13) | 113(15) | 4 027(5) |
| O(14) | 3 711(19) | −656(14) | 3 446(5) |

numerical integration and applied to the reflection data of each complex.

*Determination of the Structures.*—The structures were solved by Patterson and Fourier methods. Full-matrix least-squares refinements were carried out for the non-hydrogen atoms on an IBM 360 65 computer, with the CRYLSQ program of the '*X*-Ray' system of crystallographic programs.[8] All the atoms were refined anisotropically (stepwise, in groups) using a weighting scheme (no. 3) which downweighs the contribution of reflections with large $F_0$ and/or small $\theta$ values ($A = 0.0$, $B = 0.36$, $C = 90.0$). Final $R$ values of 0.06 for the observed intensities were obtained for both complexes. Scattering factors were taken from ref. 9 with corrections for anomalous dispersion. It should be noted that the temperature factor of C(412) of (II) did not remain positive definite during refinement and had to be kept constant. Anisotropic thermal parameters and observed and calculated structure factors are listed in Supplementary Publication No. SUP 21757 (59 pp., 1 microfiche).* Table 2 gives final positional and thermal parameters with their standard deviations. Bond lengths and angles, calculated by the program BONDLA, are summarised in Tables 3 and 4. The numbering systems are given in Figure 1. All the Figures were drawn by use of the ORTEP program of Johnson.[10] The packing within the cells is illustrated in Figure 2.

TABLE 3

Comparison of bond distances (Å) in $[IrO_2(dppm)_2][PF_6]$, (I), $[IrO_2(dppm)_2][ClO_4]$, (II), and $[IrO_2(dppe)_2][PF_6]$, (III)

| | (I) | (II) | (III) [a] |
|---|---|---|---|
| Ir–P(1)(ax) | 2.361(5) | 2.369(4) | 2.366(3) |
| Ir–P(3)(ax) | 2 368(5) | 2.337(4) | 2.353(3) |
| Ir–P(2)(eq) | 2.310(5) | 2.320(4) | 2.308(3) |
| Ir–P(4)(eq) | 2.300(5) | 2.312(4) | 2.342(3) |
| Ir–O(1) | 2.007(12) | 2.057(9) | 2.052(7) |
| Ir–O(2) | 2.002(12) | 2.048(9) | 2.062(7) |
| O(1)–O(2) | 1.453(17) | 1.486(11) | 1.52(1) |
| P(1)–C(12) | 1.84(2) | 1.85(2) | 1.87(1) |
| C(12)–P(2) | 1.87(2) | 1.85(2) | 1.85(1) |
| P(3)–C(34) | 1.84(2) | 1.84(2) | 1.88(1) |
| C(34)–P(4) | 1.86(2) | 1.85(2) | 1.84(1) |
| P(1)–C(111) | 1.80(2) | 1.82(2) | 1.84(1) |
| P(1)–C(121) | 1.80(2) | 1.82(2) | 1.83(1) |
| P(2)–C(211) | 1.82(2) | 1.82(2) | 1.82(1) |
| P(2)–C(221) | 1.83(2) | 1.83(2) | 1.83(1) |
| P(3)–C(311) | 1.82(2) | 1.82(2) | 1.82(1) |
| P(3)–C(321) | 1.80(1) | 1.82(2) | 1.83(1) |
| P(4)–C(411) | 1.81(1) | 1.82(2) | 1.82(1) |
| P(4)–C(421) | 1.81(2) | 1.81(2) | 1.83(1) |
| P(5)–F(1) | 1.54(2) | | 1.55(1) |
| P(5)–F(2) | 1.55(2) | | 1.59(1) |
| P(5)–F(3) | 1.51(2) | | 1.52(1) |
| P(5)–F(4) | 1.50(2) | | 1.52(1) |
| P(5)–F(5) | 1.54(1) | | 1.54(1) |
| P(5)–F(6) | 1.45(2) | | 1.55(1) |
| Cl–O(11) | | 1.41(2) | |
| Cl–O(12) | | 1.40(1) | |
| Cl–O(13) | | 1.41(2) | |
| Cl–O(14) | | 1.37(2) | |
| Mean C–C | 1.40(2) | 1.40(2) | 1.40(2) |

[a] From ref. 12.

TABLE 4

Comparison of angles (°) in $[IrO_2(dppm)_2][PF_6]$, (I), $[IrO_2(dppm)_2][ClO_4]$, (II), and $[IrO_2(dppe)_2][PF_6]$, (III)

| | (I) | (II) | (III) [a] |
|---|---|---|---|
| P(1)–Ir–P(3) | 170.4(2) | 169.1(1) | 175.3(3) |
| P(1)–Ir–P(2) | 70.2(2) | 71.4(1) | 83.5(1) |
| P(1)–Ir–P(4) | 102.5(2) | 103.8(1) | 99.8(1) |
| P(2)–Ir–P(3) | 103.8(2) | 99.6(1) | 99.1(1) |
| P(2)–Ir–P(4) | 96.4(2) | 95.9(1) | 97.0(1) |
| P(3)–Ir–P(4) | 70.3(2) | 70.4(1) | 83.8(1) |
| O(1)–Ir–O(2) | 42.5(5) | 42.4(3) | 43.4(3) |
| O(1)–O(2)–Ir | 68.6(7) | 68.4(5) | 67.9(4) |
| O(2)–O(1)–Ir | 68.9(6) | 69.1(5) | 68.6(4) |
| P(1)–C(12)–P(2) | 92.6(7) | 95.5(6) | |
| P(3)–C(34)–P(4) | 93.2(7) | 93.1(6) | |
| Ir–P(1)–C(12) | 94.1(6) | 94.0(4) | 108.4(3) |
| Ir–P(2)–C(12) | 95.1(5) | 95.7(4) | 106.5(3) |
| Ir–P(3)–C(34) | 93.9(5) | 94.6(4) | 107.1(3) |
| Ir–P(4)–C(34) | 95.5(5) | 95.1(4) | 108.1(3) |
| O(1)–Ir–P(1) | 96.2(4) | 96.1(2) | 86.8(2) |
| O(1)–Ir–P(2) | 113.2(3) | 112.7(2) | 111.8(2) |
| O(1)–Ir–P(3) | 93.0(4) | 93.1(2) | 88.6(2) |
| O(1)–Ir–P(4) | 149.1(3) | 149.3(3) | 151.1(2) |
| O(2)–Ir–P(1) | 94.1(3) | 95.0(3) | 84.6(2) |
| O(2)–Ir–P(2) | 151.1(4) | 151.7(3) | 153.1(2) |
| O(2)–Ir–P(3) | 94.4(3) | 95.7(3) | 91.4(2) |
| O(2)–Ir–P(4) | 110.9(3) | 111.7(3) | 108.8(2) |
| Ir–P(1)–C(111) | 114.8(5) | 120.7(5) | 114.1(3) |
| Ir–P(1)–C(121) | 122.8(5) | 121.7(4) | 117.7(3) |
| Ir–P(2)–C(211) | 127.6(5) | 127.6(4) | 123.2(3) |
| Ir–P(2)–C(221) | 114.1(5) | 113.2(4) | 115.5(3) |
| Ir–P(3)–C(311) | 122.6(5) | 120.7(4) | 121.9(3) |
| Ir–P(3)–C(321) | 114.2(6) | 119.0(4) | 114.2(4) |
| Ir–P(4)–C(411) | 126.3(5) | 128.1(4) | 122.7(3) |
| Ir–P(4)–C(421) | 116.1(6) | 114.7(4) | 114.9(3) |
| C(12)–P(1)–C(111) | 108.5(7) | 107.8(6) | 104.2(5) |
| C(12)–P(1)–C(121) | 110.6(7) | 106.8(6) | 108.6(5) |
| C(111)–P(1)–C(121) | 105.2(8) | 103.8(6) | 102.9(5) |
| C(12)–P(2)–C(211) | 104.7(8) | 106.5(6) | 106.2(5) |
| C(12)–P(2)–C(221) | 105.6(7) | 108.4(6) | 101.8(5) |
| C(211)–P(2)–C(221) | 106.5(8) | 103.9(5) | 101.5(5) |
| C(34)–P(3)–C(311) | 106.9(7) | 108.3(6) | 106.1(5) |
| C(34)–P(3)–C(321) | 110.0(7) | 107.7(5) | 105.9(5) |
| C(311)–P(3)–C(321) | 107.7(7) | 105.1(6) | 100.3(5) |
| C(34)–P(4)–C(411) | 108.5(7) | 106.6(6) | 105.5(5) |
| C(34)–P(4)–C(421) | 102.5(7) | 104.0(6) | 97.9(4) |
| C(411)–P(4)–C(421) | 104.8(7) | 105.0(6) | 104.5(4) |

[a] From ref 12.

## RESULTS AND DISCUSSION

Both structures consist of discrete cations and anions; the closest approach of fluorine or oxygen atoms in the anions to any non-hydrogen atom in the cations is >3.0 Å.

The thermal parameters of the oxygen and fluorine atoms in the anions indicate high thermal motion. In both cases, disordering of the anions could be seen from the difference-Fourier maps. This was more pronounced for the $[PF_6]^-$ anion than for the $[ClO_4]^-$ anion, and is reflected in a bigger variation in the P–F (1.45—1.55 Å) than in the Cl–O bond lengths (1.37 —1.41 Å), variations far greater than expected from the estimated standard deviations.

The cation is trigonal bipyramidal with the dioxygen ligand occupying one site in the equatorial plane. It is chiral, approximating symmetry 2, and its geometry is essentially identical in both compounds, as shown in Figure 3, projections on the mean plane of the Ir and equatorial P atoms. The mode of packing in (I) differs much from that in (II) (compare the *b* and *c* axial

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* For details see Notices to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

[8] J. M. Stewart, G. J. Kruger, H. Ammon, C. H. Dickinson, and S. R. Hall, Technical Report TR 192, University of Maryland, version of June 1972.

[9] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[10] C. K. Johnson, Report ORNL TM 3794, Oak Ridge National Laboratories, Oak Ridge, Tennessee, 1965.

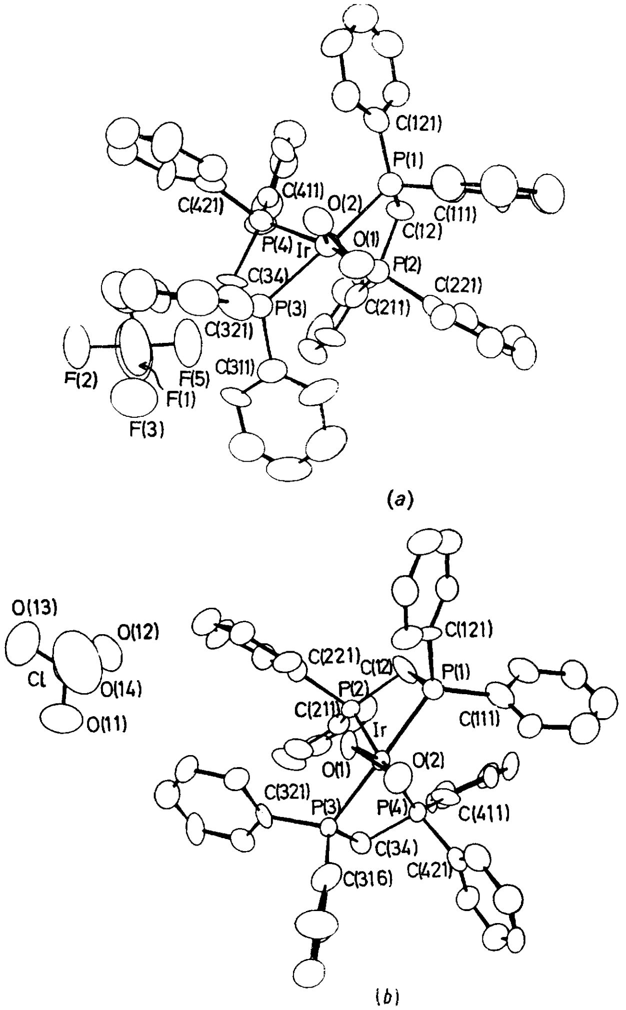

FIGURE 1 Atom-numbering system of (*a*) $[IrO_2(dppm)_2][PF_6]$ and (*b*) of $[IrO_2(dppm)_2][ClO_4]$

lengths), but in spite of this the effect on the conformation of the chelate rings is small and those differences which are observed (involving the phenyl rings) are insignificant. Hence we conclude that because of negligible variations in the phenyl rings of the chelate groups (which are in closest contact with the anions) variations in other bond parameters within the cation cannot be attributed to packing factors or variations in unit-cell dimensions.

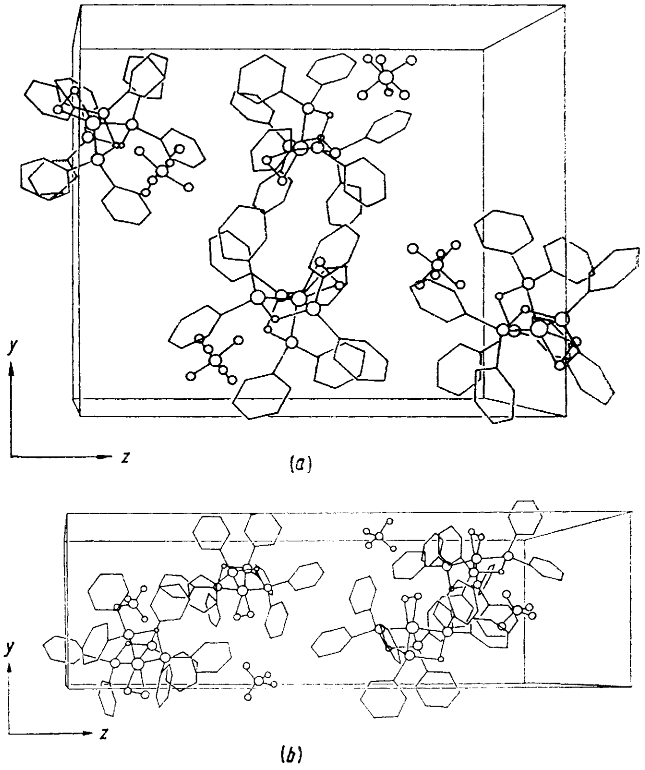

FIGURE 2 Packing of molecules in the unit cell of (*a*) (I) and (*b*) (II)

Mean values of Ir–P distances are 2.365 (I) and 2.355 Å (II) for axial and 2.305 (I) and 2.315 Å (II) for equatorial bonds. Other mean distances (Å) are: Ir–O 2.005 (I) and 2.055 (II), P–C(Me) 1.85 (I) and 1.85 (II), P–C(Ph) 1.81 (I) and 1.82 (II); C–C (Ph rings) 1.40 in both (I) and (II). The O–O bond lengths are 1.45(2) in (I) and 1.49(1) Å in (II) which, if meaningful, represent a large

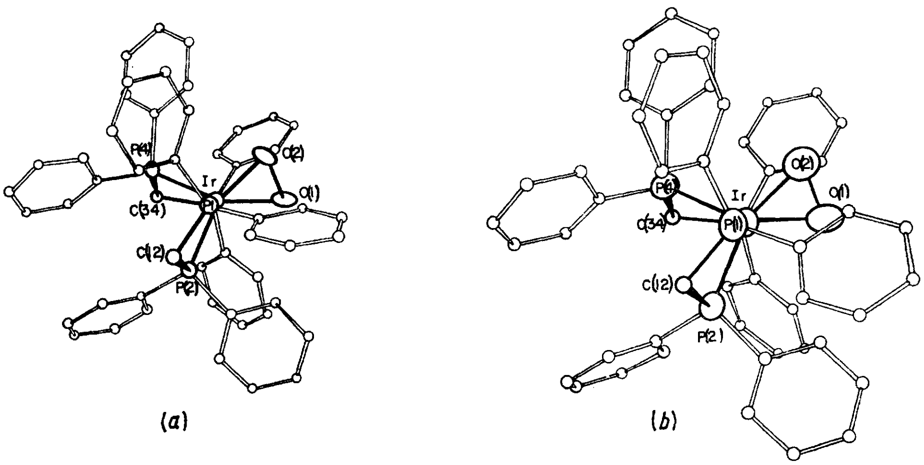

FIGURE 3 Projections of the $[IrO_2(dppm)_2]^+$ cation on the mean equatorial plane (*a*) for (I) and (*b*) for (II)

difference for the supposedly identical cations. In fact, these values differ by only 2 $\sigma$, and hence are identical within the precision of the structure determinations.

Apparently significant differences (*ca.* 5 $\sigma$) are observed between the Ir–O distances in (I) and (II), with the longer Ir–O bonds being associated with the longer O–O bond. An even more important difference ($>6\ \sigma$) of 0.03 Å is observed between the values for Ir–P(3)(ax). These apparently significant differences in Ir–P and Ir–O bond lengths for the same cation in (I) and (II) cannot be real, and merely reflect the innate limitation of the *X*-ray crystallographic methods in accurately locating light atoms in close proximity to heavy-metal atoms. The accuracy of the derived bond lengths appears to be far lower than the apparent precision deduced mathematically from the least-squares refinement, and one may conclude that the estimated standard deviations are underestimated by a factor of at least 2. Similar conclusions for other structural determinations have been drawn by other workers.[11]

In the closely related cation $[IrO_2(dppe)_2]^+$, the O–O length was originally reported [3] to be 1.625 Å, a difference of nearly 10 $\sigma$ from that in $[IrO_2(dppm)_2]^+$. The large differences between several bonding parameters in $[IrO_2(dppe)_2]^+$ and those found in the dppm analogue prompted a redetermination of the structure of (III), $[IrO_2(dppe)_2][PF_6]$, and this showed [12] that the unusually long O–O bond originally reported is an artefact caused by crystal decomposition during irradiation.

A comparison of the dimensions of the cations $[IrO_2(L\text{–}L)_2]^+$ (L–L = dppe or dppm) is given in Tables 3—5. The co-ordination geometry for the cation with the ethano-chelate ring is compared with that containing the methano-chelate ring in the two environments (I) and (II) in Figure 4. Although the co-ordination geometry of the cation can be classed as trigonal bipyramidal, all angles involving the Ir and P atoms in the dppm derivative deviate from ideality considerably more than do those in the dppe analogue: *e.g.* 70, 84, and 90° for the axial–equatorial angle within the chelate ring; 170, 175, and 180° for the axial–axial angle. The increased strain in the chelate rings of the dppm complex over that in the chelate rings of the dppe analogue is also evident in the Ir–P–C angles (95 and 107°) and P–C–P angles (94 and 110° for P–C–C). The equatorial-equatorial P–Ir–P angle is 96° in both the dppe and dppm complexes. The 'pulling back' of the two axial phosphorus atoms by the chelate ring in the dppm complex produces a more open bonding site for the dioxygen ligand: P(ax)–O 3.0 (dppe) and 3.2 Å (dppm) (Table 5). This reduction of steric repulsions at the bonding site thus explains why $[Ir(dppm)_2]^+$ forms the dioxygen complex very much faster than does $[Ir(dppe)_2]^+$.

TABLE 5

Comparison of some interatomic distances (Å) in $[IrO_2(dppm)_2][PF_6]$, (I), $[IrO_2(dppm)_2][ClO_4]$, (II), and $[IrO_2(dppe)_2][PF_6]$, (III)

| | (I) | (II) | (III) [a] |
|---|---|---|---|
| P(ax) [b] ··· O(1) | 3.26(1) | 3.30(1) | 3.04(1) |
| P(ax) ··· O(1) | 3.18(1) | 3.19(1) | 3.08(1) |
| P(ax) ··· O(2) | 3.20(1) | 3.26(1) | 2.99(1) |
| P(ax) ··· O(2) | 3.22(1) | 3.26(1) | 3.17(1) |
| C [c] ··· O(1) | 3.05(2) | 3.08(2) | 3.02(2) |
| C ··· O(2) | 2.95(2) | 3.10(2) | 2.92(2) |
| C ··· A [d] | 3.32(2) | 3.21(2) | 3.16(2) |

[a] From ref. 12. [b] Axial P atom. [c] Nearest ring C atom. [d] Shortest anion–cation atom distance.

If the O–O bond length is significantly affected by steric factors within the cation, then any alleviation of the strain would presumably have resulted in an increased O–O bond length in the dppm complex. No lengthening is observed. In a recent review [13] on transition-metal dioxygen complexes Vaska pointed out that all 'side-on' bonded dioxygen complexes of the transition metals, with the exception of some iridium complexes, have essentially constant O–O bond lengths and are 'peroxo-like' in character. He did stress however that, although the iridium–dioxygen complexes exhibit unusually long and short O–O bonds, their i.r. O–O stretching frequencies are almost identical and in the same range as those observed for the other transition-metal peroxo-complexes. Thus from this work and

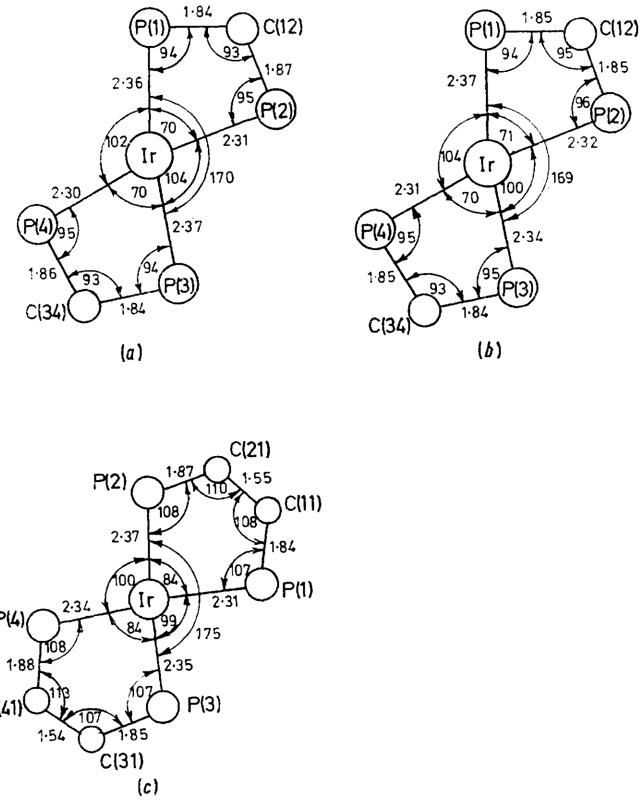

FIGURE 4 Co-ordination geometry for the methano-chelate rings (*a*) in complex (I), (*b*) in (II), and (*c*) in (III)

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[11] S. C. Abrahams, *Acta Cryst.*, 1974, **B30**, 261.

[12] M. J. Nolte, E. Singleton, and M. Laing, *J. Amer. Chem. Soc.*, 1975, **97**, 6396.

[13] L. Vaska, *Accounts Chem. Res.*, 1976, **9**, 175.

related structure determinations [5-7,12] of other rhodium and iridium dioxygen complexes one is forced to conclude that (*i*) the O–O bond length is constant irrespective of the metal or other ligands in the co-ordination sphere, (*ii*) the unusually short [1,2] and long [3] O–O bond lengths observed in iridium dioxygen complexes could be and are artefacts caused by disorder and crystal decomposition respectively, and (*iii*) there is no correlation between O–O bond length and the reversibility of metal–dioxygen 'uptake' properties. It now appears that the 'side-on' bonded dioxygen ligand in rhodium and iridium dioxygen complexes has peroxo-character and hence an O–O bond length in the range 1.45—1.50 Å; it is thus similar to all the other [13] transition-metal 'side-on' dioxygen complexes.

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