Zerovalent Platinum Chemistry. Part 11.† A Peroxo-bridged Binuclear Platinum Complex obtained by Protonation of $[Pt(O_2)(PPh_3)_2]$; the Crystal Structure of $[Pt_2(O_2)(OH)(PPh_3)_4][ClO_4]\cdot 2C_6H_6$ ‡

By **Sumit Bhaduri, Luigi Casella,** and **Renato Ugo,*** Istituto di Chimica Generale, Via Venezian 21, 20133 Milano, Italy
Paul R. Raithby and **Camillo Zuccaro,** University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW
Michael B. Hursthouse, Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS

Binuclear platinum complexes $[Pt_2(O_2)(OH)(PPh_3)_4][X]$ (X = ClO_4, BF_4, PF_6, or NO_3) and $[Pt_2(OH)_2(PPh_3)_4][X]_2$ (X = ClO_4, BF_4, or PF_6) have been prepared by the stepwise reaction of $[Pt(O_2)(PPh_3)_2]$ with HX in CH_2Cl_2–EtOH. Their formation is accompanied by production of H_2O_2. The presence of peroxo- and hydroxo-bridges between the two platinum atoms in $[Pt_2(O_2)(OH)(PPh_3)_4][ClO_4]$ has been confirmed by a single-crystal *X*-ray analysis. The complex crystallizes in space group $P\bar{1}$, with cell dimensions a = 14.884(3), b = 15.281(3), c = 16.744(4) Å, α = 90.06(2), β = 108.65(2), γ = 93.11(2)°, and Z = 2. The structure has been solved by Patterson and Fourier techniques, and refined to R 0.086 for 5 359 diffractometer data. Reaction of the peroxo-bridged species with CO yields $[Pt(CO)_2(PPh_3)_2]$, while with SO_2 the final product contains a bidentate sulphate group.

FORMATION of hydrogen peroxide by reaction of acids with complexes containing a peroxo-bridge or a dioxygen ligand has been previously reported.[1-3] However, none of these reports has described the isolation or characterization of the intermediates involved in the reaction. By treatment of $[Pt(O_2)(PPh_3)_2]$ with non-co-ordinating acids HX in a 2 : 1 mol ratio we have been able to isolate some intermediates, and these are the subject of this paper.

RESULTS AND DISCUSSION

Preparation and Characterization of $[Pt_2(O_2)(OH)(PPh_3)_4][X]$.—When an ethanolic solution of HX (X = ClO_4, BF_4, or NO_3) containing some water was added dropwise to a dichloromethane solution of $[Pt(O_2)(PPh_3)_2]$ in a *ca.* 1 : 2 mol ratio a colour change from orange to yellow occurred. The addition of excess of diethyl ether to the solution produced yellow microcrystals. These were filtered off and the filtrate titrated iodimetrically. Analytical data (Table 1) and molecular-weight measurement of the perchlorate derivative (Found: *M* 1 589. Calc.: *M* 1 588) in an associated solvent, such as chloroform, are in agreement with the stoicheiometry (1). The titration of peroxidic oxygen in the crystalline platinum complexes confirmed the presence of a peroxo-group for at least every two platinum complexes.[4] Iodimetric titrations of the resulting solutions after removal of the platinum complexes gave *ca.* 60% of the theoretical value of H_2O_2.

TABLE 1

Analytical properties of $[Pt_2(O_2)(OH)(PPh_3)_4][X]$ complexes

	Analysis (%) [a]				Λ [b]	$\tilde{\nu}$(X)
X	C	H	N	O	S cm² mol⁻¹	cm⁻¹
ClO_4	54.1 (54.5)	3.7 (3.8)		8.3 (7.1)	22.4	1 080
NO_3	55.4 (55.8)	3.8 (4.0)	0.8 (0.9)	7.0 (6.2)	21.6	1 335
BF_4	54.7 (54.9)	4.0 (3.9)			23.6	1 050
PF_6	52.5 (52.9)	3.7 (3.7)			22.8	

[a] Calculated values are given in parentheses. [b] For 10^{-3} mol dm^{-3} nitrobenzene solutions.

$$2[Pt(O_2)(PPh_3)_2] + HX + H_2O \longrightarrow [Pt_2(O_2)(OH)(PPh_3)_4][X] + H_2O_2 \quad (1)$$

All the platinum species have i.r. bands at *ca.* 3 560 cm^{-1} that can be assigned to hydroxyl groups. However, no characteristic stretching frequencies for the bridging peroxo-groups[5] could be assigned, with any certainty, in the region 800—900 cm^{-1} for any of the complexes. Conductimetric measurements established that all these complexes were 1 : 1 electrolytes (Table 1) in agreement with the i.r. spectra which show the typical pattern for anionic $[ClO_4]^-$, $[BF_4]^-$, $[PF_6]^-$, *etc.*[6] These data suggest a dimeric cationic structure in which the $[OH]^-$ and $[O_2]^{2-}$ groups bridge the two platinum moieties.

However, since iodimetric titrations of peroxidic groups in noble-metal triphenylphosphine complexes have been reported to produce lower than expected values,[5] the presence of an $[O_2H]^-$ group, instead of $[OH]^-$, could not be completely excluded. There is evidence for the formation of hydrogenperoxide anions $[O_2H]^-$ during the catalytic oxidation of PR_3 by $[Pt(O_2)(PR_3)_2]$.[7] Therefore a single-crystal *X*-ray analysis of the perchlorate derivative $[Pt_2(O_2)(OH)(PPh_3)_4][ClO_4]\cdot 2C_6H_6$[8] was undertaken, and this confirms the presence of a hydroxo-bridge.

Crystal and Molecular Structure of $[Pt_2(O_2)(OH)(PPh_3)_4][ClO_4]\cdot 2C_6H_6$.—The molecular geometry of the cation is shown in the Figure, while the bond lengths and angles for the compound are listed in Tables 2 and 3, respectively. Both Pt atoms exhibit a distorted square-planar co-ordination geometry (maximum deviation

† Part 10, R. Ugo, S. Cenini, M. F. Pilbrow, B. Deibl, and G. Schneider, *Inorg. Chim. Acta*, 1976, **18**, 113.

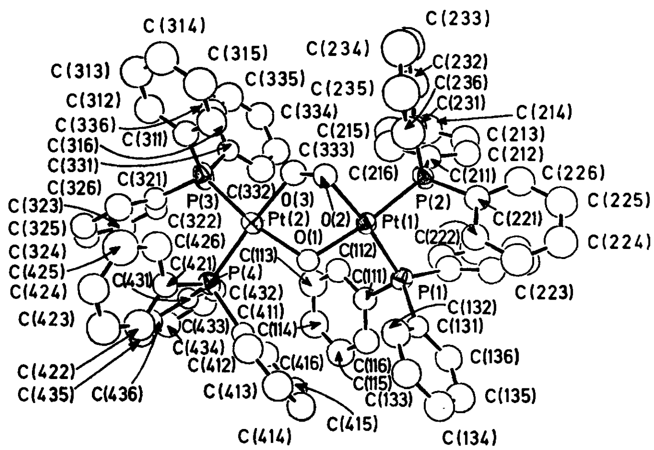
‡ The complexes whose formulae are shown are peroxobis(triphenylphosphine)platinum(II) and μ-hydroxo-μ-peroxo-bis[bis(triphenylphosphine)platinum(II)] perchlorate–benzene (1/2), respectively.

TABLE 2

Bond lengths (Å)

O(1)–Pt(1)	2.077(16)	O(1)–Pt(2)	2.096(17)
O(2)–Pt(1)	1.990(21)	O(3)–Pt(2)	2.012(19)
P(1)–Pt(1)	2.245(9)	P(3)–Pt(2)	2.274(8)
P(2)–Pt(1)	2.208(7)	P(4)–Pt(2)	2.258(7)
O(3)–O(2)	1.547(21)	C(311)–P(3)	1.749(21)
C(111)–P(1)	1.838(13)	C(321)–P(3)	1.829(13)
C(121)–P(1)	1.864(16)	C(331)–P(3)	1.830(16)
C(131)–P(1)	1.803(14)	C(411)–P(4)	1.849(16)
C(211)–P(2)	1.799(15)	C(421)–P(4)	1.766(19)
C(221)–P(2)	1.840(15)	C(431)–P(4)	1.862(13)
C(231)–P(2)	1.851(21)		

from planes is 0.11 Å), and the two planes subtend an angle of 39.8° with each other. The distortions from the idealized square-planar geometry are due to the steric requirements of the bulky triphenylphosphine ligands, with P–Pt–P angles significantly greater than 90°. The Pt · · · Pt distance of 3.475 Å can be considered as non-bonding, and is only slightly shorter than the non-bonded distance of 3.630 Å in $[Pt_3(PPh_3)_2(PPh_2)_3Ph]\cdot C_6H_6$,[9] where the metals are bridged by a



The $[Pt_2(O_2)(OH)(PPh_3)_4]^+$ cation

phosphido-ligand. The μ_2-hydroxo-bridge is not significantly asymmetric, and together with the bidentate peroxo-group forms a five-membered, puckered, $Pt(O_2)PtO$ ring. The Pt(1)–O(2)–O(3)–Pt(2) torsion angle is 79.0°. The geometry of the triphenylphosphine ligands is normal, and the Pt–P distances are similar to the values (2.232—2.282 Å) reported in the two independent determinations of the structure of the parent complex $[Pt(O_2)(PPh_3)_2]$.[10,11]

The O(2)–O(3) distance is consistent with the formulation of this group as a peroxide, and is similar to the O–O bond lengths reported in a number of peroxo-complexes.[12] The two Pt–O(peroxo) distances are in good agreement with the metal–peroxo bond values of 2.006(7) and 2.00(1) Å in $[Pt(O_2)(PPh_3)_2]\cdot 2CHCl_3$ [11] and $[Pt(O_2)(OCMe_2)(PPh_3)_2]$,[13] respectively. The Pt–O-(hydroxo) bond lengths are *ca.* 0.01 Å longer, and similar to the Pt–O(C) distance of 2.01(1) Å in the ketonic complex.[13]

This structure appears to be the first example of a cyclic peroxo-hydroxo-dibridged binuclear noble-metal complex. Although a six-membered cyclic diperoxo-bridged structure of a rhodium complex has been reported,[14] the five-membered puckered ring is typical only of cobalt(III) peroxo-complexes.[15]

As indicated by the i.r. data, the perchlorate anion, which is disordered in the solid state, is not co-ordinated to the metal complex. The closest contact distance of 2.246 Å is between H(314), the hydrogen on the phenyl carbon C(314), and O(13), related by the symmetry operation (x, y, $1 + z$). Two benzene solvent molecules were also located in the analysis, one of which was disordered, and both were well separated from the ionic species.

TABLE 3

Bond angles (°)

O(2)–Pt(1)–O(1)	81.0(7)	O(3)–Pt(2)–O(1)	85.8(7)
P(1)–Pt(1)–O(1)	91.9(6)	P(3)–Pt(2)–O(1)	168.5(5)
P(1)–Pt(1)–O(2)	169.9(5)	P(3)–Pt(2)–O(3)	83.8(6)
P(2)–Pt(1)–O(1)	170.9(6)	P(4)–Pt(2)–O(1)	90.4(5)
P(2)–Pt(1)–O(2)	90.7(5)	P(4)–Pt(2)–O(3)	176.0(6)
P(2)–Pt(1)–P(1)	96.8(3)	P(4)–Pt(2)–P(3)	100.0(3)
Pt(2)–O(1)–Pt(1)	112.7(8)	O(2)–O(3)–Pt(2)	104.0(12)
O(3)–O(2)–Pt(1)	101.5(13)	C(311)–P(3)–Pt(2)	115.5(6)
C(111)–P(1)–Pt(1)	107.5(6)	C(321)–P(3)–Pt(2)	117.1(6)
C(121)–P(1)–Pt(1)	121.4(6)	C(321)–P(3)–C(311)	105.7(8)
C(121)–P(1)–C(111)	98.1(7)	C(331)–P(3)–Pt(2)	108.6(6)
C(131)–P(1)–Pt(1)	115.7(6)	C(331)–P(3)–C(311)	104.6(8)
C(131)–P(1)–C(111)	106.3(7)	C(331)–P(3)–C(321)	104.1(6)
C(131)–P(1)–C(121)	105.5(7)	C(411)–P(4)–Pt(2)	110.5(5)
C(211)–P(2)–Pt(1)	109.2(5)	C(421)–P(4)–Pt(2)	117.7(7)
C(221)–P(2)–Pt(1)	115.7(6)	C(421)–P(4)–C(411)	103.7(7)
C(221)–P(2)–C(211)	114.1(8)	C(431)–P(4)–Pt(2)	112.8(5)
C(231)–P(2)–Pt(1)	112.0(6)	C(431)–P(4)–C(411)	100.6(7)
C(231)–P(2)–C(211)	106.1(8)	C(431)–P(4)–C(421)	109.7(7)
C(231)–P(2)–C(221)	98.9(7)	C(312)–C(311)–P(3)	121.8(5)
C(112)–C(111)–P(1)	118.2(5)	C(316)–C(311)–P(3)	118.1(5)
C(116)–C(111)–P(1)	121.7(5)	C(322)–C(321)–P(3)	119.4(5)
C(122)–C(121)–P(1)	119.2(4)	C(326)–C(321)–P(3)	120.6(5)
C(126)–C(121)–P(1)	120.7(4)	C(332)–C(331)–P(3)	120.3(6)
C(132)–C(131)–P(1)	117.8(5)	C(336)–C(331)–P(3)	119.6(6)
C(136)–C(131)–P(1)	122.2(5)	C(412)–C(411)–P(4)	118.1(5)
C(212)–C(211)–P(2)	126.5(5)	C(416)–C(411)–P(4)	121.7(5)
C(216)–C(211)–P(2)	113.4(5)	C(422)–C(421)–P(4)	120.2(6)
C(222)–C(221)–P(2)	116.8(5)	C(426)–C(421)–P(4)	119.7(6)
C(226)–C(221)–P(2)	122.7(5)	C(432)–C(431)–P(4)	116.2(5)
C(232)–C(231)–P(2)	121.7(5)	C(436)–C(431)–P(4)	123.5(4)
C(236)–C(231)–P(2)	118.3(5)		

Reactivity of $[Pt_2(O_2)(OH)(PPh_3)_4][X]$.—The complex reacts further with aqueous HX to give a white precipitate of the dihydroxo-bridged species $[Pt_2(OH)_2(PPh_3)_4][X]_2$ [16] and hydrogen peroxide according to equation (2). Infrared spectra of these complexes also

$$[Pt_2(O_2)(OH)(PPh_3)_4][X] + H_2O + HX \longrightarrow [Pt_2(OH)_2(PPh_3)_4][X]_2 + H_2O_2 \quad (2)$$

show the hydroxide stretching frequencies at *ca.* 3 560 cm^{-1}, but the hydrogen peroxide produced (titrated iodimetrically) was only 40% of the amount expected. Furthermore, the complexes $[PtX_2(PPh_3)_2]$ were only obtained when $[Pt(O_2)(PPh_3)_2]$ was treated with HX, when X^- is a strongly co-ordinating anion such as Cl^- or Br^-.

The $[Pt(O_2)(PPh_3)_2]$ undergoes addition reactions with

TABLE 4

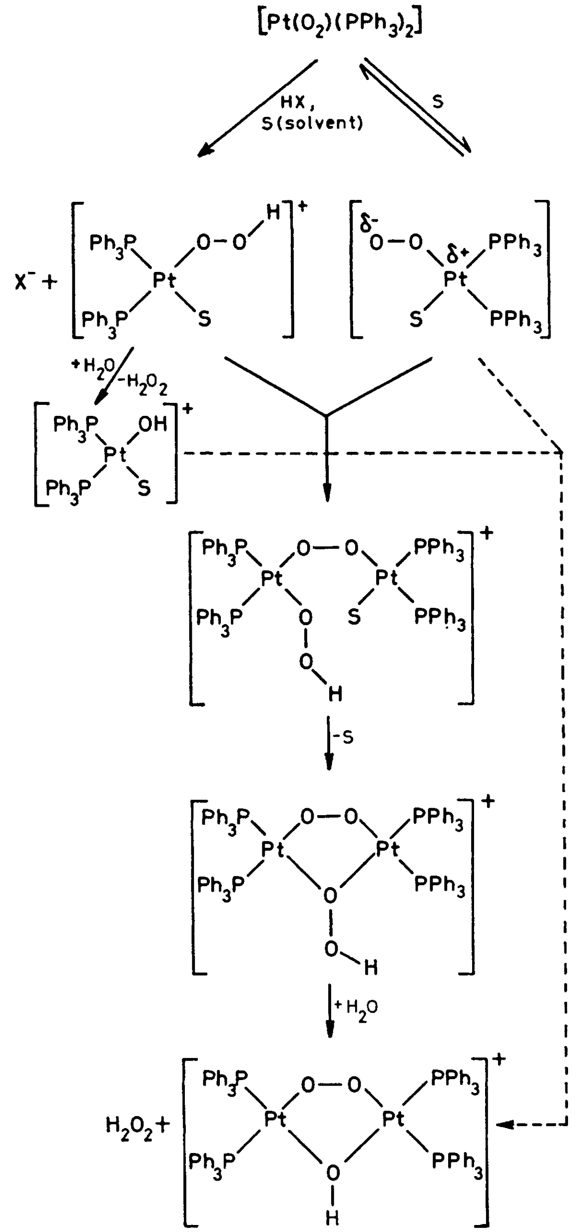
Atom co-ordinates ($\times 10^4$)

Atom	x/a	y/b	z/c
Pt(1)	6 241(1)	3 123(1)	8 078(1)
Pt(2)	4 280(1)	1 707(1)	7 910(1)
O(1)	5 648(10)	1 852(11)	7 810(11)
O(2)	5 504(11)	3 063(11)	8 882(12)
O(3)	4 472(12)	2 978(12)	8 273(13)
P(1)	6 841(4)	3 083(5)	7 008(5)
P(2)	6 838(5)	4 448(5)	8 559(6)
P(3)	2 793(5)	1 845(5)	7 979(6)
P(4)	4 152(5)	295(5)	7 471(5)
C(111)	5 896(9)	2 623(8)	6 080(9)
C(112)	4 958(9)	2 792(8)	5 994(9)
C(113)	4 224(9)	2 477(8)	5 286(9)
C(114)	4 427(9)	1 994(8)	4 663(9)
C(115)	5 364(9)	1 826(8)	4 749(9)
C(116)	6 099(9)	2 140(8)	5 457(9)
C(121)	7 148(8)	4 107(9)	6 525(9)
C(122)	8 066(9)	4 495(9)	6 840(9)
C(123)	8 295(9)	5 283(9)	6 512(9)
C(124)	7 607(9)	5 684(9)	5 869(9)
C(125)	6 690(9)	5 296(9)	5 554(9)
C(126)	6 460(9)	4 508(9)	5 882(9)
C(131)	7 838(8)	2 409(8)	7 161(9)
C(132)	7 993(8)	1 782(8)	7 788(9)
C(133)	8 740(8)	1 229(8)	7 917(9)
C(134)	9 333(8)	1 304(8)	7 419(9)
C(135)	9 178(8)	1 932(8)	6 792(9)
C(136)	8 430(8)	2 485(8)	6 663(9)
C(211)	6 150(10)	5 253(9)	7 885(9)
C(212)	6 504(10)	5 994(9)	7 573(9)
C(213)	5 879(10)	6 547(9)	7 032(9)
C(214)	4 901(10)	6 358(9)	6 803(9)
C(215)	4 548(10)	5 616(9)	7 115(9)
C(216)	5 172(10)	5 064(9)	7 656(9)
C(221)	8 129(9)	4 634(9)	8 793(8)
C(222)	8 652(9)	3 891(9)	8 863(8)
C(223)	9 614(9)	3 980(9)	8 939(8)
C(224)	10 053(9)	4 811(9)	8 946(8)
C(225)	9 530(9)	5 554(9)	8 876(8)
C(226)	8 568(9)	5 465(9)	8 800(8)
C(231)	6 768(9)	4 667(10)	9 625(11)
C(232)	6 256(9)	5 348(10)	9 781(11)
C(233)	6 234(9)	5 502(10)	10 596(11)
C(234)	6 723(9)	4 974(10)	11 254(11)
C(235)	7 234(9)	4 293(10)	11 097(11)
C(236)	7 257(9)	4 139(10)	10 282(11)
C(311)	2 716(10)	1 941(9)	8 996(10)
C(312)	1 852(10)	1 819(9)	9 152(10)
C(313)	1 811(10)	1 954(9)	9 964(10)
C(314)	2 634(10)	2 211(9)	10 619(10)
C(315)	3 498(10)	2 332(9)	10 463(10)
C(316)	3 539(10)	2 197(9)	9 651(10)
C(321)	1 883(7)	1 000(8)	7 438(8)
C(322)	1 332(7)	1 121(8)	6 603(8)
C(323)	670(7)	462(8)	6 168(8)
C(324)	558(7)	−317(8)	6 568(8)
C(325)	1 109(7)	−437(8)	7 403(8)
C(326)	1 771(7)	221(8)	7 838(8)
C(331)	2 340(9)	2 861(9)	7 466(9)
C(332)	2 697(9)	3 227(9)	6 858(9)
C(333)	2 306(9)	3 969(9)	6 430(9)
C(334)	1 558(9)	4 346(9)	6 611(9)
C(335)	1 201(9)	3 980(9)	7 219(9)
C(336)	1 592(9)	3 238(9)	7 647(9)
C(411)	5 214(8)	21(8)	7 198(9)
C(412)	5 961(8)	−335(8)	7 822(9)
C(413)	6 808(8)	−481(8)	7 667(9)
C(414)	6 909(8)	−271(8)	6 889(9)
C(415)	6 162(8)	85(8)	6 265(9)
C(416)	5 315(8)	230(8)	6 419(9)
C(421)	4 056(8)	−524(10)	8 187(11)
C(422)	4 080(8)	−1 406(10)	7 984(11)
C(423)	4 055(8)	−2 048(10)	8 570(11)
C(424)	4 007(8)	−1 808(10)	9 359(11)
C(425)	3 983(8)	−925(10)	9 562(11)
C(426)	4 008(8)	−283(10)	8 976(11)
C(431)	3 208(7)	82(8)	6 438(8)
C(432)	3 055(7)	770(8)	5 871(8)
C(433)	2 433(7)	639(8)	5 052(8)
C(434)	1 963(7)	−179(8)	4 799(8)
C(435)	2 116(7)	−867(8)	5 366(8)
C(436)	2 738(7)	−736(8)	6 185(8)
Cl(1)	1 323(2)	2 110(2)	2 757(2)
O(11)	1 090(5)	1 194(2)	2 669(5)
O(12)	476(2)	2 566(3)	2 570(5)
O(13)	1 820(3)	2 367(4)	2 191(2)
O(14)	1 906(4)	2 314(5)	3 597(2)
O(11′)	1 096(3)	1 907(5)	3 500(2)
O(12′)	805(4)	2 830(2)	2 357(4)
O(13′)	1 079(5)	1 370(3)	2 199(3)
O(14′)	2 312(2)	2 332(5)	2 971(5)
C(11)	8 411	2 892	3 332
C(12)	7 737	3 199	3 654
C(13)	8 025	3 603	4 451
C(14)	8 989	3 700	4 915
C(15)	9 663	3 392	4 583
C(16)	9 375	2 988	3 787
C(21)	8 423	349	−110
C(22)	7 779	1 009	−280
C(23)	8 081	1 860	28
C(24)	9 028	2 051	507
C(25)	9 672	1 392	677
C(26)	9 369	541	369
C(21′)	8 118	770	−186
C(22′)	8 588	1 596	−114
C(23′)	9 202	1 900	666
C(24′)	9 346	1 378	1 374
C(25′)	8 876	553	1 303
C(26′)	8 262	248	523

carbon dioxide, aldehydes and ketones, sulphur dioxide, and nitrogen monoxide.[17] With SO_2 and NO the final products contain a bidentate sulphate and two nitro-groups, respectively. As expected, the reactivity of $[Pt_2(O_2)(OH)(PPh_3)_4][ClO_4]$ is somewhat different from that of the monomeric platinum dioxygen complex. No reaction is observed between acetone and the peroxo-bridged species, either at room temperature or under reflux. The i.r. spectrum of crystals obtained from acetone solution shows only a band at 1 706 cm^{-1} that can be assigned to acetone of crystallization.

The yellow solution of $[Pt_2(O_2)(OH)(PPh_3)_4][ClO_4]$ rapidly becomes colourless when sulphur dioxide is passed through it. Addition of diethyl ether gives a white microcrystalline solid which can be formulated as $[Pt_2(OH)(SO_4)(PPh_3)_4][ClO_4]$ on the basis of the analytical data and the i.r. spectrum. This complex contains a bridging hydroxo- and a sulphato-group produced by insertion of sulphur dioxide into the peroxo-bridge. Similar reactions are not, however, observed between the peroxo-complex and NO or carbon dioxide. With carbon monoxide, instead of insertion into the peroxo-bridge, reduction of the complex leads to the formation of $[Pt(CO)_2(PPh_3)_2]$ [18] as can be seen from the i.r. spectrum of the solution.

It is well established from spectroscopy [19] and from its reactivity [20] that the dioxygen group in $[Pt(O_2)(PPh_3)_2]$ behaves as a true anionic ligand. This is reflected by its reactivity towards strong (H^+,[2] $[NO]^+$,[21] SO_2 [17] and NO_2 [17]) and weak (activated olefins,[22] ketones and aldehydes [13]) electrophiles. Our results are in agreement with a fast protonation to form an intermediate hydrogenperoxide



SCHEME

cation, as has been observed for some cobalt complexes, where the Co-OOH bond is stable enough for the corresponding complexes to be isolated.[23]

A possible mechanistic interpretation of these observations is shown in the Scheme. Such a platinum hydrogenperoxide has been suggested by other workers.[3] This positively charged species is '*per se*' an electrophile which, in the absence of excess of protons, can attack $[Pt(O_2)(PPh_3)_2]$, which is known to be in equilibrium with a reactive open form.[24] Therefore dimerization occurs *via* attack of the intermediate electrophile to form a Pt-O-O-Pt bridge. The reaction of this intermediate with water produces H_2O_2 and the dimeric species we have isolated. It is also possible that the reaction with water, to produce hydrogen peroxide, also occurs with the cationic mononuclear hydrogenperoxide intermediate to form a cationic hydroxo-species. This could also react with $[Pt(O_2)(PPh_3)_2]$ to form a Pt-O-O-Pt bridge.

In the presence of strong nucleophiles, such as Cl^- or Br^-, it has not been possible to obtain the peroxo-bridged species because they are in competition with $[Pt(O_2)(PPh_3)_2]$ for the attack on the positively charged platinum intermediate.

As expected, the peroxo-ligand in the positively charged $Pt(O_2)PtO$ ring structure reacts only with strong electrophiles, such as an excess of a strong acid or sulphur dioxide, a behaviour which is in agreement with that of peroxo-bridged binuclear cobalt(III) species.[23] Weaker electrophiles, which do react with neutral $[Pt(O_2)(PPh_3)_2]$,[17] are unreactive towards the $[O_2]^{2-}$ ligand in the framework of a positively charged structure.

EXPERIMENTAL

The complex $[Pt(O_2)(PPh_3)_2]$ was prepared by a literature method.[25] Infrared spectra were recorded on a Perkin-Elmer 257 grating instrument. Conductivities were measured in nitrobenzene with a Philips conductivity bridge. Analyses were carried out in the analytical laboratories of Milan and Cambridge University (C, H, N), and in the F. Pascher Laboratory, Bonn (O).

Preparations.—$[Pt_2(O_2)(OH)(PPh_3)_4][X]$. To a dichloromethane (10 cm^3) solution of $[Pt(O_2)(PPh_3)_2]$ (3 mmol, 2.26 g) was added dropwise, with stirring, 70% perchloric acid (1.5 mmol) in ethanol (3 cm^3). An instantaneous colour change from orange to yellow occurred. Excess of diethyl ether was added to the solution to cause precipitation of the peroxo-complex, which was recovered by filtration under nitrogen (1.7 g), yield 35.6%. The compound was crystallized from dichloromethane–benzene. The other $[Pt_2(O_2)(OH)(PPh_3)_4][X]$ ($X = BF_4$ or NO_3) species were prepared in the same way; the $[PF_6]^-$ derivative was prepared by exchange from the nitrate. Analytical data for the complexes are in Table 1.

$[Pt_2(OH)_2(PPh_3)_4][X]_2$. Perchloric acid (70%, 1.2 mmol) in ethanol (2 cm^3) was added to a dichloromethane solution of $[Pt_2(O_2)(OH)(PPh_3)_4][ClO_4]$ (0.6 mmol, 0.95 g). A white precipitate was obtained, filtered off, and washed with ethanol and dichloromethane (0.6 g), yield 60%. The $[BF_4]^-$ derivative was prepared in the same way; the $[PF_6]^-$ derivative through exchange {Found: C, 51.2; H, 3.7. Calc. for $[Pt_2(OH)_2(PPh_3)_4][ClO_4]_2$: C, 51.7; H, 3.7. Found: C, 48.8; H, 3.8. Calc. for $[Pt_2(OH)_2(PPh_3)_4][PF_6]_2$: C, 49.05; H, 3.5. Found: C, 52.1; H, 3.6. Calc. for $[Pt_2(OH)_2(PPh_3)_4][BF_4]_2$: C, 52.5; H, 3.8%}.

Reactions of $[Pt_2(O_2)(OH)(PPh_3)_4][ClO_4]$.—*With* SO_2. A SO_2-saturated solution of dichloromethane was added in small amounts to a dichloromethane solution of $[Pt(O_2)(OH)(PPh_3)_4][ClO_4]$ (0.5 g, 0.3 mmol) until the yellow solution became colourless. After reducing the volume of the solution, diethyl ether was added until a white precipitate of $[Pt_2(OH)(SO_4)(PPh_3)_4][ClO_4]$ (0.4 g) was obtained. The compound was recrystallized from dichloromethane–diethyl ether (Found: C, 52.0; H, 3.6. Calc.: C, 52.3; H, 3.7%). Λ (in nitrobenzene) = 22.2 S cm^2

mol^{-1}; $\nu(SO_4)$ at 1 275, 1 155, 1 100, and 887 cm^{-1}, $\nu(OH)$ at 3 560 cm^{-1}.

With CO. Carbon monoxide was slowly bubbled through a dichloromethane solution of the peroxo-complex, and the reaction monitored by i.r. spectroscopy. Appearance of bands at 1 991 and 1 951 cm^{-1} indicated formation of $[Pt(CO)_2(PPh_3)_2]$.[18]

X-*Ray Structural Analysis.*—Crystals of $[Pt_2(O_2)(OH)(PPh_3)_4][ClO_4]\cdot 2C_6H_6$ were deposited as pale yellow tablets from dichloromethane–benzene. They decomposed on exposure to air, so several crystals were mounted in 0.5-mm Lindemann tubes under a nitrogen atmosphere. A crystal with dimensions *ca.* $0.166 \times 0.109 \times 0.053$ mm was mounted on a Nonius CAD4 four-circle diffractometer, and data recorded using zirconium-filtered Mo-K_α radiation with a 96-step θ—2θ scan technique. Cell dimensions were derived from angular measurements of 15 strong reflections ($10 < \theta < 20°$). 10 806 Intensities were measured in the range $1.50 < \theta \leqslant 25.0°$, in the 'constant-count' mode (maximum counting time 60 s). The aperture width and scan range were varied according to the function ($A + B\tan\theta$), with $A = 3.0$ mm and $B = 0.5$ mm for the former, and $A = 1.0°$ and $B = 0.2°$ for the latter. Reflections with a net amplitude of less than 3 counts s^{-1} on a fast pre-scan were not remeasured, while those over 3 000 counts s^{-1} were measured at the fastest rate. The intensities of two check reflections were monitored every 50 measurements. They showed a 25% reduction in intensity during data collection, and the full data set was corrected accordingly in the data reduction.

Intensities were corrected for Lorentz and polarization effects, and a numerical absorption correction applied; the crystal was bounded by the (100), ($\bar{1}00$), (010), ($0\bar{1}0$), ($1\bar{1}\bar{1}$), and ($\bar{1}11$) planes. Transmission factors ranged from 0.659 to 0.817. Equivalent reflections were averaged to give 5 375 unique observed intensities [$I < 2.5\sigma(I)$].

Crystal data. $C_{84}H_{73}ClO_7P_4Pt_2$, $M = 1\,743.94$, Triclinic, $a = 14.884(3)$, $b = 15.281(3)$, $c = 16.744(4)$ Å, $\alpha = 90.06(2)$, $\beta = 108.65(2)$, $\gamma = 93.11(2)°$, $U = 3\,602.3$ Å^3, $D_c = 1.61$ g cm^{-3}, $Z = 2$, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 40.64 cm^{-1}, space group $P\bar{1}$ from successful refinement.

The two independent platinum atoms were located by multisolution sigma-2 sign expansion, and all the non-hydrogen atoms from subsequent electron-density difference syntheses. Phenyl hydrogen atoms were included in idealized positions, and the phenyl rings were refined as rigid groups with the constraints C–C 1.395, C–H 1.08 Å, C–C–C 120.0 and C–C–H 120.0°. The perchlorate oxygen atoms were disordered between two sites, and were refined as two rigid interlocking tetrahedra, with the distances within each polyhedron set at 1.42 and 2.32 Å for Cl–O and O $\cdots$ O, respectively. The two sets of positions were assigned occupancies k and $1 - k$; k refined to 0.64(2). Two benzene solvent molecules were also located in the difference map. One was refined as a regular hexagon (C–C 1.395 Å, C–C–C 120°). The other, which was disordered between two sites, was fixed as two idealized hexagons having occupancies of 0.87 and 0.13, respectively, and with each atom having an isotropic temperature factor of 0.165 Å^2. The Pt, P, and Cl atoms were assigned anisotropic thermal parameters, the C and O atoms isotropic, and the H atoms common isotropic temperature factors. The structure was refined by a blocked, sparse-matrix, least-squares technique.[26] A six-parameter mosaic anisotropy correction was also included in the refinement, the six values being 1.002(3), 1.025(4), 0.988(4), 0.239(3), 0.176(3), and 0.178(3). In the last cycles of refinement, 16 low-angle reflections suffering severely from extinction were zero weighted, and a weighting scheme of the form $w = [\sigma^2(F) + 0.0012|F|^2]^{-1}$ introduced. The final converged residuals for the 5 359 intensities were $R = 0.086$ and R' ($= \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o|$) = 0.088. A difference electron-density synthesis calculated at this stage showed peaks of *ca.* 1.8 e Å^{-3} close to the Pt atom positions but no other regions of significant electron density.

Complex neutral-atom scattering factors[27] were employed. Table 4 lists the final atomic positions. Temperature factors, hydrogen-atom co-ordinates, observed and calculated structure-factor amplitudes, and details of least-squares planes are in Supplementary Publication No. SUP 22546 (31 pp.).*

Initial data processing was carried out on the ICL 1905 computer at Queen Mary College, and the structure solution and refinement on the IBM 370/165 at the University of Cambridge using programs written by Dr. G. M. Sheldrick. The Figure was drawn using the ORTEP plotting program.

We thank the Royal Academy for a postdoctoral fellowship (to S. B.), the Universidad Metropolitan, Venezuela, for a grant (to C. Z.), and the S.R.C. for support (to P. R. R.).

[8/1839 *Received, 20th October*, 1978]

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

REFERENCES

1 A. Haim and W. K. Wilmarth, *J. Amer. Chem. Soc.*, 1961, **83**, 509.
2 G. Wilke, H. Shott, and P. Heimbach, *Angew. Chem. Internat. Edn.*, 1967, **6**, 92.
3 S. Muto and Y. Kamiya, *Bull. Chem. Soc. Japan*, 1976, **49**, 2587; S. Muto, K. Tasaka, and Y. Kamiya, *ibid.*, 1977, **50**, 2493.
4 P. J. Hayward, D. M. Blake, G. Wilkinson, and C. J. Nyman, *J. Amer. Chem. Soc.*, 1970, **92**, 5873.
5 L. Vaska, *Accounts Chem. Res.*, 1976, **9**, 175, and refs. therein.
6 K. Nakamoto, 'Infrared Spectra of Inorganic and Co-ordination Compounds,' Wiley–Interscience, New York, 1970.
7 A. Sen and J. Halpern, *J. Amer. Chem. Soc.*, 1977, **99**, 8337.
8 S. Bhaduri, P. R. Raithby, C. I. Zuccaro, M. B. Hursthouse, L. Casella, and R. Ugo, *J.C.S. Chem. Comm.*, 1978, 991.
9 N. J. Taylor, P. C. Chieh, and A. J. Carty, *J.C.S. Chem. Comm.*, 1975, 448.
10 T. Kashiwagi, N. Yasuoka, N. Kasai, M. Kakudo, S. Takahashi, and N. Hagihara, *Chem. Comm.*, 1969, 743.
11 P. T. Cheng, C. D. Cook, S. C. Nyburg, and K. Y. Wan, *Canad. J. Chem.*, 1971, **49**, 3772.
12 J. E. Lyons, 'Aspects of Homogeneous Catalysis,' vol. 3, ed. R. Ugo, D. Reidel P.C., Dordrecht, Boston, 1977, pp. 4—9.
13 R. Ugo, F. Conti, S. Cenini, R. Mason, and G. B. Robertson, *Chem. Comm.*, 1968, 1498.
14 M. Bennett and R. Donaldson, *J. Amer. Chem. Soc.*, 1971, **93**, 3307.
15 G. McLendon and A. E. Martell, *Co-ordination Chem. Rev.*, 1976, **19**, 1.
16 S. Cenini, R. Ugo, and G. La Monica, *J. Chem. Soc.* (*A*), 1971, 3441.
17 J. S. Valentine, *Chem. Rev.*, 1973, **73**, 235 and refs. therein.
18 J. Chatt and P. Chini, *J. Chem. Soc.* (*A*), 1970, 1538.
19 C. D. Cook, K. Y. Wan, K. Hamrin, G. Johanasson, E. Olson, H. Siegbahn, C. Nordling, and K. Siegbahn, *J. Amer. Chem. Soc.*, 1971, **93**, 1904.
20 S. L. Regen and G. M. Whitesides, *J. Organometallic Chem.*, 1973, **59**, 293.
21 D. A. Phillips, M. Kubota, and J. Thomas, *Inorg. Chem.*, 1976, **15**, 118.
22 R. A. Sheldon and J. A. Van Doorn, *J. Organometallic Chem.*, 1975, **94**, 115.

[23] G. Pregaglia, D. Morelli, F. Conti, G. Gregorio, and R. Ugo, *Discuss. Faraday Soc.*, 1968, **46**, 110 and refs. therein; U. Thewalt and R. G. Marsh, *J. Amer. Chem. Soc.*, 1967, **89**, 6364.
[24] S. P. Otsuka, A. Nakamura, Y. Tatsuno, and M. Miki, *J. Amer. Chem. Soc.*, 1972, **94**, 3761; G. M. Zanderighi, R. Ugo, A. Fusi, and Y. Ben Taarit, *Inorg. Nuclear Chem. Letters*, 1976, **12**, 729.
[25] C. D. Cook, P. T. Cheng, and S. C. Nyburg, *J. Amer. Chem. Soc.*, 1969, **91**, 2123.
[26] G. M. Sheldrick, personal communication.
[27] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.