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STRUCTURAL STUDIES OF COMPLEXES CONTAINING THE COORDINATED METHYLDISULPHIDO LIGAND: THE CRYSTAL STRUCTURE OF $[Os(\eta^2-S_2CH_3)(CO)_2(P(C_6H_5)_3)_2]ClO_4.\frac{1}{2}C_6H_6$.

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Summary

Crystal and molecular structures of the title compound have been determined from a three-dimensional X-ray analysis using diffractometer data. The crystals are triclinic, space group $P\bar{1}$, with $Z = 2$ in a unit cell of dimensions $a = 14.23(1)$, $b = 17.30(1)$, $c = 10.44(1)$ Å, $\alpha = 102.1(2)$, $\beta = 102.7(2)$, $\gamma = 105.5(2)°$. Full matrix least squares refinement has given a final R-factor of 0.060 for 4628 reflections for which $I > 3\sigma(I)$.

The crystal structure consists of discrete cations and anions, together with benzene molecules of crystallisation which are situated about the crystallographic centres of symmetry and serve a purely space-filling role. In the cation the coordination about the osmium atom is that of a distorted octahedron, comprising the two triphenylphosphine groups (mutually *trans*), the two carbonyl groups (mutually *cis*) and the *dihapto* S_2Me group. The Os–P distances of 2.420 and 2.419(3) Å are normal. The S_2Me group is nearly symmetrically coordinated with Os-S(1) 2.426(4) Å and Os-S(2) 2.442(4) Å. Other bonds and angles in this ligand are S(1)-S(2) 2.022(7) Å, S(1)-CH_3 1.81(2) Å, and S(2)-S(1)-CH_3 105.4(6)°. The observed geometry is similar to that in $[Ir(S_2)(Ph_2PCH_2CH_2PPh_2)_2]Cl.CH_3CN$.

Introduction

During the last decade the coordinating properties of dioxygen have been extensively studied, not only because of an intrinsic interest in the ligand itself, but also because it was anticipated that such studies might lead to a better understanding of the mechanism of oxygen uptake and transport in biological systems. Interest has been further stimulated by conflicting opinions on the nature of the metal-O_2 bonding, sometimes promulgated by misleading or erroneous structural information. The present state of knowledge has been summarised in two recent reviews - structure and bonding in metal-dioxygen complexes by Vaska [1], chemical reactivity of the coordinated ligand by Valentine [2].

By contrast there has been little investigation into the reactivity of coordinated disulphur and few structural data are available [3]. In a recent communication some new reactions of coordinated disulphur were described, together with a preliminary account of the structure of $[Os(\eta^2-S_2Me)(CO)_2(PPh_3)_2]ClO_4$ which is the product of methylation by methyltrifluoromethylsulphonate of the disulphur analogue $Os(S_2)(CO)_2(PPh_3)_2$ [4]. We now describe details of the fully refined crystal structure.

Experimental

Crystals were supplied by Dr. W.R. Roper of the University of Auckland. They were pale lemon-coloured parallelepipeds, elongated along *c*, with well-developed {100}, {010} and {101} forms. Preliminary X-ray photography showed the crystals to be triclinic with no systematically absent reflections. Unit cell dimensions were determined from precession photographs.

Crystal Data

$C_{42}H_{36}ClO_6OsP_2S_2$, M = 988.4, Triclinic, a = 14.23(1), b = 17.30(1), c = 10.44(1) Å, α = 102.1(2), β = 102.7(2), γ = 105.5(2)°, V = 2315.34 Å^3, space group $P\bar{1}$, Z = 2, d_m = 1.48 (by flotation in aqueous NaI solution), d_c = 1.42, $F(000)$ = 982, Mo-K_α radiation of λ = 0.7107 Å, graphite monochromator, $\mu(\text{Mo}K_\alpha)$ = 28.67 cm^{-1}, crystal size 0.164 x 0.182 x 0.109 mm.

The crystal selected for intensity data collection was a fragment cleaved from a longer needle. Data were collected for the layers h k 0 through h k 10 to θ_{max} = 27° with an ω scan technique on a Stoe 2-circle diffractometer. The optimum scan width was computed for each reflection [5]. The scan rate was 1°s^{-1} with stationary background measurements of 20s at each end of the scan range. Attenuators were not required as the maximum count rate was 5200 c s^{-1}. The data were corrected for Lorentz and polarisation effects, and at a later stage, for absorption using a local version of the programme ABSCOR [6]. After averaging, there remained 4628 unique reflections for which $I > 3\sigma(I)$.

The structure was solved by Patterson and Fourier syntheses. The first isotropic least-squares cycle returned R as 0.103, and a subsequent difference map clearly revealed the presence of one half of a benzene molecule of crystallisation. The refinement program used was SHELX-76 [7]. Atomic scattering factors and dispersion corrections were from standard listings [8]. The full least squares matrix was used to minimise the function $\Sigma\omega(|Fo|-|Fc|)^2$, the weights being of the form $k/(\sigma^2(F) + gF^2)$. The final refinement cycles were computed in blocks. The phenyl rings were treated as rigid groups with riding H atoms (for which the isotropic temperature parameter U

TABLE 1

POSITIONAL PARAMETERS WITH STANDARD DEVIATIONS FOR

$[Os(\eta^2\text{-}S_2Me)(CO)_2(PPh_3)_2]ClO_4\cdot\frac{1}{2}C_6H_6$

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
Os	.1629(0)	.2752(0)	.2574(1)	C(24)	.5752(7)	.3345(6)	.6327(11)
Cl(1)	.1965(5)	.8366(4)	.6290(8)	C(25)	.5530(7)	.2571(6)	.5383(11)
S(1)	−.0026(3)	.1688(2)	.1435(5)	C(26)	.4529(7)	.2129(6)	.4574(11)
S(2)	.0982(4)	.1709(3)	.0336(5)	C(31)	.2445(8)	.0974(6)	.2568(10)
P(1)	.2421(3)	.1902(2)	.3708(4)	C(32)	.1967(8)	.0174(6)	.2643(10)
P(2)	.0989(3)	.3670(2)	.1437(4)	C(33)	.1962(8)	−.0529(6)	.1695(10)
O(1)	.1523(11)	.3676(9)	.5340(17)	C(34)	.2433(8)	−.0434(6)	.0672(10)
O(2)	.3699(13)	.3874(10)	.2827(17)	C(35)	.2910(8)	.0366(6)	.0598(10)
O(3)	.2518(16)	.7942(13)	.5661(22)	C(36)	.2916(8)	.1070(6)	.1546(10)
O(4)	.0974(16)	.7819(13)	.6328(21)	C(41)	−.0315(8)	.3222(7)	.0305(11)
O(5)	.2501(19)	.9041(15)	.7448(26)	C(42)	−.0517(8)	.3152(7)	−.1092(11)
O(6)	.1697(15)	.8752(12)	.5198(21)	C(43)	−.1522(8)	.2844(7)	−.1934(11)
C(1)	.1563(13)	.3334(11)	.4291(20)	C(44)	−.2325(8)	.2605(7)	−.1380(11)
C(2)	.2939(14)	.3448(11)	.2740(18)	C(45)	−.2122(8)	.2676(7)	.0016(11)
C(3)	−.0246(14)	.0700(11)	.1846(19)	C(46)	−.1118(8)	.2984(7)	.0859(11)
C(4)	.4480(11)	−.0258(10)	.3605(14)	C(51)	.0972(7)	.4606(7)	.2619(10)
C(5)	.3964(11)	−.0466(10)	.4542(14)	C(52)	.0106(7)	.4853(7)	.2450(10)
C(6)	.4484(11)	−.0208(10)	.5937(14)	C(53)	.0097(7)	.5547(7)	.3403(10)
C(11)	.1907(7)	.1559(7)	.5001(12)	C(54)	.0953(7)	.5995(7)	.4525(10)
C(12)	.2449(7)	.1198(7)	.5842(12)	C(55)	.1819(7)	.5749(7)	.4693(10)
C(13)	.2078(7)	.0927(7)	.6859(12)	C(56)	.1828(7)	.5054(7)	.3740(10)
C(14)	.1165(7)	.1017(7)	.7034(12)	C(61)	.1749(9)	.4081(6)	.0401(11)
C(15)	.0623(7)	.1378(7)	.6193(12)	C(62)	.2004(9)	.4925(6)	.0449(11)
C(16)	.0993(7)	.1649(7)	.5176(12)	C(63)	.2587(9)	.5233(6)	−.0362(11)
C(21)	.3751(7)	.2461(6)	.4709(11)	C(64)	.2914(9)	.4695(6)	−.1219(11)
C(22)	.3974(7)	.3235(6)	.5652(11)	C(65)	.2658(9)	.3851(6)	−.1267(11)
C(23)	.4975(7)	.3677(6)	.6461(11)	C(66)	.2076(9)	.3544(6)	−.0457(11)

was fixed at 0.10, i.e. approximately 20% higher than those of their parent C atoms). All other atoms were assigned anisotropic thermal parameters. The hydrogen atoms on the methyl carbon atom were treated as a group which was free to rotate about the S(1)-C(3) bond. Their common *U* tensor refined to 0.095. The final residual, *R*, was 0.060, the weighted residual, $R_w = \{\Sigma w(|Fo|-|Fc|)^2/\Sigma w Fo^2\}^{\frac{1}{2}}$ was 0.065, and the weighting parameter, *g*, was 0.004429.

The final atomic positions with standard deviations are listed in Table 1. Bond distances and bond angles are given in Tables 2 and 3 respectively. The atomic numbering scheme is outlined in Fig. 1. Thermal parameters, hydrogen atom positions and tables of observed and calculated structure factors are available on request from the authors (G.R.C.).

TABLE 2

BOND DISTANCES (Å) AND STANDARD DEVIATIONS FOR $[Os(\eta^2-S_2Me)(CO)_2(PPh_3)_2]ClO_4.\frac{1}{2}C_6H_6$

Os - S(1)	2.426(4)	S(1) - S(2)	2.022(7)
Os - S(2)	2.442(4)	S(1) - C(3)	1.812(17)
Os - P(1)	2.420(3)	P(1) - C(11)	1.803(10)
Os - P(2)	2.419(3)	P(1) - C(21)	1.827(10)
Os - C(1)	1.898(19)	P(1) - C(31)	1.800(9)
Os - C(2)	1.878(18)	P(2) - C(41)	1.825(10)
Cl - O(3)	1.385(21)	P(2) - C(51)	1.827(10)
Cl - O(4)	1.488(21)	P(2) - C(61)	1.808(10)
Cl - O(5)	1.391(24)	C(1) - O(1)	1.152(20)
Cl - O(6)	1.469(20)	C(2) - O(2)	1.106(21)

TABLE 3

BOND ANGLES (°) AND STANDARD DEVIATIONS FOR $[Os(n^2\text{-}S_2Me)(CO)_2(PPh_3)_2]ClO_4\cdot\frac{1}{2}C_6H_6$

S(1) - Os - S(2)	49.1(2)	O(5) - Cl - O(6)	104.3(13)
S(1) - Os - P(1)	97.2(1)	Os - S(1) - S(2)	65.9(2)
S(1) - Os - P(2)	87.3(1)	Os - S(1) - C(3)	117.4(6)
S(1) - Os - C(1)	106.8(5)	S(2) - S(1) - C(3)	105.4(6)
S(1) - Os - C(2)	157.1(5)	Os - S(2) - S(1)	65.0(2)
S(2) - Os - P(1)	94.2(1)	Os - P(1) - C(11)	116.7(3)
S(2) - Os - P(2)	86.9(1)	Os - P(1) - C(21)	113.1(3)
S(2) - Os - C(1)	155.9(5)	Os - P(1) - C(31)	114.4(3)
S(2) - Os - C(2)	108.5(5)	C(11) - P(1) - C(21)	100.4(5)
P(1) - Os - P(2)	174.8(1)	C(11) - P(1) - C(31)	105.7(4)
P(1) - Os - C(1)	89.0(5)	C(21) - P(1) - C(31)	105.0(4)
P(1) - Os - C(2)	88.3(5)	Os - P(2) - C(41)	116.1(4)
P(2) - Os - C(1)	92.1(5)	Os - P(2) - C(51)	113.5(3)
P(2) - Os - C(2)	86.5(5)	Os - P(2) - C(61)	113.5(4)
C(1) - Os - C(2)	95.5(7)	C(41) - P(2) - C(51)	103.4(4)
O(3) - Cl - O(4)	114.5(12)	C(41) - P(2) - C(61)	105.1(5)
O(3) - Cl - O(5)	117.8(14)	C(51) - P(2) - C(61)	103.8(5)
O(3) - Cl - O(6)	95.6(12)	Os - C(1) - O(1)	178.9(15)
O(4) - Cl - O(5)	115.8(13)	Os - C(2) - O(2)	178.0(16)
O(4) - Cl - O(6)	105.0(11)		

Description of the structure

The crystals contain discrete monovalent complex cations, perchlorate anions, and space-filling benzene molecules of crystallisation. The overall geometry of the cation is shown in Fig. 1, which also gives the atomic numbering scheme. The coordination geometry is

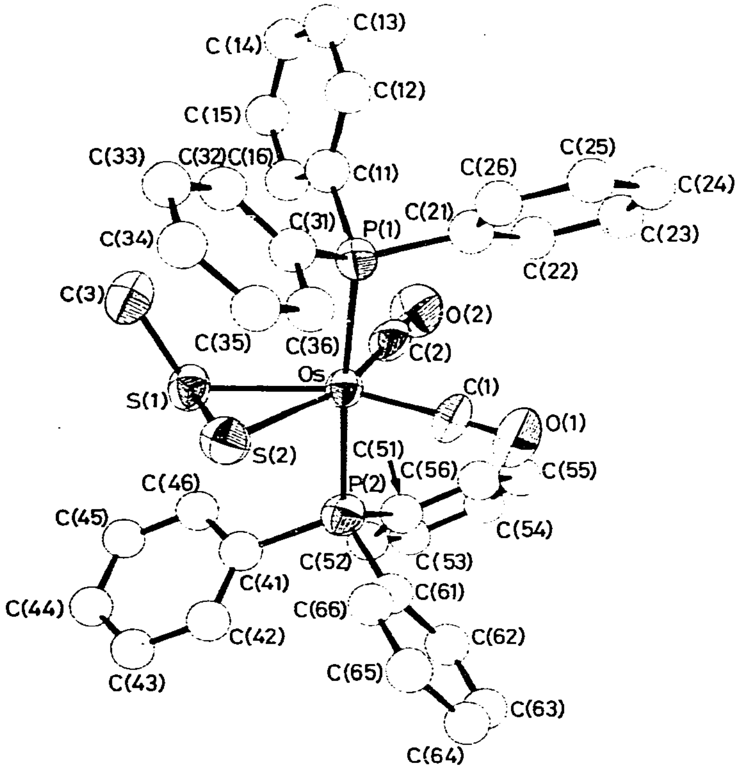

Fig. 1. The molecular geometry of the cation of $[Os(\eta^2-S_2Me)(CO)_2(PPh_3)_2]ClO_4.\frac{1}{2}C_6H_6$, the atomic numbering scheme and 50% probability anisotropic thermal ellipsoids. The perchlorate oxygen atoms are O(3) - O(6), the benzene carbon atoms are C(4) - C(6).

best described as that of a distorted octahedron, in which the triphenylphosphine ligands are mutually *trans*, the carbonyl groups are mutually *cis*, and the bidentate methyldisulphide ligand occupies the other two sites.

The Os-P distances of 2.420 and 2.419(3) Å are equivalent, and compare closely with similar bonds in the majority of other octahedral or trigonal bipyramidal osmium complexes containing *trans* triphenylphosphine ligands, e.g. 2.405(2), 2.401(3) Å in $Os(CO)_2(NO)(PPh_3)_2{}^+ClO_4{}^-$ [9]; 2.400, 2.406(7) Å in $Os(CO)(NO)(CN\text{-}p\text{-}C_6H_4CH_3)(PPh_3)_2{}^+ClO_4{}^-$ [10];

2.430, 2.431(3) Å in $Os(CO)(CS)Cl_2(PPh_3)_2$ [11]; 2.39, 2.40(2) Å in $OsCl_2(HgCl)(NO)(PPh_3)_2$ [12]; 2.411, 2.411(2) Å in $OsCl_3(NH_3)(PPh_3)_2$ [13]; 2.382, 2.371(1) Å in $OsH(CS_2CH_3)(CO)_2(PPh_3)_2 \cdot \frac{1}{2}C_6H_6$ [14]; 2.412, 2.416(2) Å in $Os[\eta^2\text{-}C(S)(p\text{-tolyl})](\eta^1\text{-}O_2CCF_3)(CO)(PPh_3)_2$ [15]; and 2.371, 2.379(2) Å in $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$ [16].

The P-Os-P angle is 174.8(1)°. The deviation from linearity is most likely due to steric interactions associated with the bulky triphenylphosphine groups, and is similar to that found in $Os[\eta^2\text{-}C(S)(p\text{-tolyl})](\eta^1\text{-}O_2CCF_3)(CO)(PPh_3)_2$, 173.9(1)° [15], $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$, 174.00(6)° [16] and many other *trans* triphenylphosphine-metal complexes.

The Os-CO bond lengths of 1.90, 1.88(2) Å are normal values, indicating little or no *trans* bond-weakening influence of the sulphur donors. It is noted that the slightly longer bond lies *trans* to the methylated sulphur atom, but the difference is not significant. The Os-C-O angles of 178.0, 178.9° deviate only very slightly from linearity.

The most interesting aspect of the structure is the geometry of the osmium-S_2Me interaction. The Os-S distances of 2.426, 2.442(4) Å are marginally different (4σ), where the shorter bond is that to the methylated sulphur atom. The S-S bond length is 2.022(7) Å, and S(1)-Me is 1.81(2) Å. This observed geometry can be compared to that found in the disulphur complex $Ir(S_2)(Ph_2PCH_2CH_2PPh_2)_2^+$ where Ir-S bond lengths are 2.389(5) and 2.422(4) Å and S-S is 2.066(6) Å [3]. The reason for the difference of 6σ in the two Ir-S bond lengths is unknown. In the Ir complex the S_2 ligand is twisted 12.8° from the P-Ir-P equatorial plane. Bonds and Ibers [3] have tabulated structural data for a series of related complexes in which O_2, NO and CO replace S_2, and where similar twists occur [17]. In the present complex the extent of this distortion is much reduced despite the fact that methylation has lowered the symmetry of the ligand. The Os-S distances differ by only 4σ, while the plane defined by Os, S(1) and

S(2) is twisted only 5.3° from the corresponding equatorial plane defined by Ir, C(1) and C(2). In the Os complex the phosphine ligands are triphenylphosphine, rather than the bridging bis(diphenylphosphino)ethane, and the P-C-C-P ring constraints do not exist. The small distortions which do occur probably result from a balancing of ligand-ligand repulsive forces.

The S-S distance of 2.022(7) Å in the present complex is a little shorter than that of 2.066(6) Å in $Ir(S_2)(Ph_2PCH_2CH_2PPh_2)_2^+$ [3]. However, both values can be compared with those of 2.060(3) Å in octasulphur [18], 2.06(2) Å in H_2S_2 [19], 2.03(1) Å in phenyl disulphide [20] and 2.007(5) Å in $[SFe(CO)_3]_2$ [21]. All of these distances lie between the values of 2.12 Å in Na_2S_2 (bond order 1) [22] and 1.889 Å in disulphur (bond order 2) [23]. That the S-S bond order is greater than 1 in $[Os(\eta^2\text{-}S_2Me)(CO)_2(PPh_3)_2]ClO_4$ is best explained by conventional metal → π*(S_2 or S_2Me) back-donation, analogous to that proposed for metal-dioxygen complexes [1].

The S(1)-methyl distance of 1.81(2) Å and the S(2)-S(1)-methyl angle of 105.4(6)° are normal.

The unit cell packing can be seen in the stereopair diagrams of Fig. 2. There are 16 intermolecular approaches shorter than

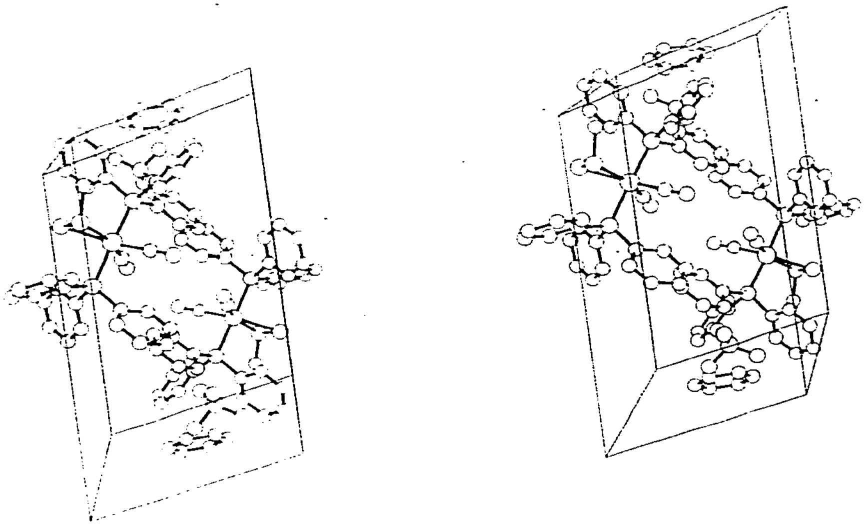

Fig. 2. Stereographic diagrams showing the molecular packing.

3.5Å. This number of close contacts is higher than usual for complexes of this type, indicating a considerable intimacy in the solid-state aggregation of the cations, anions and benzene solvate molecules. Many of the close approaches involve oxygen atoms of the perchlorate anion, and it is noted that the ClO_4^- is considerably distorted from its ideal tetrahedral geometry. The best fit with the diffraction data gives Cl-O bond distances ranging from 1.391-1.488 Å and O-Cl-O angles ranging from 95.6 to 117.8°. The ClO_4^- ion is notorious for displaying this kind of disorder [24] although much more symmetrical ions have often been observed [25].

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