Supplementary Material Available: Listing of structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Bis(chloro(dioxygen)bis(triphenylphosphine)rhodium(I))

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The compound bis(chloro(dioxygen)bis(triphenylphosphine)rhodium(I)), $[RhCl(O_2)(P(C_6H_5)_3)_2{\cdot}CH_2Cl_2]_2$, has been formed by the oxygenation of $RhCl(P(C_6H_5)_3)_3$. The crystal structure has been determined from three-dimensional x-ray data at room temperature. The compound crystallized in space group $P\bar{1}$ with one molecule per unit cell ($\rho_{obsd} = 1.470$, $\rho_{calcd} = 1.469$ g cm^{-3}). The axial parameters are $a = 13.889$ (7), $b = 13.678$ (6), $c = 11.433$ (5) Å; $\alpha = 105.73$ (4), $\beta = 115.74$ (3), $\gamma = 100.97$ (4)°. Least-squares refinement of absorption- and decomposition-corrected intensity data converged at a conventional R factor of 0.044 based on 1658 significant reflections. The structure may be described as a dimer having two trigonal-bipyramidal subunits, the bridge being formed by one oxygen atom of each subunit having a third bond to the second subunit. The dioxygen molecules thus have features similar to those of both π-bonded ligands and chelating peroxo groups.

Introduction

Two crystalline materials have been isolated in the products formed in the reaction of molecular oxygen with solutions of chlorotris(triphenylphosphine)rhodium(I) in methylene chloride. In a previous paper[1] we have given complete details of the synthesis and structural characterization of the monomeric species $RhCl(O_2)(P(C_6H_5)_3)_3{\cdot}2CH_2Cl_2$. In this paper we present structural details for the dimeric species $[RhCl(O_2)(P(C_6H_5)_3)_2{\cdot}CH_2Cl_2]_2$ on which we have published a previous communication.[2]

Experimental Section

(a) Synthesis. On bubbling oxygen for 5 min through a solution containing 0.25 g of $RhCl(P(C_6H_5)_3)_3$ in 15 mL of methylene chloride and slowly evaporating the solution at 7 °C for 2 days, red-brown diamagnetic crystals were obtained (~50% yield). All measurements were made on this material which appeared to be homogeneous. Carbon and hydrogen analyses[3] are in reasonable agreement with the formulation $RhCl(O_2)(P(C_6H_5)_3)_2{\cdot}CH_2Cl_2$. The chlorine analysis proved difficult owing to rhodium interference in the method used. Anal. Calcd: C, 57.0; H, 4.1; Cl, 13.6. Found: C, 57.7; H, 4.2; Cl, ~15. The infrared spectrum (Nujol mull) shows an absorption at 845 cm^{-1} attributable to oxygen–oxygen stretching.[4] The complex is also formed by dissolution of $RhCl(O_2)(P(C_6H_5)_3)_3$ in methylene chloride. Yields vary with concentration (less than 1×10^{-2} M solutions give ~50% yield after standing at 7 °C for 2 days). Oxygen was positively identified in the gaseous thermal decomposition products by gas chromatography after heating the complex in vacuo to 200 °C. The residue showed an absorption at 1120 cm^{-1} consistent with the formation of complexed triphenylphosphine oxide.[5,6] The complex undergoes a series of transformations on heating: 80–85 °C, dissolution in solvent of crystallization; 110–120 °C, loss of solvent; 133–134 °C, explosive decomposition.

Black diamagnetic crystals of the iodo analogue may be prepared in the same manner from $RhI(P(C_6H_5)_3)_3$ in 62% yield (mp 166–168 °C). Microanalytical analyses were satisfactory for the formulation $RhI(O_2)(P(C_6H_5)_3)_2$. Anal. Calcd: C, 54.9; H, 3.8; I, 16.1. Found: C, 54.5; H, 4.0; I, 16.2. No evidence of chlorine was found in the analysis. However, it appears that some methylene chloride of crystallization (ν 740 cm^{-1}) is initially present but is removed under vacuum. The infrared spectrum was very similar to that observed for the chloro species. However, the dioxygen stretching band is shifted slightly at 857 cm^{-1}. In both complexes the oxygen is irreversibly bound.[1]

The chloro complex is extremely stable chemically, being inert to both strong acid and base and almost insoluble in all solvents tested.

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Table I. Refined and Derived Atomic Parameters[a]

(i) Refined Coordinates

Atom	X	Y	Z	B	Atom	X	Y	Z	B	Atom	X	Y	Z	B
Rh	0.09542(7)	-0.05735(8)	0.06606(9)	2.45(b)	O(1)	-0.0255(6)	-0.1164(5)	-0.1361(7)	2.67	Cl(2)	0.223(2)	0.377(1)	0.484(2)	8.7
P(1)	0.0670(3)	-0.2351(2)	0.0442(3)	2.95	O(2)	-0.0884(6)	-0.0928(5)	-0.0666(7)	2.86	Cl(3)	0.305(3)	0.367(1)	0.606(5)	15.3
P(2)	0.2648(3)	-0.0127(2)	0.0728(3)	3.03	C(1)	0.172(2)	0.255(2)	0.492(2)	10.3	Cl(4)	0.1238(9)	0.2598(5)	0.6050(8)	15.4
Cl(1)	0.1776(3)	0.0039(2)	0.3167(3)	4.17										

Occupancy factors Cl(2), 0.42(4); Cl(3), 0.62 (4)

(a) The values in parentheses in this and the following tables represent the standard deviation of the least significant digit(s).

(b) Equivalent isotropic temperature factors corresponding to the anisotropic thermal parameters given in Table 3.

(ii) Derived coordinates

C(111)(c)	0.133(1)	0.2670(8)	0.198(1)	3.1(3)	C(216)	0.3459(6)	0.1985(7)	0.2812(9)	3.9(3)	H(125)	0.209	-0.506	-0.136	4.8
C(112)	0.0663(9)	-0.3343(6)	0.2282(9)	3.8(3)						H(126)	0.163	-0.410	0.028	4.2
C(113)	0.118(1)	-0.3600(6)	0.3448(7)	5.0(3)	C(221)	0.241(1)	-0.0358(5)	-0.1031(9)	3.2(3)					
C(114)	0.237(1)	-0.3183(8)	0.432(1)	4.5(3)	C(222)	0.1490(9)	-0.0154(6)	-0.194(1)	4.4(3)	H(132)	-0.085	-0.184	0.134	4.4
C(115)	0.3033(9)	-0.2510(6)	0.4019(9)	4.9(3)	C(223)	0.1290(9)	-0.0269(6)	-0.328(1)	5.8(3)	H(133)	-0.277	-0.277	0.068	5.9
C(116)	0.251(1)	-0.2253(6)	0.2853(7)	4.2(3)	C(224)	0.201(1)	-0.0584(5)	-0.3712(9)	6.3(4)	H(134)	-0.388	-0.448	-0.130	6.3
					C(225)	0.2940(9)	-0.0788(6)	-0.281(1)	6.1(3)	H(135)	-0.308	-0.527	-0.262	6.5
C(121)	0.0960(7)	-0.3182(5)	-0.0827(8)	3.1(3)	C(226)	0.3140(8)	-0.0675(6)	-0.147(1)	4.5(3)	H(136)	-0.116	-0.435	-0.196	4.8
C(122)	0.0727(6)	-0.2976(5)	-0.2031(9)	3.9(3)										
C(123)	0.0996(7)	-0.3538(6)	-0.2989(6)	4.6(3)	C(231)	0.3710(7)	-0.0724(7)	0.1519(7)	3.3(3)	H(212)	0.441	0.125	0.063	4.8
C(124)	0.1498(7)	-0.4305(5)	-0.2742(8)	5.0(3)	C(232)	0.3685(7)	-0.1722(6)	0.0755(8)	4.2(3)	H(213)	0.572	0.309	0.203	5.7
C(125)	0.1731(6)	-0.4510(5)	-0.1538(9)	4.4(3)	C(233)	0.4474(8)	-0.2165(5)	0.143(1)	6.0(3)	H(214)	0.560	0.423	0.392	5.5
C(126)	0.1462(7)	-0.3948(6)	-0.0581(6)	3.9(3)	C(234)	0.5289(7)	-0.1610(7)	0.2865(7)	6.0(3)	H(215)	0.417	0.353	0.441	5.7
					C(235)	0.5314(7)	-0.0611(6)	0.3629(8)	5.4(3)	H(216)	0.286	0.169	0.302	4.3
C(131)	-0.0850(5)	-0.3020(7)	-0.0251(9)	2.8(2)	C(236)	0.4524(8)	-0.0168(5)	0.296(1)	3.9(3)					
C(132)	-0.1318(7)	-0.2561(5)	0.0515(9)	4.1(3)						H(222)	0.097	0.007	-0.162	4.8
C(133)	-0.2434(8)	-0.3102(7)	0.0128(8)	5.4(3)	H(112)	-0.019	-0.364	0.165	4.1	H(223)	0.062	-0.012	-0.392	6.3
C(134)	-0.3083(5)	-0.4099(7)	-0.1026(9)	5.7(3)	H(113)	0.070	-0.408	0.365	5.4	H(224)	0.187	-0.067	-0.468	6.9
C(135)	-0.2614(7)	-0.4557(5)	-0.1792(9)	5.9(3)	H(114)	0.274	-0.337	0.515	4.9	H(225)	0.346	-0.101	-0.312	6.7
C(136)	-0.1498(8)	-0.4018(7)	-0.1405(8)	4.4(3)	H(115)	0.388	-0.221	0.464	5.3	H(226)	0.380	-0.082	-0.082	4.9
					H(116)	0.299	-0.177	0.264	4.6					
C(211)	0.3531(6)	0.1322(5)	0.1712(9)	3.1(3)						H(232)	0.310	-0.212	-0.028	4.6
C(212)	0.4363(8)	0.1728(7)	0.1425(9)	4.4(3)	H(122)	0.037	-0.242	-0.221	4.3	H(233)	0.446	-0.288	0.088	6.6
C(213)	0.5123(6)	0.2797(7)	0.2237(9)	5.2(3)	H(123)	0.083	-0.339	-0.385	5.1	H(234)	0.586	-0.193	0.335	6.6
C(214)	0.5051(6)	0.3459(5)	0.3337(9)	5.0(3)	H(124)	0.169	-0.471	-0.343	5.5	H(235)	0.590	-0.021	0.466	5.9
C(215)	0.4219(8)	0.3053(7)	0.3625(9)	5.2(3)						H(236)	0.454	0.055	0.350	4.3

(c) The numbering of the phenyl group atoms Cijk proceeds as follows: i, phosphine number; j, phenyl group number in phosphine; k, number in ring.

Table II. Refined Rigid-Body Parameters[a]

Group	*x*	*y*	*z*	*D*	*E*	*F*
11	0.1848 (5)	−0.2967 (4)	0.3151 (5)	4.210 (4)	3.026 (9)	5.267 (9)
12	0.1229 (4)	−0.3743 (4)	−0.1785 (5)	2.712 (4)	1.647 (5)	3.889 (5)
13	−0.1966 (4)	−0.3559 (4)	−0.0638 (5)	0.680 (4)	0.445 (6)	0.198 (6)
21	0.4291 (4)	0.2391 (4)	0.2525 (5)	0.598 (5)	0.871 (6)	4.332 (6)
22	0.2215 (5)	−0.0471 (4)	−0.2372 (6)	2.202 (5)	1.800 (7)	3.215 (8)
23	0.4499 (4)	−0.1167 (4)	0.2192 (6)	2.879 (5)	2.434 (5)	5.514 (5)

[a] The coordinates *x*, *y*, and *z* describe the center of gravity of the ring and the angles *D*, *E*, and *F* are inclination angles (in radians).

Slow dissolution does take place in pyridine and an orange crystalline product is formed. Analysis of this complex proved unsatisfactory.

(b) X-Ray Crystallography. Brown crystals of $[RhCl(O_2)(P(C_6H_5)_3)_2\cdot CH_2Cl_2]_2$ were examined under a microscope and found to be prone to twinning with the twin boundary clearly visible. Crystals cleaved along the diagonal were free of such defects. Examination of preliminary Weissenberg and precession photographs indicated that the complex crystallizes in the triclinic crystal system. The density ($\rho_{obsd} = 1.470$ g cm^{-3}), measured by flotation in aqueous potassium iodide, was in excellent agreement with the calculated value ($\rho_{calcd} = 1.469$ g cm^{-3}) assuming one dimeric unit per unit cell.

A crystal with faces of the forms {100}, {010}, {001}, and {$\bar{3}$21} was mounted on a Picker manual four-circle diffractometer with the c^* axis coincident with the diffractometer ϕ axis. Precise lattice parameters were determined as $a = 13.889$ (7), $b = 13.678$ (6), $c = 11.433$ (5) Å; $\alpha = 105.73$ (4), $\beta = 115.74$ (3), $\gamma = 100.97$ (4)° (from the setting angles of 16 accurately aligned high-angle reflections showing resolvable α_1–α_2 splitting (Cu Kα_1, λ 1.54051 Å). No significant variations were observed after data collection. Data were collected using nickel-filtered Cu K$\bar{\alpha}$ radiation and a peak height analyzer tuned to accept 95% of the Cu K$\bar{\alpha}$ peak. Coupled ω–2θ scans were made with a $(2\theta \pm 1)°$ scan width and scan speed of 2° min^{-1}. Background counts were estimated from a linear interpolation of two 30-s stationary counts taken at the limits of the scan. No evidence of twinning was found on examination of peak profiles. As indicated by the preliminary photography, data were only measured to a limit of $(\sin\theta)/\lambda = 0.45$ Å^{-1}. This rapid falloff in intensity was consistent with a relatively low degree of order in the crystals. A total of 2151 reflections were measured and of this number 1658 were found to be statistically reliable using the criteria $I \leq 3\sigma(I)$ for rejection. During data collection seven standard reflections were measured at eight hourly intervals and some slight decomposition of the crystal was found. Peaks having a count rate $>10^4$ counts s^{-1} were recollected at lower tube currents and scaled into the data by comparison with peaks of lower intensity recollected under the same conditions.

The observed data were reduced to structure amplitudes after correction for Lorentz–polarization effects, decomposition (up to 8%), and absorption (μ, 72 cm^{-1}; transmission factors range from 0.633 to 0.809). Standard deviations for observed structure amplitudes were calculated using an uncertainty factor[7] of 0.03.

Table III. Anisotropic Thermal Parameters ($Å^2 \times 10^3$)[a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	33.4 (7)	31.6 (6)	31.0 (7)	15.9 (5)	16.6 (5)	13.8 (5)
P(1)	46 (2)	35 (2)	33 (2)	20 (2)	19 (2)	15 (2)
P(2)	38 (2)	41 (2)	35 (2)	17 (2)	16 (2)	16 (2)
Cl(1)	73 (2)	52 (2)	34 (2)	29 (2)	25 (2)	17 (2)
O(1)	33 (5)	45 (5)	31 (5)	22 (4)	16 (4)	11 (4)
O(2)	32 (5)	34 (5)	38 (5)	19 (4)	16 (4)	19 (4)
C(1)	180 (20)	120 (20)	70 (10)	50 (20)	70 (20)	100 (10)
Cl(2)	100 (10)	120 (10)	120 (20)	46 (8)	70 (10)	37 (8)
Cl(3)	180 (20)	120 (10)	250 (30)	60 (10)	150 (20)	70 (10)
Cl(4)	250 (10)	80 (10)	150 (10)	21 (6)	150 (10)	22 (5)

[a] Anisotropic thermal parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

Table IV. Selected Interatomic Distances (Å)

Rh-P(1)	2.314 (3) [2.316 (3)[a]]	P(1)-C(131)	1.829 (7)
Rh-P(2)	2.277 (3) [2.281 (3)]	P(2)-C(211)	1.833 (7)
Rh-Cl(1)	2.390 (3) [2.402 (3)]	P(2)-C(221)	1.821 (8)
Rh-O(1)	1.980 (7)	P(2)-C(231)	1.832 (7)
Rh-O(2)	2.198 (7)	O(1)-O(2)	1.44 (1)
Rh'-O(1)	2.778 (7)	C(1)-Cl(2)	1.70 (3)
Rh-O(2)'	2.069 (7)	C(1)-Cl(3)	1.80 (3)
P(1)-C(111)	1.815 (7)	C(1)-Cl(4)	1.70 (3)
P(1)-C(121)	1.829 (7)		

[a] Distances corrected for riding.

Table V. Selected Intramolecular Angles (deg)

P(1)-Rh-P(2)	100.3 (1)	O(2)-Rh-O(2)'	76.9 (3)
P(1)-Rh-Cl(1)	90.6 (1)	Rh-P(1)-C(111)	121.3 (3)
P(1)-Rh-O(1)	87.5 (2)	Rh-P(1)-C(121)	115.5 (3)
P(1)-Rh-O(2)	92.5 (2)	Rh-P(1)-C(131)	107.4 (3)
P(1)-Rh-O(2)'	169.4 (2)	Rh-P(2)-C(211)	114.5 (3)
P(2)-Rh-Cl(1)	95.7 (1)	Rh-P(2)-C(221)	110.7 (3)
P(2)-Rh-O(1)	106.2 (3)	Rh-P(2)-C(231)	120.6 (3)
P(2)-Rh-O(2)	143.4 (2)	Cl(2)-C(1)-Cl(3)	47 (1)
P(2)-Rh-O(2)'	89.2 (2)	Cl(2)-C(1)-Cl(4)	116 (1)
Cl(1)-Rh-O(1)	158.0 (3)	Cl(3)-C(1)-Cl(4)	100 (1)
Cl(1)-Rh-O(2)	118.4 (2)	O(1)-O(2)-Rh	61.7 (1)
Cl(1)-Rh-O(2)'	93.4 (2)	O(1)-O(2)-Rh'	103.4 (5)
O(1)-Rh-O(2)	39.9 (3)	Rh-O(2)-Rh'	103.0 (3)
O(1)-Rh-O(2)'	85.2 (3)		

Table VI. Selected Intramolecular Nonbonded Contacts (Å)

Rh-Rh^1	3.340 (2)	Rh-H(222)	2.98
O(2)-O(2)^1	2.65 (1)	O(1)-H(222)	2.33
O(1)-O(1)^1	3.49 (1)	O(1)-H(122)	2.25
O(1)-O(2)^1	2.75 (1)	O(2)-H(132)	2.88

Table VII. Selected Intermolecular Contacts

Atom 1-atom 2	Symmetry operation (on atom 2)	Dist, Å
H(115)-H(236)	$\bar{x} + 1, \bar{y}, \bar{z} + 1$	2.43
H(223)-H(223)	$\bar{x}, \bar{y}, \bar{z} - 1$	2.46
H(115)-H(236)	$\bar{x} + 1, \bar{y}, \bar{z} - 1$	2.43

Structure Solution and Refinement

Examination of a three-dimensional Patterson map gave approximate coordinates for the rhodium, two phosphorus, and one chlorine atoms. This initial solution was consistent with the space group $P\bar{1}$ with the two rhodium atoms of the unit cell being separated by only ~3.5 Å. The remaining atoms were located in electron density difference maps although the methylene chloride molecule was not well defined and some disorder seemed likely. To reduce the number of parameters of the model the phenyl groups were treated as rigid bodies through all stages of refinement with carbon–carbon and carbon–hydrogen distances fixed at 1.392 and 1.0 Å, respectively. Hydrogen atoms of the phenyl groups were allowed individual isotropic temperature factors 10% greater than those of the attached carbon atoms. The initial sequence of refinements was based on a single-site model, which in its most sophisticated form allowed anisotropic thermal parameters for the rhodium, chlorine, phosphorus, and oxygen atoms. The refinement of this model converged at $R_1 = 0.055$, $R_2 = 0.060$ where

$$R_1 = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|}$$

$$R_2 = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w|F_o|^2}\right]^{1/2}$$

and $\omega = 1/\sigma^2(F)$. Scattering factors (except those of hydrogen) were those of Cromer and Mann[8] and included both real and imaginary corrections for anomalous scattering.[9] The hydrogen scattering factors were those of Mason and Robertson.[10]

When the methylene chloride region of an electron density difference map ($R = 0.075$; methylene chloride atoms excluded from calculation) was examined, reasonably well-defined sites were found for the carbon atom and one chlorine atom (Cl(4)). However, the other chlorine atom position was represented by a banana-shaped region of electron density having an approximate radius of 1.7–1.8 Å (about C(1)) and subtending an approximate angle at C(1) of 65°. Some resolution into two distinct sites could be seen. Considerable rotation and disorder of the molecule about the Cl(4)–C(1) axis was occurring. A hindered-rotor description of this section of the structure seemed desirable; however, no program was available. As the methylene chloride molecule had no significant contacts with the rest of the structure, the considerable amount of effort required to describe this motion did not seem warranted. Thus a partial description of the methylene chloride was attempted by including the semiresolved sites as anisotropic chlorine atoms of variable occupancy (Cl(2), 0.42 (4); Cl(3), 0.62 (4)).[30] The total model was then refined to convergence (average shift/σ = 0.07; $R_1 = 0.044$; $R_2 = 0.055$). Since the observed structure was unexpected, it was considered necessary to be absolutely certain that the bridging groups were dioxygen molecules. When the scattering factors for nitrogen were used for these atoms, the atomic thermal parameters assumed negative values and both R_1 and R_2 (0.051 and 0.069, respectively) ensured that the nitrogen could be rejected at better than the 0.005 confidence level.[11]

A final electron density difference map was then calculated. The largest positive and negative peaks were 0.4 and –0.4 e $Å^{-3}$, respectively (cf. carbon ~3 e $Å^{-3}$), and were located in the vicinity of the disordered methylene chloride molecule. Programs used in this study include FORDAP,[12] SFLS5HR,[13] GONO9,[14] ORFFE II,[15] and ORTEP.[16]

Discussion

The primitive unit cell contains one molecule of the dimeric complex $[RhCl(O_2)(P(C_6H_5)_3)_2]_2$ situated at an inversion center and two molecules of methylene chloride. The structure of the complex is shown in Figure 1. The coordination of the rhodium atoms can be described in terms of a trigonal bipyramid as follows. The equatorial sites are occupied by a triphenylphosphine (P(2)), a chlorine atom (Cl(1)), and a dioxygen molecule (O(1) and O(2)). The axial sites are occupied by the other triphenylphosphine (P(1)) and an oxygen atom (O(2)') of the inversion center related subunit. Thus the two dioxygen molecules of the dimer act as most unusual bridges and exhibit a geometry that is a combination of the more common sideways π-bonded dioxygen complexes[17,18] and the trans peroxo-bridged species.[19-21] There are general

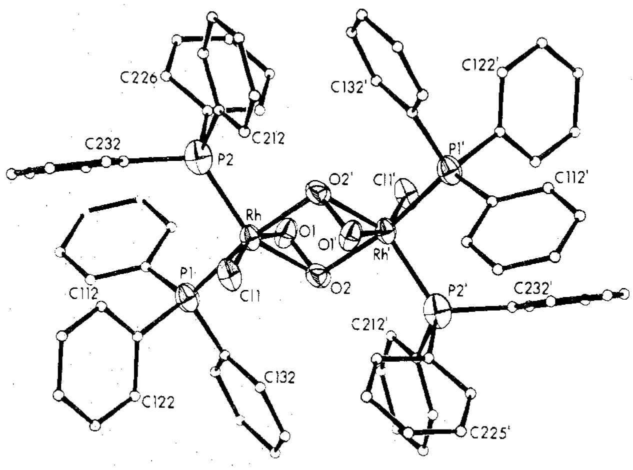
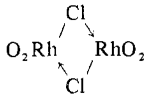


Figure 1. Perspective view of $[RhCl(O)_2(P(C_6H_5)_3)_2]_2$.

structural similarities to bis[tricarbonyl(3-chloro-2-methylnitrosobenzene)iron][22] despite the differences in interatomic distances.

The rhodium–oxygen distances are significantly different (Rh–O(1) = 1.980 (7), Rh–O(2) = 2.198 (7) Å), the shorter distance involving the nonbridging atom. The rhodium–oxygen distances to the symmetry-related subunit are Rh–O(1)′ = 2.778 (7) and Rh–O(2)′ = 2.069 (7) Å and the oxygen–oxygen bond length is 1.44 (1) Å.

The bonding in this complex may be described using the conventional molecular orbital scheme for oxygen with the oxygen molecule assumed to have the configuration $\pi^{*2}\pi^{*0}$. Within the subunit fragment Rh–O(1)–O(2) the bonding can then be rationalized by a ligand to metal donation from a fully occupied π orbital accompanied by back-donation from the metal to the empty dioxygen π^* orbital.[23] The bridging bond is then considered to involve overlap between the filled π^* orbital not taking part in the π bonding and the d_{z^2} orbital of the rhodium atom in the other subunit[21,24] (the "z" axis being the pseudo-threefold rotation axis of the trigonal-bipyramidal subunit).



$$O_2Rh\overset{Cl}{\underset{Cl}{\rightleftarrows}}RhO_2$$

Although the chlorine-bridged species seems geometrically feasible, it does not appear to be formed. This suggests that a particularly favorable energy relationship exists between the dioxygen π^* and the rhodium d_{z^2} orbitals. An alternative method of describing the structure would be to consider rhodium as Rh(III) and the dioxygen molecules as chelating peroxide anions, the bridges being formed from one of the lone pairs of each peroxide ion. This latter description now seems more appropriate.[4] Although variations are present in the Cl–C–Cl angles in the methylene chloride molecule,[25,26] no conclusions can be drawn due to the extremely high thermal motion and inadequacies of the model. It does not appear to be coordinated to the complex as it is situated at least 5.6 Å from the central coordination and has no significant contacts with other atoms. In Table VIII, the dimer is compared with the monomeric complex $RhClO_2(P(C_6H_5)_3)_3 \cdot 2CH_2Cl_2$[1] and the parent catalyst $RhCl(P(C_6H_5)_3)_3$.[27] In the dioxygen species the large changes occur in both the axial and equatorial rhodium–phosphorus distances. In the tris(phosphine)–dioxygen complex, these distances are longer than those of the dimer by approximately 0.06 and 0.08 Å, respectively. This difference must be mainly due to the different axial ligands (P(3) and O(2)′). The oxygen in the axial position has no vacant orbitals in a suitable geometry to accept π electrons from the rhodium. Thus in $RhClO_2P'_3$ there are four ligands (3 P′ and O_2) competing for π-electron density[28] whereas in the half-unit of the dimer there are only three ligands (2 P′ and O_2). It would be reasonable to expect the observed trend but not perhaps the magnitude. The asymmetry of the rhodium–oxygen distances could involve a trans effect[1] or may, in the case of the dimer, be a result of extra bond formation involving the oxygen atom with the longer bond length. Little more can be inferred until any doubts concerning rhodium–oxygen and oxygen–oxygen distances in related complexes are dispelled.[4,18,29]

Table VIII. Selected Distances and Angles in Related Complexes

	$[RhCl(O_2)P'_2]_2$[a]	$RhCl(O_2)P'_3$[a]	$RhClP'_3$[a]	
			Red	Orange
	(i) Distances, Å			
	Equatorial Atoms			
Rh–Cl(1)	2.390 (3)	2.391 (3)	2.376 (4)	2.404 (4)
Rh–P(2)	2.277 (3)	2.357 (3)	2.214 (4)	2.225 (4)
Rh–O_2	2.198 (7) 1.980 (7)	2.081 (8) 2.005 (8)		
	Axial Atoms			
Rh–P(1)	2.314 (3)	2.362 (4)	2.334 (3)	2.304 (4)
Rh–P(3)	2.069 (7)	2.387 (4)	2.322 (4)	2.338 (4)
	(ii) Angles, Deg			
P(1)–Rh–Cl(1)	90.6 (1)	85.1 (1)	85.2 (2)	85.3 (1)
P(1)–Rh–P(2)	100.3 (1)	102.7 (1)	97.9 (2)	97.7 (1)
P(1)–Rh–P(3)	169.4 (2)[b]	154.4 (1)	152.8 (1)	159.1 (2)
P(2)–Rh–Cl(1)	95.7 (1)	101.3 (1)	156.2 (2)	166.7 (2)
P(2)–Rh–P(3)	89.2 (2)[b]	101.6 (1)	100.4 (1)	96.4 (2)
P(3)–Rh–Cl(1)	93.4 (2)[b]	82.5 (1)	86.1 (2)	84.5 (1)

[a] P′ = triphenylphosphine. [b] Second or last atom is O(2)′.

The differences in geometries of the two oxygenation products and the red and orange forms of the parent catalyst $RhCl(P(C_6H_5)_3)_3$ may be summarized as (i) a major angular change between a phosphine and the chlorine atom, (ii) increase in the rhodium–phosphorus bond lengths, and (iii) little change in rhodium–chlorine distances.

A recent paper[31] qualitatively accounts for the trigonal bipyramidal geometries in both complexes. Other calculations[32] suggest that σ effects are of importance in dioxygen–metal donation and that metal–phosphine $\sigma + \pi$ orbitals may influence dioxygen coordination.

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Registry No. $[RhCl(O_2)(P(C_6H_5)_3)_2 \cdot CH_2Cl_2]_2$, 62623-64-7; $[RhI(O_2)(P(C_6H_5)_3)_2]_2$, 62521-12-4; $RhCl(O_2)(P(C_6H_5)_3)_3$, 62521-13-5; $RhCl(P(C_6H_5)_3)_3$, 14694-95-2.

Supplementary Material Available: Listing of structure factor amplitudes (4 pages). Ordering information is given on any current masthead page.

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Crystal Structure and Polarized Electronic Spectrum of μ-Hydroxo-bis[pentaaminechromium(III)] Chloride Dihydrate

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The crystal structure of μ-hydroxo-bis[pentaaminechromium(III)] chloride dihydrate has been determined from three-dimensional x-ray diffractometer data. The compound crystallizes in the monoclinic space group $C2/c$ with $a = 23.656$ (9) Å, $b = 7.36$ (1) Å, $c = 16.718$ (8) Å, and $\beta = 128.1$ (1)°. Least-squares refinement of 1112 independent reflections led to a final R value of 0.091. The dimeric $[(NH_3)_5CrOHCr(NH_3)_5]^{5+}$ complexes are oriented with their twofold axes parallel to the b axis of the unit cell. Single-crystal absorption spectra in the region of single pair excitations ${}^4A_{2g}{}^4A_{2g} \rightarrow {}^4A_{2g}{}^2E_g$, ${}^4A_{2g}{}^2T_{1g}$ have been measured down to liquid helium temperatures. The structural and spectroscopic informations are combined to determine the polarizations of the optical transitions with respect to the symmetry axes of the dinuclear complexes. There are at least two intensity-gaining mechanisms active in this region. The most prominent absorption bands are shown to arise through an exchange-induced mechanism.

Introduction

Exchange interactions in the classical dinuclear rhodo and erythro chromium(III) complexes have been studied by magnetic susceptibility measurements as well as spectroscopic methods.[1-4] The spectroscopic investigations have been hampered somewhat by a lack of crystal structure information. Two crystal structure determinations of acid rhodo chloride monohydrate have been reported, but neither of the published structures[2,5] is compatible with the results of a spectroscopic study.[4]

The information gained by single-crystal absorption or emission spectroscopy can only partly be used if the orientation of the dinuclear complexes with respect to the optical extinction directions of the crystal is unknown. A knowledge of the polarizations of pair transitions with respect to the symmetry axes of the complex is particularly important if one is interested in the mechanisms by which those transitions gain their intensity. Several intensity-gaining mechanisms have been found to be operative in chromium(III) pair transitions. As in mononuclear complexes, spin-forbidden electric dipole transitions may arise through combined action of spin–orbit coupling and odd-parity crystal field. Pair transitions due to this single-ion mechanism have been found in the spectrum of ruby.[6] At least part of the intensity of the spin-forbidden bands in trigonal $Cs_3Cr_2Br_9$ appears to be due to this mechanism.[7] Another possibility for spin-forbidden transitions in dinuclear complexes to gain intensity is through an exchange-induced electric dipole mechanism first proposed by Tanabe.[8] Some of the most prominent bands in the chromium(III)-pair spectra of Al_2O_3,[6] $LaAlO_3$,[9] and $ZnGa_2O_4$,[10] have been found to be due to this mechanism. Finally, there has been strong evidence for the existence of a vibronically induced exchange mechanism,[11] particularly in the absorption spectrum of the basic rhodo chromium(III) complex, where we have a linear Cr–O–Cr arrangement.

In order to create a basis for an analysis of the polarized absorption spectrum we decided to determine the crystal structure of acid rhodo chromium dihydrate. Crystals of this compound are most suitable for spectroscopic investigations. Various sets of spectra can be measured perpendicular to the well-developed faces of the crystal.

Experimental Section

Collection and Reduction of the X-Ray Data. Acid rhodo chromium chloride was prepared by the method of Linhard and Weigel.[12] Crystals of the dihydrate were grown by slow evaporation of a saturated solution at 5 °C and pH 4. For the x-ray experiments a crystal had to be sealed into a capillary of Lindemann glass together with some mother liquor to prevent decomposition. The crystal was aligned with its b axis approximately parallel to the capillary tube. Weissenberg photographs showed that the crystals belong to the monoclinic system. The systematic absences observed on the diffraction pattern were $h + k$ even for hkl and l even for $h0l$, which indicates that the space group is either Cc (C_s^4) or $C2/c$ (C_{2h}^6). The intensity distribution[13-16] clearly suggests that the centrosymmetric space group $C2/c$ is the more probable one. The following expectation values for various functions of the normalized structure factor E were obtained: $\langle|E|\rangle = 0.806$, $\langle|E|^2\rangle = 1.009$, $\langle||E|^2 - 1|\rangle = 0.958$. These indications are supported by the different distribution of vectors in the Patterson function for the two space groups.[17] The cell constant b was determined from an oscillation photograph along the b axis. The other cell constants were calculated by a least-squares procedure from eight reflections with $\theta > 67°$ measured on a zero-layer Weissenberg photograph calibrated with Si-powder lines. The wavelengths were assumed as λ(Cu Kα_1) 1.54051 Å and λ(Cu Kα_2) 1.54433 Å. The

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