Crystal and Molecular Structure of Potassium Bis(dimethylphenylphosphine)bis(dithiocarbonato)rhodate(III) Trihydrate

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The structure of the title compound (II), $K[Rh(S_2CO)_2(PMe_2Ph)_2]\cdot3H_2O$ has been determined. Crystals are monoclinic, space group $P2_1/c$, with a = 18.798, b = 6.516, c = 23.924 Å, β = 113.91°. There are two independent anions per unit cell with crystallographic C_i ($\bar{1}$) symmetry. They are essentially identical, and the planar dithiocarbonate ligands have Rh–S 2.37, C–S 1.725, C–O 1.25 Å; S–Rh–S 73.5, S–C–S 111, and S–C–O 125°.

In a recent publication,[1] the reaction between *mer*-$[RhCl_3(PMe_2Ph)_3]$ and excess of potassium dithiocarbonate heated under reflux in ethanol was reported to give four products: $K[RhCl_2(S_2CO)(PMe_2Ph)_2]$ (I) (7%), $[RhCl(S_2CO)(PMe_2Ph)_3]$ (16%), *trans*-$[Rh(S_2CO)(S_2COEt)(PMe_2Ph)_2]$ (17.5%), and its *cis*-isomer (35%). The formulation of (I) was based on elemental analyses [Found: C, 34.9; H, 3.8%. (I) requires C, 35.1; H, 3.8%), qualitative detection of chlorine by *X*-ray fluorescence, and conductivity measurements indicating a 1 : 1 electrolyte in nitromethane solution. A strong band in the i.r. spectrum at 320 cm^{-1} was assigned to ν(Rh–Cl), and peaks at 1 640 and 1 610 cm^{-1} to ν(C–O) (S_2CO^{2-}).[2] Furthermore, ^1H n.m.r. studies in deuterioacetone showed a single triplet at τ 8.22, suggesting *trans*-phosphine groups. The *X*-ray structural analysis reported here indicates that this compound, after drying, is in fact *trans*-$K[Rh(S_2CO)_2(PMe_2Ph)_2]$ (II), which requires C, 35.9; H, 3.7%.

EXPERIMENTAL

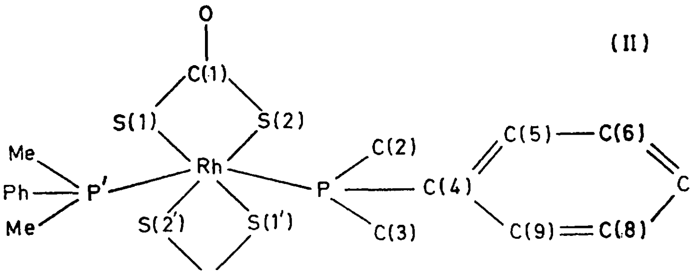
Crystal Data.—$C_{18}H_{22}KO_2P_2RhS_4\cdot3H_2O$, Monoclinic, M = 657, a = 18.798(4), b = 6.516(2), c = 23.924(5) Å, β = 113.91(1)°, U = 2 697 Å^3, D_m = 1.611 g cm^{-3}, Z = 4, D_c = 1.617 g cm^{-3}, $F(000)$ = 1 336. Space group $P2_1/c$. Mo-K_α radiation, λ = 0.7107 Å; μ(Mo-K_α) = 12.2 cm^{-1}.

Intensity Data, Structure, and Refinement.—Intensity data were collected with zirconium-filtered Mo-K_α radiation on a computer-controlled Nonius three-circle diffractometer (θ—2θ scan). Of the 2 480 attainable symmetry-independent reflections within the limit $\theta < 20°$, 1 648 reflections were considered observed, having intensities $I > 3\sigma(I)$, based on counting statistics. No absorption correction was applied. The structure was solved by a combination of Patterson and direct methods.[3] From the Patterson synthesis, two independent rhodium atoms were placed on special positions; these atoms only contribute to reflections in parity groups *ggg* and *uuu*. A Wilson-type plot for these reflections, and a Wilson plot for the remaining reflections, gave overall temperature parameters B_H and B_L, for the rhodium atoms and for the remaining atoms respectively. After subtraction of the scaled heavy-atom contribution from the observed value of the structure factors, normalised structure factors for the remaining light-atom structure were calculated. With the sign-correlation procedure,[4] using a starting set of 50 reflections signed by the heavy atoms, 2 reflections to specify completely the origin, and 20 reflections with symbolic signs, 738 reflections were signed, and all symbols eliminated. A subsequent Fourier synthesis showed all light atom positions except hydrogen. Refinement was carried out by full-matrix least squares, including anisotropic thermal parameters for rhodium, sulphur, potassium, and phosphorus atoms, and isotropic temperature factors for all other atoms, no attempt being made to locate hydrogen atoms. The least-squares weights were $w = \sin\theta/0.3$ for $\sin\theta < 0.3$, and $w = 1$ otherwise. The final refinement resulted in a residual R 0.053 for all ' observed ' reflections. Standard crystallographic calculations were carried out by use of ' *X*-Ray '70 ' [5] as implemented at the Computing Centre of the University of Nijmegen.

Positional and thermal parameters are given in Table 1, and the structure factors are listed in Supplementary Publication No. SUP 21696 (5 pp., 1 microfiche).†

DISCUSSION

Bond lengths and angles for the two independent complex ions are given in Tables 2 and 3, the numbering scheme adopted being given in (II), and a projection of the unit cell along *b* in the Figure.



(II)

Numbering of the atoms in an asymmetric unit of the two complex ions (1) and (2). The oxygen atoms of the water molecules are O(3), O(4), and O(5)

The rhodium atoms are both on crystallographic centres of symmetry with distorted octahedral coordination. In both complexes, the rhodium atom and the two dithiocarbonate ligands are essentially coplanar, the maximum deviation from the plane defined by the relevant atoms being 0.019 [complex (1)] and 0.015 Å

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† See Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue.

[1] D. J. Cole-Hamilton and T. A. Stephenson, *J.C.S. Dalton*, 1974, 1818.

[2] J. M. Burke and J. P. Fackler, jun., *Inorg. Chem.*, 1972, **11**, 2744.

[3] P. T. Beurskens and J. H. Noordik, *Acta Cryst.*, 1971, **27**, 187.

[4] P. T. Beurskens, *Acta Cryst.*, 1964, **17**, 462, and ' Lecture Notes,' N.A.T.O. Advanced Study Institute on Direct Methods in Crystallography, Erice, 1974.

[5] ' *X*-Ray ' system of programs,' 1970 version of Technical Report TR 67 58, University of Maryland Computer Science Center, 1970.

TABLE 1

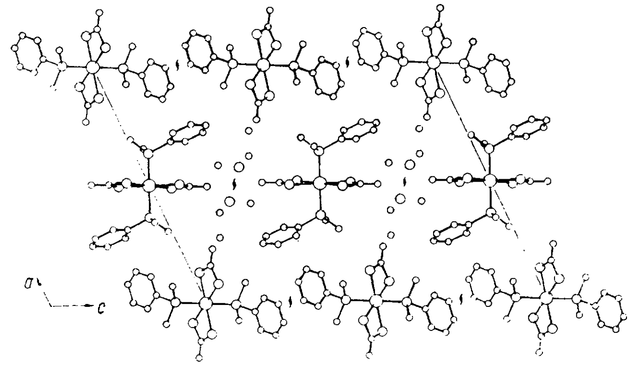
Fractional co-ordinates ($\times 10^4$) with standard deviations and isotropic thermal parameters (Å$^2 \times 10^4$) for complex ions (1) and (2) of (II)

Atom	Complex (1)				Complex (2)			
	x	y	z	U	x	y	z	U
Rh	0	0	0	*	5 000	0	5 000	*
S(1)	819(2)	2 545(5)	648(2)	*	5 032(2)	−1 555(6)	5 904(2)	*
S(2)	1 304(2)	−1 084(6)	249(2)	*	4 879(2)	2 712(6)	5 623(2)	*
P	−65(2)	−1 504(6)	872(2)	*	3 660(2)	−725(6)	4 578(2)	*
O	2 300(6)	1 696(17)	962(5)	640	4 930(5)	1 215(15)	6 671(4)	475
C(1)	1 603(8)	1 132(22)	672(6)	398	4 946(7)	888(20)	6 162(6)	329
C(2)	−736(8)	−3 670(24)	732(6)	484	3 451(9)	−3 429(26)	4 651(7)	609
C(3)	856(8)	−2 511(23)	1 443(6)	460	3 070(9)	597(24)	4 914(7)	563
C(4)	−370(7)	229(21)	1 325(5)	323	3 165(7)	− 188(21)	3 757(6)	350
C(5)	181(8)	1 561(21)	1 765(6)	381	2 809(9)	1 713(24)	3 578(7)	529
C(6)	−71(8)	2 948(23)	2 103(6)	490	2 461(10)	2 236(28)	2 931(7)	675
C(7)	−855(9)	3 034(25)	1 996(7)	556	2 504(11)	722(26)	2 518(8)	692
C(8)	−1 382(9)	1 762(24)	1 591(7)	526	2 804(9)	−1 110(27)	2 697(7)	616
C(9)	−1 158(8)	347(22)	1 235(6)	433	3 166(8)	−1 616(24)	3 336(6)	489
K	4 287(2)	6 980(5)	2 123(2)	*				
O(3)	3 826(6)	736(18)	1 681(5)	741				
O(4)	4 193(7)	3 593(19)	2 713(5)	784				
O(5)	2 786(7)	5 911(19)	1 340(5)	765				

* Anisotropic thermal parameters (Å$^2 \times 10^4$). Temperature factors are of the form $\exp(-2\pi^2\sum_i\sum_j h_i a^*_i h_j a^*_i U_{ij})$.

Atom	Complex (1)						Complex (2)					
	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	280	301	286	−5	115	−43	353	302	281	−25	113	0
S(1)	393	316	345	−104	164	−125	368	333	264	−4	106	42
S(2)	263	433	388	67	132	6	483	286	328	58	126	−49
P	322	306	250	−23	137	−34	297	452	300	−36	89	11
K	573	455	548	−12	241	33						

[complex (2)]. The only distortion of the dithiocarbonate ions from their ideal C_{2v} (*mm*) symmetry is the marginally significant difference between the angles S(1)-C(1)-O and S(2)-C(2)-O, also reflected in the Rh-S(1) and Rh-S(2) bond lengths, in both complexes. This is probably the result of the involvement of the oxygen atoms in hydrogen bonding, and potassium co-ordination.



Projection of (II) along *b*. The large unconnected circles are potassium ions, while the small ones are water molecules

TABLE 2

Bond lengths (Å) in the complex ions (1) and (2) of (II)

Bond	Complex (1)	Complex (2)
Rh-S(1)	2.364(4)	2.368(4)
Rh-S(2)	2.383(4)	2.382(4)
Rh-P	2.352(4)	2.351(4)
S(1)-C(1)	1.718(15)	1.739(15)
S(2)-C(1)	1.722(15)	1.720(15)
C(1)-O	1.264(16)	1.247(18)
P-C(2)	1.831(16)	1.827(19)
P-C(3)	1.838(12)	1.829(18)
P-C(4)	1.813(15)	1.834(12)
Mean C-C (Ph)	1.405(20)	1.399(20)

The dimethylphenylphosphine ligands have C_s (*m*) symmetry within the accuracy of the structure determination; the angle between the plane defined by the phenyl ring and that defined by P, C(4), and the mid-point between C(2) and C(3) is 85° in complex (1) and 88° in complex (2). The essential difference between the two complex ions lies in the orientation of the phosphine group with respect to the rest of the complex. It is indicated by the pseudo-torsion angle C(4)-P-Rh-C(1), which is 90° in complex (1) and 150° in complex (2).

TABLE 3

Bond angles (°) in the complex ions (1) and (2) of (II)

Angle	Complex (1)	Complex (2)
S(1)-Rh-S(2)	73.35(13)	73.68(13)
S(1)-Rh-P	87.96(13)	86.15(13)
S(2)-Rh-P	94.15(13)	93.47(13)
Rh-S(1)-C(1)	87.9(3)	87.8(3)
Rh-S(2)-C(1)	87.3(3)	87.7(3)
S(1)-C(1)-S(2)	111.0(7)	110.8(8)
S(1)-C(1)-O	123.2(11)	123.0(10)
S(2)-C(1)-O	125.8(11)	126.1(11)
Rh-P-C(2)	116.1(3)	112.8(3)
Rh-P-C(3)	115.9(3)	116.9(3)
Rh-P-C(4)	114.1(3)	114.3(3)
C(2)-P-C(3)	103.1(5)	102.7(5)
C(2)-P-C(4)	103.5(5)	104.5(5)
C(3)-P-C(4)	102.2(5)	104.2(5)
P-C(4)-C(5)	120.7(11)	118.1(12)
P-C(4)-C(9)	120.6(11)	120.4(12)
Mean C-C-C (Ph)	120.0(13)	120.0(15)

The potassium ions have distorted trigonal prismatic co-ordination, with K · · · O distances varying from 2.66 to 2.92 Å. Each potassium ion shares an O(2) and an O(4) with one ion below and one above it about a screw axis, and is also co-ordinated by an O(3) and an

O(5). The hydrogen bonding as well is associated with these columns about the screw axes at $\frac{1}{2},y,\frac{1}{4}$ and $\frac{1}{2},y,\frac{3}{4}$. There are four recognisable hydrogen bonds, and although the hydrogen atoms were not found, it is possible to assign unambiguously the sense of each hydrogen bond: $O(5)\cdots O(1)$ 2.91, $O(3)\cdots O(1)$ 2.77, $O(3)\cdots O(2)$ (at $x, \frac{1}{2} - y, z - \frac{1}{2}$) 2.88, and $O(4)\cdots O(3)$ 2.9 Å. Among the atoms found, there are no other intermolecular contacts <3.3 Å.

The structure found for (II) agrees with the evidence used to assign it to (I), except for the qualitative finding of chlorine, which appears to have been an impurity, and the assignment of an i.r. band to ν(RhCl). As this band appears in a complex region of the spectrum, it could be otherwise assigned, probably to ν(RhS).

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