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The Crystal Structure of Di-μ-chloro-bis(triphenyl phosphite)-(cyclo-octa-1,5-diene)dirhodium(I)

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The crystal structure of di-μ-chloro-bis(triphenyl phosphite)(cyclo-octa-1,5-diene)dirhodium(I) has been determined by three-dimensional Patterson and Fourier techniques using automatic diffractometer data. The atomic parameters were refined by the least-squares method to a final R index of 0·066 for 2500 observed reflexions. The cell dimensions are $a=12{\cdot}863\pm0{\cdot}006$, $b=13{\cdot}146\pm0{\cdot}007$, $c=25{\cdot}130\pm0{\cdot}010$ Å, $\beta=99{\cdot}98\pm0{\cdot}01°$ with the space group $P2_1/c$ and 4 molecules per unit cell. The coordination of the Rh atoms is square planar, displaying a folded $RhCl_2Rh$ bridge with an angle of $122{\cdot}6\pm0{\cdot}2°$ between the lines extending from the Rh atoms to the centre of the line joining the two Cl atoms.

Introduction

The structure analysis of $Rh_2[P(OC_6H_5)_3]_2(C_8H_{12})Cl_2$ (Haines, 1969) was undertaken at the request of Dr W. Robb and Mrs L. Haines of the National Chemical Research Laboratories as the structure of the $RhCl_2Rh$ bridge is relevant to their kinetic studies of this and related compounds. Two structure analyses of compounds containing $RhCl_2Rh$ bridges have hitherto been reported. Ibers & Snyder (1962) showed that the dimer of RhCl(cyclo-octa-1,5-diene) is planar in that the $RhCl_2Rh$ bridge is planar and the centres of the C=C bonds (towards which the $\sigma-\pi$ bonds between the rhodium atoms and the C_8H_{12} rings are directed) form square-planar arrays with the halves of the bridge. In contrast, Dahl, Martell & Wampler (1961) found a more complicated situation in $Rh_2(CO)Cl_2$. Each rhodium atom is surrounded by two chlorine atoms and two carbonyl groups in a square-planar arrangement. The $RhCl_2Rh$ bridge is severely bent with an angle of 124° between the two lines joining the rhodium atoms with the centre of the line between the

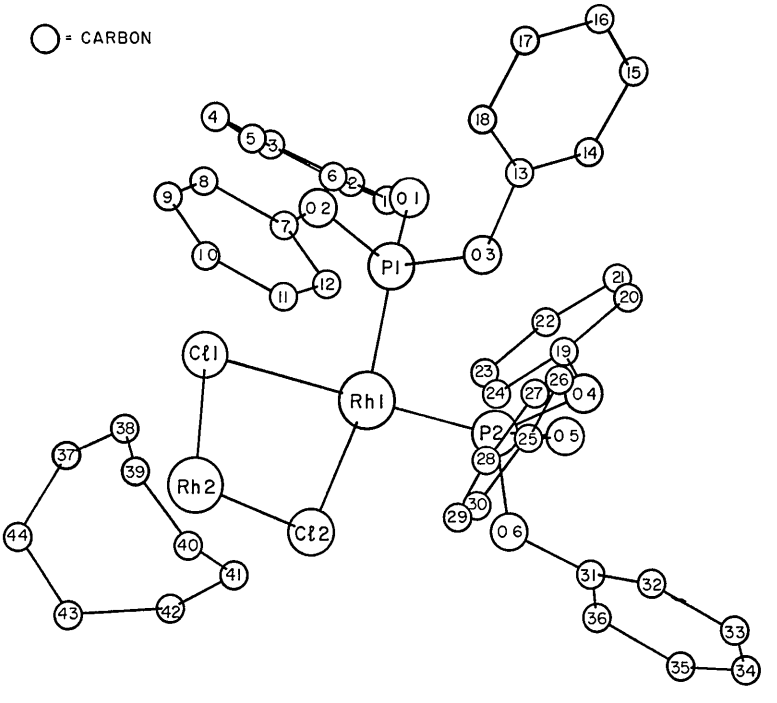

Fig. 1. A view of the molecule along the [221] axis showing the atomic numbering used.

chlorine atoms and they consider the rhodium atom to be six-coordinated. The increased coordination is caused by two rhodium atoms, *viz.* (*a*) one in an adjacent dimer at a distance of 3·31 Å which is in keeping with other metal–metal bonds as referenced by Dahl *et al.* (1961), and (*b*) the second rhodium atom of the bridge itself. Dahl *et al.* describe this atom as making a 'bent' bond with the central atom, and this is held responsible for the diamagnetism exhibited by the compound in the solid state.

Experimental

Crystals of suitable size and quality were prepared and provided by Mrs L. Haines. The crystals were amber coloured and had intricate faceting which resulted in many of them being nearly spherical. Preliminary oscillation, Weissenberg and precession photographs showed them to be monoclinic with space group $P2_1/c$ ($h0l$ absent for l odd, $0k0$ absent for k odd). Spot positions were accurately measured with a Hilger &

Table 1. *Final atomic parameters (fractional coordinates and isotropic temperature factors)*

Standard deviations are given in parentheses.

	x/a	*y/b*	*z/c*	*B*
Rh(1)	0·7077 (1)	0·2180 (1)	0·6085 (1)	3·74 (3)
Rh(2)	0·7348 (1)	0·4218 (1)	0·5473 (1)	4·52 (4)
Cl(1)	0·5832 (3)	0·3503 (4)	0·5758 (1)	4·68 (10)
Cl(2)	0·7690 (4)	0·2495 (4)	0·5252 (2)	5·16 (11)
P(1)	0·6480 (4)	0·2054 (4)	0·6825 (2)	3·78 (10)
P(2)	0·8165 (3)	0·0954 (3)	0·6316 (2)	3·36 (9)
O(1)	0·5510 (8)	0·1317 (8)	0·6876 (4)	4·53 (24)
O(2)	0·6018 (9)	0·3070 (8)	0·7056 (4)	4·58 (25)
O(3)	0·7289 (8)	0·1610 (9)	0·7334 (4)	4·62 (26)
O(4)	0·7763 (8)	−0·0141 (8)	0·6475 (4)	4·24 (24)
O(5)	0·9048 (8)	0·1015 (8)	0·6857 (4)	4·08 (24)
O(6)	0·8827 (8)	0·0689 (8)	0·5857 (4)	4·36 (23)
C(1)	0·4543 (13)	0·1304 (13)	0·6510 (6)	4·6 (4)
C(2)	0·4322 (16)	0·0393 (16)	0·6255 (8)	6·4 (5)
C(3)	0·3239 (22)	0·0314 (22)	0·5921 (11)	10·2 (7)
C(4)	0·2622 (20)	0·1132 (21)	0·5901 (10)	8·8 (6)
C(5)	0·2857 (18)	0·2009 (18)	0·6177 (8)	7·4 (5)
C(6)	0·3907 (17)	0·2108 (18)	0·6488 (8)	6·9 (5)
C(7)	0·6567 (13)	0·3995 (13)	0·7159 (6)	4·0 (4)
C(8)	0·5928 (15)	0·4826 (15)	0·7203 (7)	5·4 (4)
C(9)	0·6442 (15)	0·5775 (15)	0·7331 (7)	5·9 (4)
C(10)	0·7518 (15)	0·5870 (15)	0·7417 (7)	5·4 (4)
C(11)	0·8120 (14)	0·5033 (15)	0·7361 (7)	4·9 (4)
C(12)	0·7674 (13)	0·4041 (13)	0·7238 (6)	4·6 (4)
C(13)	0·7036 (13)	0·1382 (14)	0·7842 (7)	4·1 (4)
C(14)	0·6971 (15)	0·0375 (16)	0·7975 (8)	6·3 (5)
C(15)	0·6770 (17)	0·0123 (17)	0·8503 (9)	7·1 (5)
C(16)	0·6618 (15)	0·0893 (17)	0·8850 (8)	6·2 (5)
C(17)	0·6670 (15)	0·1902 (16)	0·8720 (8)	6·0 (5)
C(18)	0·6881 (14)	0·2158 (15)	0·8193 (7)	4·9 (4)
C(19)	0·6954 (14)	−0·0720 (14)	0·6157 (7)	4·3 (4)
C(20)	0·6651 (15)	−0·1557 (15)	0·6426 (7)	5·4 (4)
C(21)	0·5856 (16)	−0·2184 (17)	0·6136 (8)	6·6 (5)
C(22)	0·5448 (15)	−0·1981 (16)	0·5602 (8)	5·7 (5)
C(23)	0·5760 (14)	−0·1128 (14)	0·5347 (7)	5·2 (4)
C(24)	0·6555 (14)	−0·0493 (14)	0·5616 (7)	4·7 (4)
C(25)	0·9632 (13)	0·1888 (13)	0·7022 (7)	4·0 (4)
C(26)	0·9787 (15)	0·2041 (16)	0·7579 (8)	5·5 (5)
C(27)	1·0418 (15)	0·2922 (16)	0·7765 (8)	6·3 (4)
C(28)	1·0791 (16)	0·3541 (16)	0·7420 (9)	6·7 (5)
C(29)	1·0616 (15)	0·3367 (16)	0·6864 (8)	6·6 (5)
C(30)	0·9994 (14)	0·2502 (14)	0·6656 (7)	5·0 (4)
C(31)	0·9482 (13)	−0·0153 (13)	0·5850 (7)	4·3 (4)
C(32)	1·0349 (18)	−0·0273 (18)	0·6215 (9)	7·5 (6)
C(33)	1·1014 (20)	−0·1159 (21)	0·6179 (11)	9·1 (7)
C(34)	1·0771 (17)	−0·1816 (16)	0·5761 (9)	7·2 (5)
C(35)	0·9945 (23)	−0·1639 (23)	0·5367 (11)	10·7 (8)
C(36)	0·9267 (20)	−0·0776 (21)	0·5408 (10)	9·6 (7)
C(37)	0·6645 (13)	0·5659 (14)	0·5358 (7)	4·7 (4)
C(38)	0·7254 (14)	0·5615 (14)	0·5888 (7)	6·1 (4)
C(39)	0·8292 (17)	0·6136 (16)	0·6047 (8)	6·9 (5)
C(40)	0·9236 (18)	0·5452 (18)	0·6014 (9)	6·9 (6)
C(41)	0·8943 (14)	0·4596 (14)	0·5566 (7)	6·0 (4)
C(42)	0·8448 (15)	0·4827 (14)	0·5029 (7)	5·3 (4)
C(43)	0·8153 (14)	0·5925 (15)	0·4824 (7)	5·9 (4)
C(44)	0·7027 (15)	0·6228 (15)	0·4895 (7)	5·5 (4)

Watts four-circle diffractometer and all the cell constants were determined from these by means of least-squares methods to give:

$$a = 12{\cdot}863 \pm 0{\cdot}006 \text{ Å}$$
$$b = 13{\cdot}146 \pm 0{\cdot}007$$
$$c = 25{\cdot}130 \pm 0{\cdot}010$$
$$\beta = 99{\cdot}98 \pm 0{\cdot}01°.$$

The density measured by flotation was 1·59 g.cm^{-3} indicating four formula units of mass 1005·5 in the unit cell which gave a calculated density of 1·60 g.cm^{-3}.

A crystal of spherical shape with a diameter of 0·2 mm was selected for the intensity measurements. The intensities of 2500 independent reflexions with $\theta \leq 20°$ were measured. Mo $K\alpha$ (Zr, β-filtered) radiation was used in conjunction with the ω-scan technique. The intense 102 reflexion was used as a reference standard and remeasured after each set of 5 reflexions. Maximum variation over the 14 days taken to collect the intensities was ±2%. Background corrections were made from slow scans of intensity against θ parallel to central lattice rows but sufficiently far from them in ω to ensure that the tails of the diffraction peaks were not intersected. The usual Lp corrections were made and absorption corrections were obviated by the low value of $\mu R \simeq 0{\cdot}10$.

Structure refinement

The trial structure which followed from three-dimensional Patterson and Fourier syntheses was refined to $R = 0{\cdot}066$, $[R = (\sum||F_o| - |F_c||)/\sum|F_o|]$, by using a full-matrix least-squares program which minimizes the function $\sum w(|F_o| - |kF_c|)^2$ (Busing, Martin & Levy, 1962) with individual isotropic thermal parameters for all the atoms. The form factors used were those of Hanson, Herman, Lea & Skillman (1964) after minimal adjustment for anomalous dispersion according to *International Tables for X-ray Crystallography* (1962). All measurable intensities were included in the refinement with equal weight and those of magnitude less than three times the background count (the unobserved

Table 2. *Bond distances* (Å)

Standard deviations in parentheses.

Rh(1)–Cl(1)	2·410 (5)	C(11)–C(12)	1·43 (2)
Rh(1)–Cl(2)	2·398 (5)	C(12)–C(7)	1·40 (2)
Rh(1)–P(1)	2·138 (5)		
Rh(1)–P(2)	2·146 (5)	C(13)–C(14)	1·37 (2)
Rh(2)–Cl(1)	2·383 (5)	C(14)–C(15)	1·43 (3)
Rh(2)–Cl(2)	2·391 (5)	C(15)–C(16)	1·37 (3)
		C(16)–C(17)	1·37 (3)
Rh(2)–C(37)	2·10 (2)	C(17)–C(18)	1·43 (2)
Rh(2)–C(38)	2·12 (2)	C(18)–C(13)	1·39 (2)
Rh(2)–C(41)	2·08 (2)		
Rh(2)–C(42)	2·10 (2)	C(19)–C(20)	1·38 (2)
		C(20)–C(21)	1·41 (2)
Rh(2)···Rh(1)*	3·138 (2)	C(21)–C(22)	1·38 (2)
Cl(1) ···Cl(2)*	3·185 (7)	C(22)–C(23)	1·38 (2)
		C(23)–C(24)	1·40 (2)
P(1)–O(1)	1·61 (1)	C(24)–C(19)	1·40 (2)
P(1)–O(2)	1·59 (1)		
P(1)–O(3)	1·61 (1)	C(25)–C(26)	1·39 (2)
P(2)–O(4)	1·60 (1)	C(26)–C(27)	1·44 (3)
P(2)–O(5)	1·60 (1)	C(27)–C(28)	1·35 (3)
P(2)–O(6)	1·61 (1)	C(28)–C(29)	1·39 (3)
		C(29)–C(30)	1·43 (2)
O(1)–C(1)	1·41 (2)	C(30)–C(25)	1·37 (2)
O(2)–C(7)	1·41 (2)		
O(3)–C(13)	1·40 (2)	C(31)–C(32)	1·33 (4)
O(4)–C(19)	1·42 (2)	C(32)–C(33)	1·45 (3)
O(5)–C(25)	1·41 (2)	C(33)–C(34)	1·35 (3)
O(6)–C(31)	1·39 (2)	C(34)–C(35)	1·34 (3)
		C(35)–C(36)	1·44 (3)
C(1)–C(2)	1·37 (3)	C(36)–C(31)	1·37 (3)
C(2)–C(3)	1·48 (4)		
C(3)–C(4)	1·34 (3)	C(37)–C(38)	1·42 (2)
C(4)–C(5)	1·35 (3)	C(38)–C(39)	1·49 (3)
C(5)–C(6)	1·44 (3)	C(39)–C(40)	1·52 (3)
C(6)–C(1)	1·34 (3)	C(40)–C(41)	1·59 (3)
		C(41)–C(42)	1·42 (2)
C(7)–C(8)	1·38 (2)	C(42)–C(43)	1·56 (3)
C(8)–C(9)	1·42 (2)	C(43)–C(44)	1·54 (3)
C(9)–C(10)	1·37 (2)	C(44)–C(37)	1·53 (2)
C(10)–C(11)	1·37 (2)	Mean aromatic C=C	1·39 (3)

* Interatomic distance across $RhCl_2Rh$ bridge.

Table 3. *Bond angles* (°)

Standard deviations in parentheses.

Rh(1)–Cl(1) –Rh(2)	81·8 (2)		
Rh(1)–Cl(2) –Rh(2)	81·9 (2)		
Cl(1) –Rh(1)–Cl(2)	82·9 (2)	P(2)—O(4)—C(19)	125·4 (1·0)
Cl(1) –Rh(1)–P(1)	91·9 (2)	P(2)—O(5)—C(25)	123·7 (1·0)
Cl(2) –Rh(1)–P(2)	94·0 (2)	P(2)—O(6)—C(31)	125·8 (9)
Cl(1) –Rh(2)–Cl(2)	83·7 (2)		
P(1)—Rh(1)–P(2)	91·3 (2)	C(37)–C(38)–C(39)	123·6 (1·6)
		C(38)–C(39)–C(40)	113·5 (1·8)
Rh(1)–P(1)–O(1)	121·1 (5)	C(39)–C(40)–C(41)	113·2 (1·7)
Rh(1)–P(1)–O(2)	117·4 (5)	C(40)–C(41)–C(42)	122·3 (1·7)
Rh(1)–P(1)–O(3)	116·0 (5)	C(41)–C(42)–C(43)	123·7 (1·6)
Rh(1)–P(2)–O(4)	121·2 (5)	C(42)–C(43)–C(44)	112·4 (1·5)
Rh(1)–P(2)–O(5)	121·4 (5)	C(43)–C(44)–C(37)	113·1 (1·5)
Rh(1)–P(2)–O(6)	112·1 (5)	C(44)–C(37)–C(38)	122·2 (1·6)
P(1)–O(1)–C(1)	124·4 (1·0)	Mean O–P–O	99·5 (6)
P(1)–O(2)–C(7)	125·2 (1·0)	Mean O–C–C	117·4 (1·6)
P(1)–O(3)–C(13)	125·4 (1·0)	Mean C–C–C (benzene)	119·5 (2·0)
Rh(1)Cl(1)Cl(2)/Rh(2)Cl(1)Cl(2) interplanar angle			122·6 (2)

reflexions) were excluded according to the suggestion of Dunning & Vand (1969). The final positional and thermal parameters are listed in Table 1.

Interatomic distances and bond angles were calculated (Fig. 1) with the aid of the crystallographic program *ORFFE* of Busing, Martin & Levy (1964). These values are summarized in Tables 2 and 3. Observed and calculated structure factors are listed in Table 4.

Discussion

The atomic numbering and the molecular geometry are illustrated in Figs. 1 and 2. Fig. 1 shows a view of the molecule perpendicular to the (221) crystal plane, while the molecular geometry can be seen from the stereoscopic diagram in Fig. 2. The principal bonding parameters of the structure are given in Fig. 3.

Table 4. *Observed and calculated structure factors*

The columns are l, $10|F_{obs}|$, and $10F_{calc}$.

Table 4 (*cont.*)

Table 5. *Comparison of the molecular parameters associated with the* $RhCl_2Rh$ *bridge in* $Rh_2(CO)_4Cl_2$ *and* $Rh_2[P(OC_6H_5)_3]_2(C_8H_{12})Cl_2$

Interatomic distance	Bond angle	$Rh_2(CO)_4Cl_2$	$Rh_2[P(OC_6H_5)_3]_2(C_8H_{12})Cl_2$
Rh–Cl		2·38 Å	2·39 Å
Rh···Rh		3·12	3·14
	Cl(1)Rh(1)Rh(2)	85·0°	82·9°
	Cl(1)Rh(2)Cl(2)	85·0	83·7
	P(1)Rh(1)P(2)	—	91·3
	C–Rh–C	91·0	—
	Rh(1)Cl(1)Cl(2)/ Rh(2)Cl(1)Cl(2) interplanar angle	124·0	122·6

A detailed examination of the interatomic parameters shows two points of interest. Firstly, the $RhCl_2Rh$-bridge atoms are not coplanar. Table 5 shows a comparison of the bonding parameters associated with the folded $RhCl_2Rh$ bridge in the two species $Rh_2(CO)_4Cl_2$ and $Rh_2[P(OC_6H_5)_3]_2(C_8H_{12})Cl_2$. The intersecting angles of the two planes defined by the atoms Rh(1)Cl(1)Cl(2) and Rh(2)Cl(1)Cl(2) are almost equal in both molecules. This agreement between the interatomic distances and bond angles listed in Table 5 leads to the conclusion that the bridge geometry is essentially identical in the two molecules.

Secondly, whereas Dahl *et al.* observed an intermolecular Rh–Rh distance of 3·31 Å for $Rh_2(CO)_4Cl_2$ which led to their postulation of octahedral hybridization for the metal atoms, the closest approach of two Rh atoms in neighbouring molecules of the species $Rh_2[P(OC_6H_5)_3]_2(C_8H_{12})Cl_2$ is found to be 6·4 Å. This result precludes the necessity of an intermolecular metal–metal bond in inducing the folded conformation.

The equation of the best plane through Rh(2) and its four ligands, *viz.* Cl(1), Cl(2), P(1) and P(2), is

$$0{\cdot}5940X+0{\cdot}6717Y+0{\cdot}4427Z-12{\cdot}4198=0^*.$$

If it is assumed that the bonding of the metal to the cyclo-octadiene ring is directed towards the centre of the double bond, the best plane through Rh(1) and its 4 ligands, *viz.* Cl(1), Cl(2), the centre of C(37)=C(38) and the centre of C(41)=C(42), is given by the equation

$$0{\cdot}3281X-0{\cdot}1221Y+0{\cdot}9367Z-14{\cdot}3432=0\,.$$

The perpendicular distances from the atoms or ligands defined above to the corresponding planes are given in Table 6. In both cases the 5 sets of positional coordinates deviate from the respective planes by less than 0·1 Å. It thus appears that the arrangement of the ligands around the two Rh atoms of

$$Rh_2[P(OC_6H_5)_3]_2(C_8H_{12})Cl_2$$

must be seen as square planar coordination.

Table 6. *Perpendicular distances (σ) between the atoms or groups involved in the square-planar arrangement around the two* Rh *atoms and the best plane through each set of atoms*

	σ		σ
Rh(1)	0·002 Å	Rh(2)	−0·014 Å
Cl(1)	−0·054	Cl(1)	0·080
Cl(2)	0·052	Cl(2)	−0·075
P(1)	0·055	Centre of C(37)C(38)	−0·084
P(2)	−0·055	Centre of C(41)C(42)	0·093

The unusually long C=C bond distance of 1·42 Å in the cyclo-octadiene ring is a direct result of the $\sigma-\pi$ bonding with the Rh atom (Ibers & Snyder, 1962). The mean Rh–P and O–P bond lengths of 2·142 (La Placa & Ibers, 1965) and 1·605 Å (Davies & Stanley, 1962) show consistency with literature values. The three phenyl rings on each of the two phosphite groups are arranged in a propeller-like manner (Fig. 2) with a mean aromatic C=C bond length of 1·39 ± 0·03 Å. The shortest intermolecular contact distance (3·56 Å) occurs between the carbon atoms (C(16) and C(42), the parent molecules of which are related by a glide plane. The closest approach of two rhodium atoms (6·4 Å) is observed between Rh(2) atoms in neighbouring molecules related by a centre of symmetry.

* *X*, *Y* and *Z* are the orthogonalized coordinates parallel to *a*, *b* and *c**.

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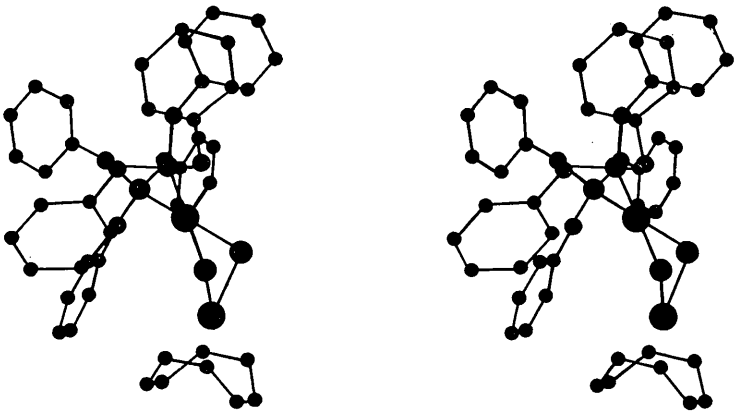

Fig. 2. Stereoscopic pair showing the molecular geometry of $Rh_2[P(OC_6H_5)_3]_2(C_8H_{12})Cl_2$.

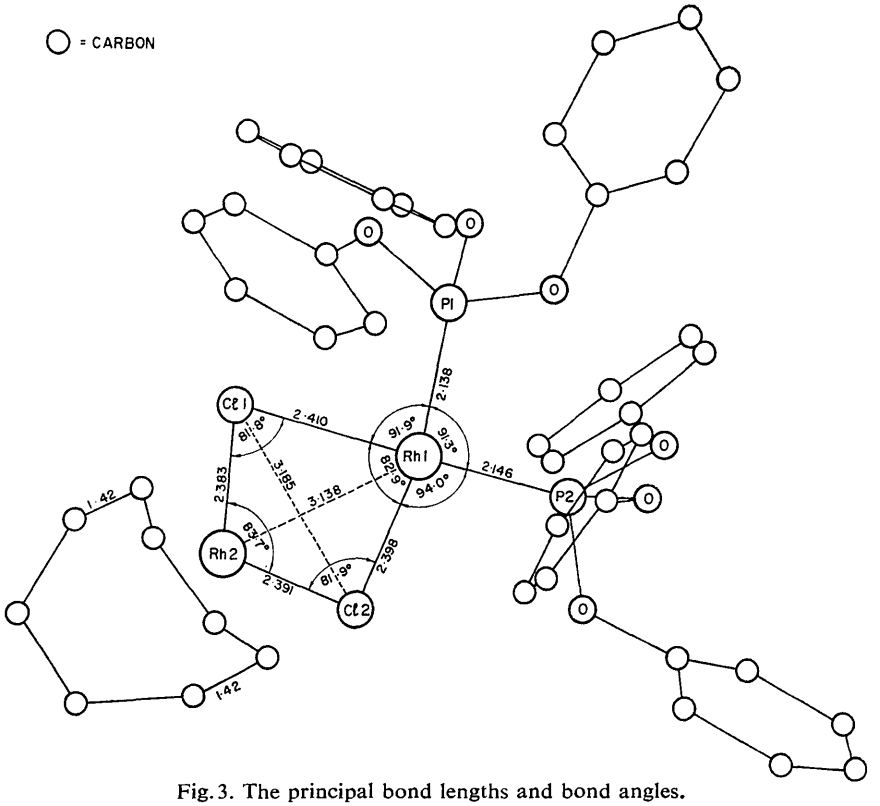

Fig. 3. The principal bond lengths and bond angles.

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The Crystal and Molecular Structure of Coriose

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The crystal structure of coriose, $C_7H_{14}O_7$, a natural 3-heptulose, has been determined by the use of a symbolic addition procedure. The space group is $P2_1$ with two molecules in the unit cell of dimensions $a=11{\cdot}33$, $b=7{\cdot}460$, $c=5{\cdot}205$ Å and $\beta=90{\cdot}75°$. The molecule is found in a novel α-furanose form with three *cis* hydroxyl groups. Owing to the twist of the five-membered ring, similar to that in adenosine monophosphate, three groups attached to the ring are quasi-equatorial and the other two are quasi-axial.

Introduction

Coriose, $C_7H_{14}O_7$, is a naturally occurring heptulose, extracted from *Coriaria japonica* A. Gray. The crystal of coriose is obtained solvent-free either from aqueous ethanol, methanol or water. The same crystal (m.p. = 169–171 °) is obtained also by evaporation of an aqueous solution to dryness at higher temperature, or by