

form assemblies  $W_3O_{13}$ , four of which assemblies share edges to form the unit  $W_{12}O_{40}$ , which has at its centre four oxygens disposed tetrahedrally and defining a cavity wherein the phosphorus is located. Whereas our description of the 12-molybdophosphate anion does differ only in detail, we note that the environment of each Mo atom is more appropriately described as a tetragonal pyramid, with an oxygen of the central  $PO_4^{3-}$  ion making a reasonably close approach on the open side of the pyramid, as is shown in Fig. 1. Thus the base of the pyramid is formed by two atoms each of type O(1) and O(2), with Mo–O bond lengths of 1.91 Å in each case. The Mo atom does not lie in this basal plane, but is displaced axially by 0.41 Å towards O(3). The Mo–O(3) bond length is 1.70 Å. By contrast the other axial approach, Mo–O(4), is 2.46 Å, and the atom O(4) is distinctly displaced from the Mo–O(3) axis. This geometry is very similar to that reported about the molybdenum atom in the structure of  $MoOPO_4$  (Kierkegaard & Westerland, 1964). This can formally be described in terms of  $MoO_6$  octahedra and  $PO_4$  tetrahedra, but again the authors noted that whereas the octahedra are considerably distorted, one neighbour oxygen is at a much greater distance than the remaining five, and exclusion of this one leaves a reasonably regular tetragonal pyramid about the molybdenum.

On this basis the anion may be described in terms of tetragonal pyramidal  $MoO_5$  units, each sharing two basal edges to form an assembly  $Mo_{12}O_{36}$ . The atoms Mo, O(1), O(2) form an almost spherical shell, with bonds Mo–O(3) projecting radially. The radius (to the

Mo atom) is 3.56 Å, so that the shell is of appropriate size to house a guest orthophosphate ion. The  $PO_4^{3-}$  ion is perfectly tetrahedral by space group requirement, and the P–O bond length is slightly short but within error of the values normally observed, 1.51–1.55 Å (*International Tables for X-ray Crystallography*, 1962). The orientation of the orthophosphate ion within the cage is such as to minimize repulsive interactions between atom O(4) and the oxygen atoms of the shell [the shortest contact O(4)···O(2) is 2.63 (2) Å]. The 12-molybdophosphate ion is thus described as a clathrate, and it may well be that this is the essential basis of the formation of the heteropolyacids.

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## Tri- $\mu$ -chloro-hexakis(dimethylphenylphosphine)diruthenium(II) Hexafluorophosphate

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**Abstract.**  $[Ru_2Cl_3(PMe_2Ph)_6]PF_6$ ,  $Ru_2Cl_3P_7F_6C_{48}H_{66}$ ,  $M = 1282$ . Monoclinic,  $P2_1/c$ ,  $a = 14.43$  (1),  $b = 16.41$  (1),  $c = 23.86$  (2) Å,  $\beta = 97.5$  (1)°,  $V = 5601$  Å<sup>3</sup>,  $D_m = 1.55$  (1),  $D_c = 1.53$  g cm<sup>-3</sup>,  $Z = 4$ ,  $\mu = 9.25$  cm<sup>-1</sup>.  $R = 0.069$  for 4983 observed data; two Ru, seven P and three Cl atoms anisotropic. The Ru atoms are approximately octahedrally coordinated: Ru···Ru = 3.39, Ru–Cl range from 2.46 to 2.52, Ru–P from 2.28 to 2.30 Å; average Ru–Cl–Ru = 86°.

**Introduction.** During an investigation of the reactivity of cationic hydrazine complexes of Ru (Hough & Singleton, 1972), it was found that addition of the

appropriate stoichiometric amount of  $PMe_2Ph$  to  $[CODRuH(NH_2NMe_2)_3]PF_6$  under nitrogen yielded either  $[CODRuH(PMe_2Ph)_3]PF_6$  or  $[RuH(PMe_2Ph)_5]PF_6$ . Reaction of  $[CODRuH(NH_2NMe_2)_3]PF_6$  with three moles of  $PMe_2Ph$  per Ru in acetone–ethanol solvent in the presence of air gave the unusual triply bridged hydroxo salt  $[Ru_2(OH)_3(PMe_2Ph)_6]PF_6$ . When the above reaction was done in a chloroform–ethanol mixture a different compound formed. It was isolated as a  $PF_6$  salt and chemical and spectroscopic studies suggested that it was  $[Ru_2Cl_3(PMe_2Ph)_6]PF_6$  (Ashworth & Singleton, 1975; Chatt & Hayter, 1961; Chatt, Shaw &

Field, 1964; Head & Nixon, 1975). A structure determination was undertaken to confirm the chemical deductions and to compare the structure with that of the trihydroxo analogue (Ashworth, Nolte & Singleton, 1975). Crystals of the chloro compound, supplied by Mr T. V. Ashworth and Dr E. Singleton, were well formed canary-yellow parallelepipeds.

Data were collected on a Philips four-circle diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda=0.7107$  Å) for  $\theta$  between 3 and 22°. The  $\omega$ -2 $\theta$  scan technique was used; the scan width was 0.9°, the scan time 30 s, and the background was counted for 30 s. Of the 7146 reflexions measured, 4983 were classed as observed,  $I > 1.65\sigma(I)$ . Three reflexions were used as standards and remeasured after every 60 reflexions; no crystal decomposition was detected. The intensities were corrected for Lorentz and polarization effects only. The two Ru atoms were located from a temperature-sharpened Patterson map and the remaining atoms were found from subsequent Fourier maps. The structure was refined by block-diagonal least squares with the two Ru, three Cl and seven P atoms anisotropic and all C and F atoms isotropic. Weighting was proportional to  $1/F_o$  for  $F_o > 96$  and to  $F_o$  for  $F_o < 96$  with a proportionality constant that gave a weight = 1 for  $F_o = 96$ . Scattering factors for neutral atoms were used (*International Tables for X-ray Crystallography*, 1962); that of Ru was corrected for anomalous dispersion. The refinement converged with  $R=0.059$  for the 4983 observed data.\* A final difference map was featureless except for peaks of about  $1e \text{ \AA}^{-3}$  near the positions of the F atoms in the anion. Final positional and thermal parameters are given in Table 1, bond lengths and angles in Table 2.

**Discussion.** The two Ru atoms in the cation have distorted octahedral coordination and are linked by three bridging Cl atoms (Figs. 1 and 2). The Ru...Ru separation is 3.39 Å. Ru-Cl range in length from 2.46 to 2.52 Å; the Ru-Cl-Ru angles are: Cl(1) 87, Cl(2) 86, Cl(3) 85°. The bond lengths and angles in the Ru<sub>2</sub>Cl<sub>3</sub>P<sub>6</sub> framework are similar to those observed in related compounds, especially [Ru<sub>2</sub>Cl<sub>3</sub>(PEt<sub>2</sub>Ph)<sub>6</sub>]<sup>+</sup> (Table 3). Similar M-P and M-Cl lengths have also been found in the Ir compound [Ir<sub>2</sub>Cl(SPh)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>H<sub>2</sub>]<sup>+</sup> (Roberts, Ferguson & Senoff, 1975). The mean P-C length is 1.85 ( $\pm 0.03$ ) Å. The C-C lengths in the phenyl rings lie between 1.35 and 1.45 Å, with a mean of 1.40 Å. The angles about the P atom in each of the phosphine ligands show the same distortion: one Ru-P-CH<sub>3</sub> angle is close to 122° while the other is far smaller, about 114°, and the Ru-P-C(phenyl) is about 117°. The C-P-C angles lie between 97 and 102°, mean 100°.

Table 1. *Atomic coordinates and thermal parameters*

Estimated standard deviations in the last significant figure are shown in parentheses.

(a) Fractional atomic coordinates and isotropic thermal parameters

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
Ru(1)	0.18960 (6)	0.11550 (6)	0.23810 (4)	
Ru(2)	0.33030 (6)	0.20210 (6)	0.34700 (4)	
P(1)	0.0308 (2)	0.1348 (2)	0.2298 (1)	
P(2)	0.1891 (2)	-0.0218 (2)	0.2246 (1)	
P(3)	0.2000 (2)	0.1462 (2)	0.1453 (1)	
P(4)	0.2645 (2)	0.2900 (2)	0.4047 (1)	
P(5)	0.4159 (2)	0.1264 (2)	0.4154 (1)	
P(6)	0.4538 (2)	0.2870 (2)	0.3360 (1)	
P(7)	0.7439 (3)	0.1042 (3)	0.0162 (2)	
Cl(1)	0.1991 (2)	0.1060 (2)	0.3417 (1)	
Cl(2)	0.2259 (2)	0.2602 (2)	0.2647 (1)	
Cl(3)	0.3613 (2)	0.1094 (2)	0.2671 (1)	
F(1)	0.8320 (8)	0.1583 (8)	0.0277 (5)	9.1 (3)
F(2)	0.6559 (11)	0.0491 (10)	0.0068 (7)	12.7 (4)
F(3)	0.8045 (9)	0.0247 (8)	0.0241 (5)	9.3 (3)
F(4)	0.6790 (9)	0.1801 (8)	0.0087 (5)	9.9 (3)
F(5)	0.7525 (8)	0.1011 (7)	-0.0495 (5)	8.1 (3)
F(6)	0.7360 (7)	0.1078 (7)	0.0822 (4)	7.1 (2)
C(1.1)	-0.0339 (8)	0.0735 (8)	0.2752 (5)	3.1 (2)
C(1.2)	-0.0225 (9)	0.0876 (8)	0.3333 (5)	3.4 (3)
C(1.3)	-0.0648 (10)	0.0370 (9)	0.3703 (6)	4.8 (3)
C(1.4)	-0.1218 (11)	-0.0292 (10)	0.3479 (6)	5.3 (3)
C(1.5)	-0.1362 (11)	-0.0411 (10)	0.2906 (7)	5.6 (4)
C(1.6)	-0.0935 (9)	0.0105 (8)	0.2538 (5)	3.7 (3)
C(1.7)	-0.0013 (10)	0.2386 (9)	0.2512 (6)	4.1 (3)
C(1.8)	-0.0466 (10)	0.1257 (9)	0.1602 (6)	4.5 (3)
C(2.1)	0.1981 (9)	-0.0854 (8)	0.2889 (5)	3.5 (3)
C(2.2)	0.2738 (12)	-0.1345 (11)	0.3042 (7)	6.3 (4)
C(2.3)	0.2744 (15)	-0.1866 (13)	0.3528 (9)	8.3 (5)
C(2.4)	0.1969 (12)	-0.1880 (11)	0.3823 (8)	6.7 (4)
C(2.5)	0.1240 (11)	-0.1376 (10)	0.3667 (7)	5.5 (4)
C(2.6)	0.1251 (9)	-0.0869 (8)	0.3200 (7)	4.0 (3)
C(2.7)	0.2878 (10)	-0.0588 (9)	0.1900 (6)	4.4 (3)
C(2.8)	0.0909 (10)	-0.0739 (9)	0.1819 (6)	4.3 (3)
C(3.1)	0.3205 (9)	0.1562 (8)	0.1288 (6)	3.8 (3)
C(3.2)	0.3629 (9)	0.0926 (8)	0.1025 (6)	3.9 (3)
C(3.3)	0.4565 (10)	0.1020 (10)	0.0904 (6)	5.2 (3)
C(3.4)	0.5046 (10)	0.1723 (9)	0.1034 (6)	5.1 (3)
C(3.5)	0.4609 (11)	0.2387 (10)	0.1283 (7)	5.8 (4)
C(3.6)	0.3680 (10)	0.2291 (9)	0.1414 (6)	4.6 (3)
C(3.7)	0.1459 (10)	0.0842 (9)	0.0842 (6)	4.3 (3)
C(3.8)	0.1523 (10)	0.2487 (9)	0.1228 (6)	4.5 (3)
C(4.1)	0.1512 (9)	0.2614 (8)	0.4276 (5)	3.4 (3)
C(4.2)	0.1460 (9)	0.1893 (8)	0.4569 (6)	4.0 (3)
C(4.3)	0.0636 (10)	0.1668 (9)	0.4801 (6)	4.6 (3)
C(4.4)	-0.0126 (11)	0.2202 (10)	0.4733 (6)	5.3 (4)
C(4.5)	-0.0096 (12)	0.2908 (12)	0.4436 (7)	6.7 (4)
C(4.6)	0.0744 (11)	0.3136 (10)	0.4188 (7)	5.3 (3)
C(4.7)	0.2375 (10)	0.3896 (9)	0.3719 (6)	4.6 (3)
C(4.8)	0.3247 (10)	0.3200 (9)	0.4756 (6)	4.8 (3)
C(5.1)	0.3549 (9)	0.0707 (8)	0.4673 (5)	3.5 (3)
C(5.2)	0.3592 (10)	0.1022 (9)	0.5229 (6)	4.4 (3)
C(5.3)	0.3149 (10)	0.0561 (9)	0.5630 (6)	4.8 (3)
C(5.4)	0.2668 (11)	-0.0138 (10)	0.5476 (6)	5.3 (3)
C(5.5)	0.2602 (11)	-0.0425 (10)	0.4924 (6)	5.1 (3)
C(5.6)	0.3056 (10)	0.0003 (9)	0.4509 (6)	4.8 (3)
C(5.7)	0.5162 (10)	0.1703 (9)	0.4637 (6)	4.6 (3)
C(5.8)	0.4759 (11)	0.0410 (10)	0.3862 (6)	5.2 (3)
C(6.1)	0.5651 (9)	0.2387 (8)	0.3222 (6)	3.8 (3)
C(6.2)	0.5670 (10)	0.1959 (9)	0.2723 (6)	4.6 (3)
C(6.3)	0.6488 (11)	0.1574 (10)	0.2591 (7)	5.9 (4)
C(6.4)	0.7303 (12)	0.1651 (11)	0.3003 (7)	6.1 (4)
C(6.5)	0.7300 (11)	0.2065 (10)	0.3480 (7)	5.8 (4)
C(6.6)	0.6467 (9)	0.2458 (9)	0.3626 (6)	4.2 (3)
C(6.7)	0.4964 (10)	0.3650 (9)	0.3889 (6)	4.6 (3)
C(6.8)	0.4322 (10)	0.3536 (9)	0.2725 (6)	4.3 (3)

\* A table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31587 (28 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1 (cont.)

(b) Anisotropic thermal parameters ( $\times 10^5$ ). The expression for the thermal parameters is

$$\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})].$$

	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Ru(1)	277 (5)	178 (4)	93 (2)	26 (7)	46 (4)	-15 (5)
Ru(2)	253 (5)	232 (4)	96 (2)	39 (8)	26 (4)	13 (5)
P(1)	272 (16)	226 (14)	132 (7)	40 (24)	3 (16)	-45 (15)
P(2)	382 (18)	200 (13)	133 (7)	-14 (26)	97 (18)	-42 (15)
P(3)	393 (19)	269 (14)	89 (6)	-9 (26)	77 (17)	-28 (15)
P(4)	365 (18)	297 (15)	105 (6)	121 (28)	-1 (17)	-72 (16)
P(5)	293 (17)	400 (17)	129 (7)	76 (29)	27 (17)	126 (18)
P(6)	300 (17)	291 (15)	143 (7)	-91 (27)	29 (17)	0 (17)
P(7)	680 (26)	363 (18)	156 (8)	31 (36)	-15 (23)	-102 (20)
Cl(1)	291 (15)	231 (12)	96 (5)	-33 (22)	63 (14)	15 (14)
Cl(2)	342 (16)	180 (12)	107 (6)	34 (22)	-17 (15)	6 (13)
Cl(3)	272 (15)	270 (13)	124 (6)	88 (24)	76 (15)	7 (15)

The bond lengths and angles in the PF<sub>6</sub><sup>-</sup> anion are normal, P-F lengths between 1.55 and 1.59 Å, F-P-F angles between 88 and 92°.

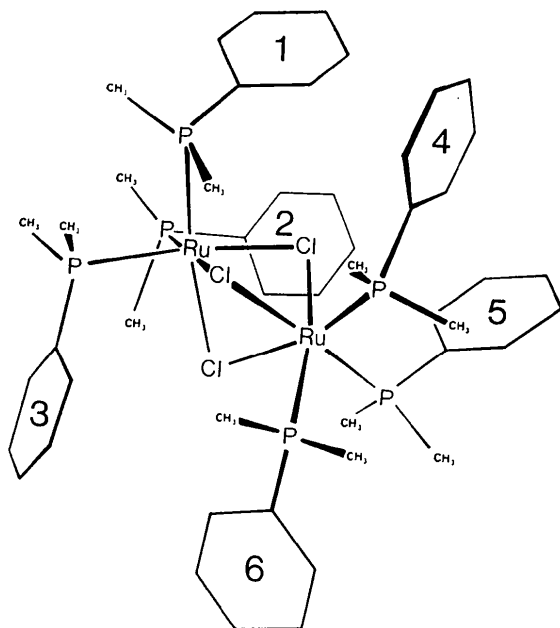


Fig. 1. A projection of the cation down  $y$ . Phenyl rings 1 to 6 are bonded to atoms P(1) to P(6) respectively.

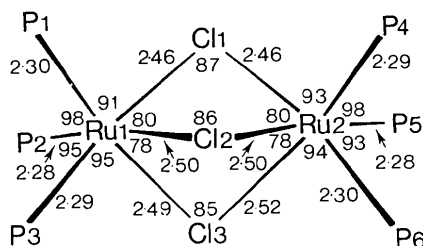


Fig. 2. The geometry of the Ru<sub>2</sub>Cl<sub>3</sub>P<sub>6</sub> unit. Bond lengths and some bond angles are shown.

Table 2. Bond lengths and angles

(a) Bond lengths (Å) ( $\pm 0.01$  Å)

Ru(1)-Cl(1)	2.46	Ru(1)-P(1)	2.30
Ru(1)-Cl(2)	2.50	Ru(1)-P(2)	2.28
Ru(1)-Cl(3)	2.49	Ru(1)-P(3)	2.29
Ru(2)-Cl(1)	2.46	Ru(2)-P(4)	2.29
Ru(2)-Cl(2)	2.50	Ru(2)-P(5)	2.28
Ru(2)-Cl(3)	2.52	Ru(2)-P(6)	2.30
P(1)-C(1.1)	1.82	P(4)-C(4.1)	1.85
P(1)-C(1.7)	1.85	P(4)-C(4.7)	1.83
P(1)-C(1.8)	1.88	P(4)-C(4.8)	1.86
P(2)-C(2.1)	1.85	P(5)-C(5.1)	1.85
P(2)-C(2.7)	1.84	P(5)-C(5.7)	1.87
P(2)-C(2.8)	1.84	P(5)-C(5.8)	1.83
P(3)-C(3.1)	1.84	P(6)-C(6.1)	1.86
P(3)-C(3.7)	1.86	P(6)-C(6.7)	1.85
P(3)-C(3.8)	1.87	P(6)-C(6.8)	1.86

(b) Bond angles (°) ( $\pm 1^\circ$ )

Cl(1)-Ru(1)-P(1)	91	Cl(1)-Ru(2)-P(4)	93
Cl(1)-Ru(1)-P(2)	94	Cl(1)-Ru(2)-P(5)	92
Cl(1)-Ru(1)-P(3)	169	Cl(1)-Ru(2)-P(6)	170
Cl(2)-Ru(1)-P(1)	94	Cl(2)-Ru(2)-P(4)	89
Cl(2)-Ru(1)-P(2)	167	Cl(2)-Ru(2)-P(5)	169
Cl(2)-Ru(1)-P(3)	90	Cl(2)-Ru(2)-P(6)	94
Cl(3)-Ru(1)-P(1)	168	Cl(3)-Ru(2)-P(4)	165
Cl(3)-Ru(1)-P(2)	89	Cl(3)-Ru(2)-P(5)	95
Cl(3)-Ru(1)-P(3)	95	Cl(3)-Ru(2)-P(6)	94
Cl(1)-Ru(1)-Cl(2)	80	Cl(1)-Ru(2)-Cl(2)	80
Cl(1)-Ru(1)-Cl(3)	78	Cl(1)-Ru(2)-Cl(3)	78
Cl(2)-Ru(1)-Cl(3)	78	Cl(2)-Ru(2)-Cl(3)	78
P(1)-Ru(1)-P(2)	98	P(4)-Ru(2)-P(5)	98
P(1)-Ru(1)-P(3)	94	P(4)-Ru(2)-P(6)	94
P(2)-Ru(1)-P(3)	95	P(5)-Ru(2)-P(6)	93
Ru(1)-P(1)-C(1.1)	117	C(1.1)-P(1)-C(1.7)	100
Ru(1)-P(1)-C(1.7)	113	C(1.1)-P(1)-C(1.8)	101
Ru(1)-P(1)-C(1.8)	122	C(1.7)-P(1)-C(1.8)	100
Ru(1)-P(2)-C(2.1)	116	C(2.1)-P(2)-C(2.7)	102
Ru(1)-P(2)-C(2.7)	114	C(2.1)-P(2)-C(2.8)	99
Ru(1)-P(2)-C(2.8)	122	C(2.7)-P(2)-C(2.8)	101
Ru(1)-P(3)-C(3.1)	114	C(3.1)-P(3)-C(3.7)	101
Ru(1)-P(3)-C(3.7)	124	C(3.1)-P(3)-C(3.8)	100
Ru(1)-P(3)-C(3.8)	114	C(3.7)-P(3)-C(3.8)	99
Ru(2)-P(4)-C(4.1)	118	C(4.1)-P(4)-C(4.7)	102
Ru(2)-P(4)-C(4.7)	113	C(4.1)-P(4)-C(4.8)	97
Ru(2)-P(4)-C(4.8)	122	C(4.7)-P(4)-C(4.8)	102
Ru(2)-P(5)-C(5.1)	119	C(5.1)-P(5)-C(5.7)	100
Ru(2)-P(5)-C(5.7)	122	C(5.1)-P(5)-C(5.8)	100
Ru(2)-P(5)-C(5.8)	112	C(5.7)-P(5)-C(5.8)	99
Ru(2)-P(6)-C(6.1)	117	C(6.1)-P(6)-C(6.7)	101
Ru(2)-P(6)-C(6.7)	122	C(6.1)-P(6)-C(6.8)	99
Ru(2)-P(6)-C(6.8)	113	C(6.7)-P(6)-C(6.8)	99

Table 3. Parameters in related compounds

Compound	Ru···Ru (Å)	Ru-Cl (Å) (bridge)	Ru-P (Å) (terminal)	P-Ru-P (°)	Ru-Cl-Ru (°)
[Ru <sub>2</sub> Cl <sub>3</sub> (PEt <sub>2</sub> Ph) <sub>6</sub> ] <sup>+</sup>	3.44	2.46-2.50	2.31-2.32	95-98	87-88 (Raspin, 1969)
[Ru <sub>2</sub> Cl <sub>4</sub> (PEt <sub>2</sub> Ph) <sub>5</sub> ]	3.37	2.43-2.54	2.26-2.34	97-100	85-86 (Alcock & Raspin, 1968)
[Ru <sub>2</sub> Cl <sub>4</sub> (PPh <sub>3</sub> ) <sub>4</sub> CS]	3.35	2.45-2.58	2.26-2.36	99-103	83-86 (Fraser & Gould, 1974)
[Ru <sub>2</sub> Cl <sub>5</sub> (PBut <sub>3</sub> ) <sub>4</sub> ]	3.12	2.37-2.51	2.32-2.34	102	79-80 (Chioccola & Daly, 1968)
[Ru <sub>2</sub> Cl <sub>3</sub> (CO) <sub>5</sub> SnCl <sub>3</sub> ]	3.16	2.39-2.46	-	-	80-81 (Elder & Hall, 1970)
[Ru <sub>2</sub> (OH) <sub>3</sub> (PMe <sub>2</sub> Ph) <sub>6</sub> ] <sup>+</sup>	3.08	-	2.27-2.30	92-99	- (Ashworth, Nolte & Singleton, 1975)

The average volume per non-hydrogen atom is 21.2 Å<sup>3</sup>, distinctly larger than the usual value of 18-19 Å<sup>3</sup> (Laing, 1975). This low packing density appears to be characteristic of this class of dimeric bridged compound and is especially noticeable in [Ru<sub>2</sub>Cl<sub>5</sub>(PBut<sub>3</sub>)<sub>4</sub>] whose density is only 1.23 g cm<sup>-3</sup> compared with 1.35 g cm<sup>-3</sup> in [Ru<sub>2</sub>Cl<sub>4</sub>(PEt<sub>2</sub>Ph)<sub>5</sub>] and 1.55 g cm<sup>-3</sup> in the present case.

The differences in Ru···Ru distances, caused by changes both in oxidation state of the Ru atoms and in the ligands attached to them, have been discussed recently (Crozat & Watkins, 1972). It is evident that the Ru···Ru separation in the present case corresponds to a bond order of zero. However, by the same criterion, the tri-μ-hydroxo analogue would appear to have a Ru···Ru bond order between 0.5 and 1.0 as Ru···Ru of 2.96 Å was considered to have a bond order of 1.0. This conclusion seems anomalous because both the tri-μ-chloro and tri-μ-hydroxo cations formally have the same number of bonding orbitals and electrons in the RuX<sub>3</sub>Ru system.

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