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STRUCTURAL CHARACTERISATION OF HYDROXO-BRIDGED ARENE-RUTHENIUM AND -OSMIUM COMPLEXES: FURTHER REACTIONS OF HYDROXO-BRIDGED COMPLEXES

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Summary

Reaction of $[\{M(\eta\text{-}C_6H_6)Cl_2\}_2]$ with an excess of either aqueous NaOH or Na_2CO_3 followed by addition of $Na[BPh_4]$ gave two products, previously formulated as $[\eta\text{-}C_6H_6(OH)M(OH)_2M(H_2O)(\eta\text{-}C_6H_6)]BPh_4$ (II) and $[(\eta\text{-}C_6H_6)M(OH)_3M(\eta\text{-}C_6H_6)]BPh_4 \cdot Me_2CO$ (M = Ru (III), Os (IV)). X-ray structural analyses now reveal that the latter should be reformulated as the novel $[M_4(\eta\text{-}C_6H_6)_4(\mu_2\text{-}OH)_4(\mu_4\text{-}O)](BPh_4)_2 \cdot 2Me_2CO$ tetramers containing a tetrahedrally coordinated O^{2-} ion. In contrast, with substituted arenes the binuclear triple hydroxo-bridged cations of type III are formed as evidenced by the X-ray crystal structure determination of $[Ru_2(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)_2(OH)_3]Cl \cdot 3H_2O$ (V). Reaction of these various hydroxo-bridged complexes with HX (X = Cl, Br, I) gives either $[Ru_2(\eta\text{-}arene)_2X_3]^+$ and/or $[\{Ru(\eta\text{-}arene)X_2\}_2]$ whereas with CF_3CO_2H in the presence of arene′, the dications $[Ru(arene)(arene')]^{2+}$ are formed.

Results and discussion

Recently we reported that reaction of $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ with aqueous sodium carbonate (1/2 molar ratio) gave the unusual tetrameric cation $[\{Ru(\eta\text{-}C_6H_6)(OH)\}_4]^{4+}$ (I) [1], whereas treatment with an excess of sodium carbonate or hydroxide gave two products, formulated as the binuclear cations $[(\eta\text{-}C_6H_6)(OH)Ru(OH)_2Ru(H_2O)(\eta\text{-}C_6H_6)]^+$ (II) (major species) and $[(\eta\text{-}C_6H_6)Ru(OH)_3Ru(\eta\text{-}C_6H_6)]^+$ (III) [2]. Recrystallisation of II from acetone leads to irreversible, complete conversion to III (see eq. 1 in ref. 2). We now report the results of X-ray structural analyses on the "triple hydroxo-bridged" cation III, (and its osmium analogue IV), which reveal that they should be reformulated as the novel tetranuclear complexes $[M_4(\eta\text{-}C_6H_6)_4(\mu_2\text{-}OH)_4(\mu_4\text{-}O)](BPh_4)_2 \cdot 2Me_2CO$. The analyses indicate that these cations can be thought of as two binuclear $[M_2(\eta\text{-}C_6H_6)_2(\mu_2\text{-}OH)_2]^+$ units which share a common bridging oxygen vertex, (see Fig. 1

TABLE 1

SELECTED INTRAMOLECULAR DISTANCES AND ANGLES IN III (M = Ru) AND IV (M = Os) ATOMS X(1) TO X(4) REPRESENT THE CENTRES OF THE RINGS BONDED TO THE METAL ATOMS WITH THE SAME NUMBERS (Distances are given in Å and angles in degrees)

Compound III

Ru(1)–Ru(2)	3.001(4)	Ru(3)–Ru(4)	3.008(4)
Ru(1)–O(1)	2.113(20)	Ru(3)–O(3)	2.060(21)
Ru(1)–O(2)	2.047(21)	Ru(3)–O(4)	2.076(20)
Ru(1)–O(5)	2.114(19)	Ru(3)–O(5)	2.085(19)
Ru(1)–X(1)	1.68(3)	Ru(3)–X(3)	1.65(3)
Ru(1)–C(1)	2.20(4)	Ru(3)–C(13)	2.13(3)
Ru(1)–C(2)	2.23(4)	Ru(3)–C(14)	2.14(4)
Ru(1)–C(3)	2.29(3)	Ru(3)–C(15)	2.18(4)
Ru(1)–C(4)	2.22(3)	Ru(3)–C(16)	2.20(3)
Ru(1)–C(5)	2.29(4)	Ru(3)–C(17)	2.13(4)
Ru(1)–C(6)	2.13(4)	Ru(3)–C(18)	2.19(4)
Ru(2)–O(1)	2.118(20)	Ru(4)–O(3)	2.047(21)
Ru(2)–O(2)	2.109(21)	Ru(4)–O(4)	2.116(20)
Ru(2)–O(5)	2.137(19)	Ru(4)–O(5)	2.159(19)
Ru(2)–X(2)	1.64(3)	Ru(4)–X(4)	1.67(3)
Ru(2)–C(7)	2.19(3)	Ru(4)–C(19)	2.19(3)
Ru(2)–C(8)	2.18(4)	Ru(4)–C(20)	2.24(4)
Ru(2)–C(9)	2.19(4)	Ru(4)–C(21)	2.20(4)
Ru(2)–C(10)	2.15(4)	Ru(4)–C(22)	2.19(4)
Ru(2)–C(11)	2.15(4)	Ru(4)–C(23)	2.16(3)
Ru(2)–C(12)	2.18(4)	Ru(4)–C(24)	2.24(3)

O(1)–Ru(1)–O(2)	78.1(8)	O(5)–Ru(3)–X(3)	136.0(13)
O(1)–Ru(1)–O(5)	74.7(7)	O(3)–Ru(4)–O(4)	76.8(8)
O(1)–Ru(1)–X(1)	132.9(13)	O(3)–Ru(4)–O(5)	71.3(8)
O(2)–Ru(1)–O(5)	73.3(8)	O(3)–Ru(4)–X(4)	134.9(13)
O(2)–Ru(1)–X(1)	135.5(13)	O(4)–Ru(4)–O(5)	71.3(7)
O(5)–Ru(1)–X(1)	136.9(13)	O(4)–Ru(4)–X(4)	132.6(13)
O(1)–Ru(2)–O(2)	76.7(8)	O(5)–Ru(4)–X(4)	142.3(13)
O(1)–Ru(2)–O(5)	74.1(7)	Ru(1)–O(1)–Ru(2)	90.4(8)
O(1)–Ru(2)–X(2)	132.8(13)	Ru(1)–O(2)–Ru(2)	92.5(8)
O(2)–Ru(2)–O(5)	71.6(8)	Ru(3)–O(3)–Ru(4)	94.2(9)
O(2)–Ru(2)–X(2)	136.4(13)	Ru(3)–O(4)–Ru(4)	91.7(8)
O(5)–Ru(2)–X(2)	138.6(13)	Ru(1)–O(5)–Ru(2)	89.8(7)
O(3)–Ru(3)–O(4)	77.4(8)	Ru(1)–O(5)–Ru(3)	124.0(9)
O(3)–Ru(3)–O(5)	72.5(8)	Ru(1)–O(5)–Ru(4)	117.2(9)
O(3)–Ru(3)–X(3)	136.8(13)	Ru(2)–O(5)–Ru(3)	120.8(9)
O(4)–Ru(3)–O(5)	73.5(8)	Ru(2)–O(5)–Ru(4)	117.7(9)
O(4)–Ru(3)–X(3)	134.1(13)	Ru(3)–O(5)–Ru(4)	90.2(7)

Compound IV

Os(1)–Os(2)	3.0768(25)	Os(3)–Os(4)	3.0777(23)
Os(1)–O(1)	2.078(21)	Os(3)–O(3)	2.147(23)
Os(1)–O(2)	2.082(23)	Os(3)–O(4)	2.080(25)
Os(1)–O(5)	2.156(23)	Os(3)–O(5)	2.130(23)
Os(1)–X(1)	1.627(25)	Os(3)–X(3)	1.654(22)
Os(1)–C(1)	2.180(25)	Os(3)–C(13)	2.155(22)
Os(1)–C(2)	2.199(25)	Os(3)–C(14)	2.182(22)
Os(1)–C(3)	2.177(25)	Os(3)–C(15)	2.191(22)
Os(1)–C(4)	2.023(25)	Os(3)–C(16)	2.172(22)
Os(1)–C(5)	2.118(25)	Os(3)–C(17)	2.145(22)

TABLE 1 (continued)

Compound IV			
Os(1)–C(6)	2.140(25)	Os(3)–C(18)	2.136(22)
Os(2)–O(1)	2.075(21)	Os(4)–O(3)	2.055(23)
Os(2)–O(2)	2.118(23)	Os(4)–O(4)	2.071(22)
Os(2)–O(5)	2.163(23)	Os(4)–O(5)	2.132(23)
Os(2)–X(2)	1.635(24)	Os(4)–X(4)	1.613(23)
Os(2)–C(7)	2.151(24)	Os(4)–C(19)	2.101(23)
Os(2)–C(8)	2.133(24)	Os(4)–C(20)	2.092(23)
Os(2)–C(9)	2.131(24)	Os(4)–C(21)	2.124(23)
Os(2)–C(10)	2.146(24)	Os(4)–C(22)	2.163(23)
Os(2)–C(11)	2.165(24)	Os(4)–C(23)	2.172(23)
Os(2)–C(12)	2.167(24)	Os(4)–C(24)	2.141(23)
O(1)–Os(1)–O(2)	75.1(8)	O(5)–Os(3)–X(3)	140.6(10)
O(1)–Os(1)–O(5)	71.5(8)	O(3)–Os(4)–O(4)	75.9(9)
O(1)–Os(1)–X(1)	137.3(11)	O(3)–Os(4)–O(5)	73.5(9)
O(2)–Os(1)–O(5)	72.1(9)	O(3)–Os(4)–X(4)	132.0(10)
O(2)–Os(1)–X(1)	135.0(11)	O(4)–Os(4)–O(5)	69.3(9)
O(5)–Os(1)–X(1)	137.6(11)	O(4)–Os(4)–X(4)	136.9(10)
O(1)–Os(2)–O(2)	74.5(8)	O(5)–Os(4)–X(4)	141.2(10)
O(1)–Os(2)–O(5)	71.4(8)	Os(1)–O(1)–Os(2)	95.6(9)
O(1)–Os(2)–X(2)	135.0(10)	Os(1)–O(2)–Os(2)	94.2(9)
O(2)–Os(2)–O(5)	71.3(9)	Os(3)–O(3)–Os(4)	94.2(9)
O(2)–Os(2)–X(2)	135.7(10)	Os(3)–O(4)–Os(4)	95.7(9)
O(5)–Os(2)–X(2)	140.4(10)	Os(1)–O(5)–Os(2)	90.9(9)
O(3)–Os(3)–O(4)	73.7(9)	Os(1)–O(5)–Os(3)	120.6(10)
O(3)–Os(3)–O(5)	71.7(9)	Os(1)–O(5)–Os(4)	117.8(10)
O(3)–Os(3)–X(3)	135.6(10)	Os(2)–O(5)–Os(3)	118.6(10)
O(4)–Os(3)–O(5)	69.1(9)	Os(2)–O(5)–Os(4)	119.2(10)
O(4)–Os(3)–X(3)	136.5(10)	Os(3)–O(5)–Os(4)	92.5(9)

and Table 1 for selected intramolecular distances and angles). In both (isomorphous) compounds, the two M $\cdots$ M vectors across a triple bridge are orthogonal and other M $\cdots$ M distances are in the range 3.65–3.72 Å. The environment of the central oxygen atom is a flattened tetrahedron. Despite small distortions which may be related to hydrogen-bonded solvent, the cation is very close to having $\bar{4}$ (S_4) symmetry, centred on O(5). Coordinates for such idealised units are given in Table 2a, together with the averaged values of equivalent distances and angles from the structures (Table 2b) which were used to define the idealised unit. The difference between the M–O(5) and M–O(1) distances is probably not significant. The main significant difference between the two compounds is the difference in M $\cdots$ M along the bridge, which is 0.070 Å longer in the osmium compound IV. This difference is reflected in the angle at the bridging oxygen, (2.7° larger in IV), and the distance from the metal atoms to the ring centres (0.02 Å shorter in IV). Omitting the benzene rings, the cations have $\bar{4}2m(D_{2d})$ symmetry, but these are rotated by 9.5° from the orientations required by that symmetry. The presence of two acetone molecules was detected and these are both hydrogen-bonded to the hydroxo groups (O(3) and O(4)) of the same bridge with O $\cdots$ O distances of 2.88 and 2.84 Å

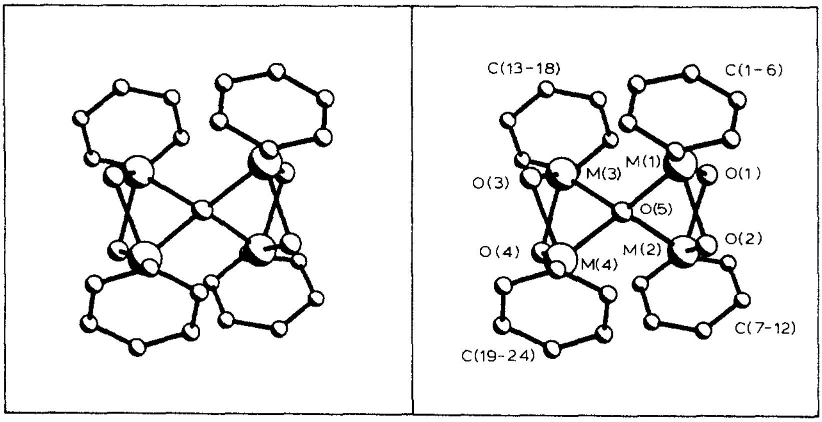


Fig. 1. The molecular structure of the cations $[M_4(\eta\text{-}C_6H_6)_4(OH)_4(O)]^{2+}$ (M = Ru, Os).

TABLE 2a

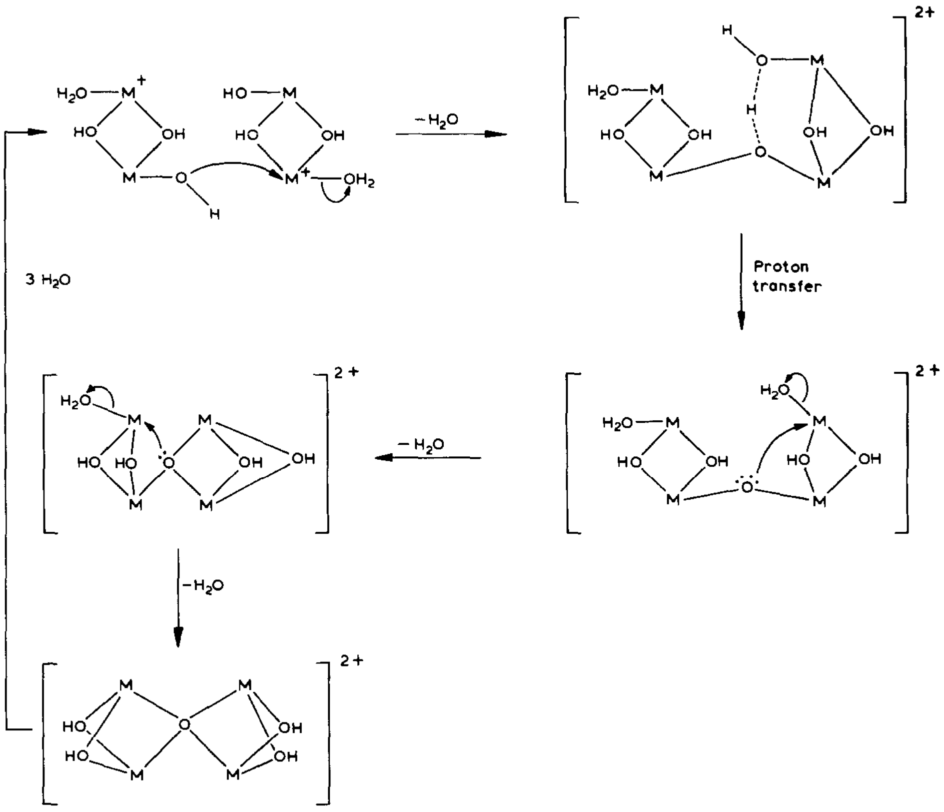
IDEALISED COORDINATES FOR A STRICTLY S_4 ($\bar{4}$) CATION IN III (M = Ru) AND IV (M = Os) (Coordinates are given in a cartesian reference frame with z as the unique axis. The relevant symmetry operators are: x, y, z; $\bar{x}, \bar{y}, z$; $\bar{y}, x, \bar{z}$; $y, \bar{x}, \bar{z}$. Approximate D_{2d} symmetry will further relate C(1) and C(4), C(2) and C(3), and C(5) and C(6). X represents a ring centre.)

Atoms	III			IV		
	x	y	z	x	y	z
O(5)	0.0	0.0	0.0	0.0	0.0	0.0
M(1,2,3,4)	1.502	0.0	1.500	1.539	0.0	1.497
O(1,2,3,4)	0.0	1.302	2.131	0.0	1.266	2.115
C(1,7,13,19)	3.161	−1.340	1.818	3.165	−1.336	1.842
C(2,8,14,20)	3.243	−0.837	0.520	3.260	−0.846	0.539
C(3,9,15,21)	3.243	0.542	0.305	3.266	0.530	0.310
C(4,10,16,22)	3.150	1.416	1.388	3.176	1.417	1.384
C(5,11,17,23)	3.062	0.913	2.686	3.081	0.927	2.687
C(6,12,18,24)	3.067	−0.465	2.901	3.076	−0.449	2.916
X(1,2,3,4)	3.154	0.040	1.603	3.171	0.036	1.613

TABLE 2b

DISTANCES AND ANGLES FOR IDEALISED CATION (with the e.s.d. of the mean in (), and the number of independent observations in []. Bridging and non-bridging groups are indicated by (b) and (n))

Atoms	Distance (Å)		Atoms	Angle (deg.)	
	III (M = Ru)	IV (M = Os)		III (M = Ru)	IV (M = Os)
M–M′ (b) [2]	3.005(4)	3.078(2)	M–O(5)–M′ (b) [2]	90.0(2)	91.7(8)
M–M′ (n) [4]	3.676(20)	3.697(19)	M–O(5)–M′ (n) [4]	119(3)	119.1(10)
M–O(5) [4]	2.12(3)	2.146(14)	O(5)–M–O(1) [8]	72.8(12)	71.2(13)
M–O(1) [8]	2.09(3)	2.09(3)	O(1)–M–O(1′) [4]	77.2(6)	74.8(8)
M–X [4]	1.659(14)	1.632(15)	O(5)–M–X [4]	138.5(24)	140.0(14)
M–C [24]	2.19(4)	2.15(4)	O(1)–M–X [8]	134.5(15)	135.5(15)
			M–O(1)–M′	92.2(13)	94.9(7)

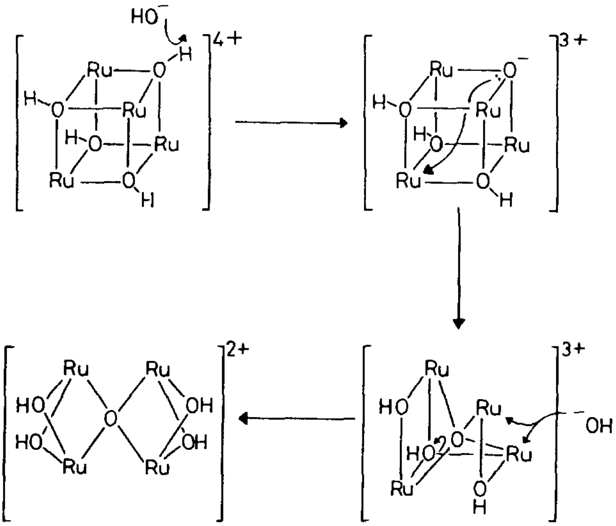


SCHEME 1. A possible mechanism for the formation of the $[M_4(\eta\text{-}C_6H_6)_4(OH)_4(O)]^{2+}$ dications (n.b. benzene rings omitted for clarity).

respectively. The two tetraphenylborate ions have the expected geometry with B–C distances ranging from 1.61 to 1.78 Å.

Only a few examples of tetrahedrally coordinated oxygen in discrete coordination complexes are known, notably in the beryllium compounds $Be_4O(O_2CR)_6$ and in some zinc complexes [3]. This appears to be the first example in transition metal chemistry, although a closely related complex with a trigonally coordinated oxygen is $[Rh_3(\eta\text{-}C_5Me_5)_3H_3(O)]\ PF_6 \cdot H_2O$ obtained from the reaction of $[Rh_2(\eta\text{-}C_5Me_5)_2(OH)_3]PF_6$ with hydrogen in isopropanol [4].

A possible mechanism of formation of $[M_4(\eta\text{-}C_6H_6)_4(\mu_2\text{-}OH)_4(\mu_4\text{-}O)]^{2+}$ from $[(\eta\text{-}C_6H_6)(OH)M(OH)_2M(H_2O)(\eta\text{-}C_6H_6)]^+$ is outlined in Scheme 1. This involves intermolecular displacement of an aqua ligand and subsequent proton transfer and loss of two coordinated water molecules. Interestingly, this dication can also be formed by reaction of $[\{Ru(\eta\text{-}C_6H_6)OH\}_4](SO_4)_2 \cdot 12H_2O$ with an excess of aqueous sodium hydroxide [1]. Although this may involve a rate determining cleavage step to give a binuclear unit, this appears unlikely since no $[(\eta\text{-}C_6H_6)OHRu(OH)_2\text{-}Ru(H_2O)(\eta\text{-}C_6H_6)]^+$ cation can be trapped out by addition of $NaBPh_4$. Therefore a more probable reaction pathway is shown in Scheme 2, namely deprotonation by hydroxide ion and subsequent rearrangement to $[Ru_4(\eta\text{-}C_6H_6)(OH)_4O]^{2+}$ without further structural disruption.



SCHEME 2. A mechanism for the formation of $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)]^{2+}$ from $[\{Ru(\eta\text{-}C_6H_6(OH)\}_4]^{4+}$ (n.b. benzene rings omitted for clarity).

Although the structures have now been unequivocally determined in the solid state, it is still conceivable that in solution, $[M_2(\eta\text{-}C_6H_6)_2(OH)_3]^+$ cation formation is favoured. In order to check this possibility the conductance of the crystals dissolved in dry nitromethane were measured over a concentration range. The linear $\Lambda_0 - \Lambda_e$ vs. $C_e^{1/2}$ plots of slope 630 (Ru), 395 (Os), are characteristic of those expected for 2 : 1 electrolytes [5]. Furthermore, the ^1H NMR spectra of these compounds were recorded in dry, freshly-distilled CD_3NO_2. Initially, only singlets at δ 5.56 (Ru), 6.08 ppm (Os), (previously attributed [2] to the $\eta\text{-}C_6H_6$ resonances in the $[M_2(\eta\text{-}C_6H_6)_2(OH)_3]^+$ cations) were observed. On addition of small amounts of water, a second signal, at δ 5.33 (Ru), 5.97 ppm (Os) (from $[\eta\text{-}C_6H_6(OH)M(OH)_2\text{-}M(H_2O)(\eta\text{-}C_6H_6)]^+$) grew at the expense of the initial signal. After a period of 24 h, the ^1H NMR spectra appeared identical to those previously reported [2] for the

TABLE 3

INTRAMOLECULAR DISTANCES AND ANGLES FOR V (X(1) and X(2) represent the ring centres for the rings bonded to Ru(1) and Ru(2) respectively)

Atoms	Distance (Å)	Atoms	Angle (deg.)
Ru(1)–Ru(2)	2.989(3)	OH–Ru(1)–X(1)	135.2(4)
Ru(1)–C(1)	2.163(15)	OH–Ru(1)–OH′	75.3(5)
Ru(1)–X(1)	1.625(9)	OH–Ru(2)–X(2)	135.7(4)
Ru(1)–OH	2.087(10)	OH–Ru(2)–OH′	74.4(5)
Ru(2)–C(4)	2.175(11)	Ru(1)–OH–Ru(2)	90.9(4)
Ru(2)–X(2)	1.666(10)		
Ru(2)–OH	2.109(10)		

Primed atoms are related to unprimed by rotation about the three-fold axis at 0,0,*z* initial products of the $[\{M(\eta\text{-}C_6H_6)Cl_2\}_2]$ NaOH reaction ie. two signals of relative intensity ca. 6/1 at δ 5.40; 5.56 ppm (Ru); δ 5.97; 6.08 ppm (Os) respectively. Hence, all this evidence strongly indicates that the tetrameric $[M_4(\eta\text{-}C_6H_6)_4(OH)_4(O)]^{2+}$ units are retained in solution, although facile conversion to $[(\eta\text{-}C_6H_6)(OH)M(OH)_2M(H_2O)(\eta\text{-}C_6H_6)]^+$ occurs on treatment with water.

In contrast, the complexes prepared from substituted arenes [2] appear to contain conventional triple hydroxo bridges, as demonstrated by X-ray structural analysis studies on $[Ru_2(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)_2(OH)_3]Cl \cdot 3H_2O$ (V).

A possible explanation for the different nature of these products may be that the benzene ring can pack more compactly and hence increase crystal stability, whereas in the case of substituted benzenes a similar tetranuclear structure would result in severe steric congestion (cf. the inability to form $[\{Ru(\eta\text{-arene})OH\}_4]^{4+}$ cations for arenes other than benzene [1]). Hence, intramolecular elimination of water from the $[Ru_2(\eta\text{-arene})_2(OH)_3(H_2O)]^+$ intermediates is apparently favoured for substituted benzenes.

Some intramolecular distances and angles for cation V are given in Table 3 and a perspective drawing with the atom numbering is shown in Fig. 2. The geometry at the ruthenium atom is identical to that found in $[\{Ru(\eta\text{-}C_6H_6)OH\}_4]^{4+}$ (I) [1] and the two ruthenium atoms are not significantly different from one another. The angle at the hydroxo group is, not surprisingly less in V than in I since it bridges two not three ruthenium atoms. The distance between the two ruthenium atoms effectively rules out any metal–metal bonding. The constraints on the refinement of the mesitylene molecules result in their having only one adjustable parameter, the ring C–C bond. In the refined structure, this is 1.40(2) Å for the ordered ring and 1.43(3) Å for the disordered ring. The related methyl groups are 1.54 and 1.57 Å respectively from the rings.

The molecules stack in columns up z; the distance between neighbouring rings is 3.35 Å, but the partial staggering makes the closest contact of ring carbons 3.38 Å, and of methyl groups 3.46 Å. The disorder is explained further by consideration of the packing normal to z. All atoms, other than ruthenium, lie within 0.32 Å of planes at $z = 0$, 1/3 and 2/3. Two alternative arrangements for the plane $z = 0$ are shown in Figs. 3a and 3b. The hydroxo groups and the ordered ring are invariant. The two

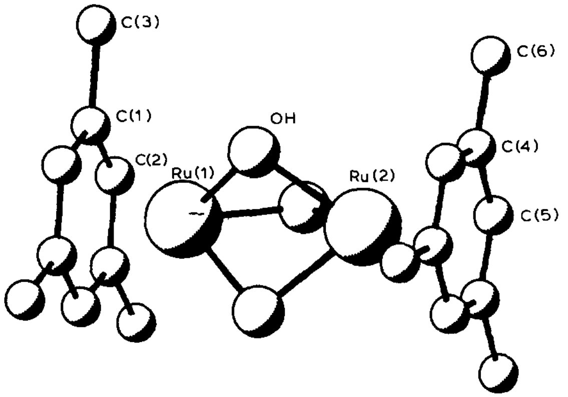


Fig. 2. The molecular structure of the cation $[Ru_2(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)_2(OH)_3]^+$.

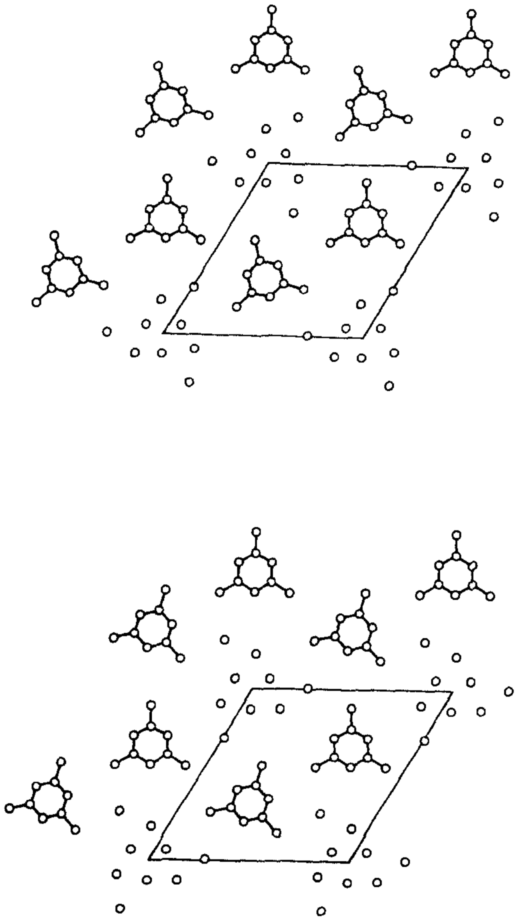


Fig. 3. Packing diagrams for V, viewed along the c axis, including only those atoms within 0.5 Å of $z = 0$. The two alternative arrangements are shown, with unconnected circles representing oxygen or chlorine atoms.

diagrams show all the disordered rings in one orientation or the other, but the true structure will be a random mixture of these. Each mesitylene does order three water molecules near it, as they would otherwise make contacts of 2.7 Å with it. Each water molecule in turn rules out one possible chloride site. Both sites make contacts of 2.91 Å with the hydroxo groups and 2.96 Å with one another, and water and chloride may in fact be distributed over all these sites. Otherwise, the only contacts less than 3.5 Å are ones of 3.46 and 3.35 Å between the disordered methyl group (C(3)) and two positions probably occupied by chloride ions or water molecules.

The stacking of parallel rings up z may be compared with that in the cation I [1]. In that tetramer, the rings are fully staggered and do not approach so closely. In V, the approach is as close as that of the planes in graphite, and may be related to the slight lengthening observed in the C–C bond lengths. The rings of adjoining molecules are partially staggered; the intramolecular torsion angle C(4)–Ru(2)–Ru(1)–C(1) is 16°, compared with the fully staggered value of 30°. Full staggering would bring the methyl groups of adjacent molecules in the xy plane too close together (3.30 Å). The conformation and packing may thus be rationalised as a compromise between the competing requirements for meshing the gear-like mesitylene molecules in the *z* direction and in the *xy* plane.

Further reactions of hydroxo-bridged complexes

As reported elsewhere [2], reaction of these hydroxo-bridged complexes with the weak acids ROH (R = Me, Et) gave the binuclear triple-alkoxo-bridged cations $[M_2(\eta\text{-arene})_2(OR)_3]^+$, now confirmed by X-ray crystallography [6] for $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$.

The compounds $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)][BPh_4]_2 \cdot 2Me_2CO$ and $[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2(OH)_3][BPh_4]$ will also react with the stronger acids, HX (X = Cl, Br, I), to give well-known [7] neutral and cationic halide-bridged complexes. Thus treatment of $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)][BPh_4]_2 \cdot 2Me_2CO$ with HCl in CH_3NO_2 gives $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ and $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3][BPh_4]$, whereas with HX (X = Br, I) only the neutral $[\{Ru(\eta\text{-}C_6H_6)X_2\}_2]$ compounds were isolated. The reaction of $[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2(OH)_3][BPh_4]$ with HCl gives exclusively $[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2Cl_3][BPh_4]$, (whose structure has been verified by X-ray analysis [8]), whilst HBr gives $[\{Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Br_2\}_2]$ and the $[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2Br_3]^+$ cation but with HI only $[\{Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)I_2\}_2]$ is formed.

The complex $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)][BPh_4]_2 \cdot 2Me_2CO$ has also proved to be a useful precursor for synthesis of the bis-arene cations $[Ru(\eta\text{-}C_6H_6)(\eta\text{-arene})]^{2+}$ (arene = C_6H_6, 1,3,5-$C_6H_3Me_3$).

Two routes to these complexes have been known for some time. The Fischer-Hafner method [9] gives rise to the symmetric bisareneruthenium(II) cations, $[Ru(\eta\text{-arene})_2]^{2+}$. More recently the asymmetric cations $[Ru(\eta\text{-arene})(\eta\text{-arene}')]^{2+}$ have been obtained by treatment of $[\{Ru(\eta\text{-arene})Cl_2\}_2]$ with silver salts followed by exchange of solvent molecules for arene in the intermediate complexes in the presence of acid (CF_3CO_2H, HBF_4 or HPF_6) [10]. The preparation of asymmetric bisarene complexes by direct reaction of $[\{Ru(\eta\text{-arene})Cl_2\}_2]$ with arenes in refluxing trifluoroacetic acid has recently appeared in the literature [11].

The preparation reported here involves treatment of the hydroxo complex with acetone/CF_3CO_2H, to generate in situ $[Ru(\eta\text{-}C_6H_6)(Me_2CO)_3]^{2+}$, and subsequent treatment with arene/CF_3CO_2H and $[Bu^n_4N][BF_4]$ then yields $[Ru(\eta\text{-arene})(\eta\text{-}C_6H_6)][BF_4]_2$. Although we have not carried out extensive investigations these preliminary studies indicate that a wide range of such complexes could be synthesised by this route.

Experimental

Microanalyses were by the University of Edinburgh Chemistry Department. Infrared spectra were recorded in the range 250–4000 cm^{-1} on a Perkin–Elmer 577 grating spectrometer using Nujol mulls on caesium iodide plates. Hydrogen-1 NMR spectra were obtained on a Bruker WP 80 spectrometer. Conductivity measurements were made at 303 K using a model 310 Portland Electronics conductivity bridge. As described earlier [5] plots of $\Lambda_0 - \Lambda_e$ against $C_e^{1/2}$ gave a straight line whose gradient is a function of the ionic charges.

The complexes "$[M_4(\eta\text{-}C_6H_6)_4(OH)_4O][BPh_4]_2 \cdot 2Me_2CO$", (M = Ru, Os) [Ru$_2$-

(η-1,3,5-$C_6H_3Me_3)_2(OH)_3]Cl \cdot 3H_2O$ and $[Ru_2(\eta$-1,4-$MeC_6H_4CHMe_2)_2(OH)_3]$-BPh_4 were prepared as described previously [2]. Anhydrous hydrogen halides were prepared using standard literature methods [12]. All other reagents were obtained from normal commercial suppliers.

Reactions of hydroxo complexes with anhydrous hydrogen halides

Tri-μ-chlorobis[(η-benzene)ruthenium(II)] tetraphenylborate. The compound $[Ru_4(\eta$-$C_6H_6)_4(OH)_4(O)][BPh_4]_2 \cdot 2Me_2CO$ (0.12 g, 0.07 mmol) was dissolved in CH_3NO_2 (10 cm^3) and HCl gas passed through the solution for 20 min. The red solid formed was filtered off, washed with diethyl ether and air dried. This product was identified as *di-μ-chlorobis[chloro(η-benzene)ruthenium(II)]*, (Yield 30 mg, 42%). The remaining solution was evaporated to dryness and the residue dissolved in methanol (5 cm^3). Addition of $Na[BPh_4]$ (0.14 g, 0.40 mmol) gave an orange precipitate which was filtered off, washed with methanol and air dried (50 mg, 45%).

Di-μ-bromobis[bromo(η-benzene)ruthenium(II)]. The compound $[Ru_4(\eta$-$C_6H_6)_4(OH)_4(O)][BPh_4]_2 \cdot 2Me_2CO$ (0.12 g, 0.07 mmol) was dissolved in CH_3NO_2 (10 cm^3) and HBr passed through the solution for 20 min. The dark precipitate which formed was filtered off, washed with diethyl ether and air dried (80 mg, 85%).

Di-μ-iodobis[iodo(η-benzene)ruthenium(II)] was prepared similarly by reaction with HI (110 mg, 91%).

Di-μ-iodobis[iodo(η-p-cymene)ruthenium(II)] was prepared in a similar manner from $[Ru_2(\eta$-1,4-$MeC_6H_4CHMe_2)_2(OH)_3][BPh_4]$ and HI (120 mg, 72%).

Tri-μ-chlorobis[(η-p-cymene)ruthenium(II)] tetraphenylborate. The compound $[Ru_2(\eta$-1,4-$MeC_6H_4CHMe_2)_2(OH)_3][BPh_4]$ (0.15 g, 0.17 mmol) was dissolved in CH_3NO_2 (10 cm^3) and HCl passed through the solution. The solvent was then removed under vacuo and the residue redissolved in methanol (5 cm^3) to which $Na[BPh_4]$ (0.14 g, 0.40 mmol) was added. The orange precipitate which formed was filtered off, washed with methanol and air dried (120 mg, 75%).

Tri-μ-bromobis[(η-p-cymene)ruthenium(II)] tetraphenylborate was prepared similarly by reaction with HBr (60 mg, 34%).

Di-μ-bromobis[bromo(η-p-cymene)ruthenium(II)] which was also formed in this reaction was removed by filtration prior to evaporation of the solvent (75 mg, 56%). The identity of all these well-known halide complexes was confirmed by elemental analyses and ^1H NMR spectroscopy (see ref. 7).

Bis(η-benzene)ruthenium tetrafluoroborate. The compound $[Ru_4(\eta$-$C_6H_6)_4$-$(OH)_4(O)][BPh_4]_2 \cdot 2Me_2CO$ (0.12 g, 0.07 mmol) was warmed with CF_3CO_2H (3 cm^3) and acetone (3 cm^3) for 10 min. The solvent was removed and the residue treated with CF_3CO_2H (5 cm^3) and benzene (5 cm^3) and then refluxed for 30 min. The solvent was removed for a second time and the residue treated with methanol (5 cm^3) to which was added $[Bu^n_4N]BF_4$ (0.25 g, 0.70 mmol). The off-white precipitate was filtered off, washed with methanol and air dried (30 mg, 10%) (^1H NMR in $(CD_3)_2SO$ at 301 K: δ 6.87(s) ppm).

Similarly prepared was *(η-benzene)(η-mesitylene)ruthenium tetrafluoroborate* by the reaction of $[Ru_4(\eta$-$C_6H_6)_4(OH)_4(O)][BPh_4]_2 \cdot 2Me_2CO$ with CF_3CO_2H/1,3,5-$C_6H_3Me_3$, (45 mg, 17%) (^1H NMR in $(CD_3)_2SO$ at 301 K: δ 6.91(s), 6.84(s), 2.36(s) ppm).

Crystal structure determination of $[Ru_4(\eta\text{-}C_6H_6)_4(\mu_2\text{-}OH)_4(\mu_4\text{-}O)](BPh_4)_2 \cdot 2Me_2CO$ *(III)*

Crystal data: $C_{78}H_{76}B_2O_7Ru_4$, $M = 1551$, monoclinic, a 13.267(8), b 12.227(3), c 41.864(8) Å, β 98.23(3)°, U 6721 Å^3, D_m 1.50, D_c 1.53 g cm^{-3}, $Z = 4$, μ(Mo-K_α) 9.2 cm^{-1}, space group $P2_1/c$ from systematic absences.

Intensities were collected on a CAD-4 diffractometer for 8175 independent reflections; the solution and refinement are based on 3110 with $I > 2.5\sigma(I)$. The four independent ruthenium atoms were found by direct methods [13] and the remaining nonhydrogen atoms were located by subsequent difference electron density syntheses. Refinement of the structure by least squares reduced the R-factor to 0.080 in 5 cycles with Ru and O atoms refined anisotropically and the phenyl groups of the tetraphenylborate anions constrained to be idealised planar hexagons. Because of the large number of atoms in the structure, hydrogen atoms were not included in the structure factor calculation in the usual way. Instead, the data were modified to allow for hydrogen atoms in idealised positions (C–H 1.1 Å), and refinement continued on the modified data. At convergence based on unmodified data, $R = 0.076$ ($R_w = 0.085$). The maximum shift/e.s.d. at this stage was 0.031. The strongest peak on a difference map had a height of about 1 ε Å^{-3} near one of the benzene rings in the cation.

Final fractional coordinates for the atoms of the cation are given in Table 4.

Crystal structure determination of $[Os_4(\eta\text{-}C_6H_6)_4(\mu_2\text{-}OH)_4(\mu_4\text{-}O)](BPh_4)_2 \cdot 2Me_2CO$ *(IV)*

Crystal data: $C_{78}H_{76}B_2O_7Os_4$, $M = 1908$, monoclinic, a 13.262(4), b 12.226(2), c 41.834(16) Å, β 98.21(3)°, U 6714 Å^3, D_c 1.89 g cm^{-3}, $Z = 4$, μ(Mo-K_α) 80.7 cm^{-1}, space group $P2_1/c$ from systematic absences.

Intensities were collected on a CAD-4 diffractometer for 6252 independent reflections; the refinement is based on 2490 with $I > 3.0\sigma(I)$. The structure is isomorphous with that of the ruthenium analogue, and was refined starting from the parameters of that structure. In this case, however, absorption corrections were applied using the DIFABS procedure [14] giving maximum corrections of ±23% based on F. In this structure, only the osmium atoms were refined anisotropically, and all benzene rings were constrained to be regular, with C–C 1.395 Å. Hydrogen atoms were omitted from all calculations. The structure refined to $R = 0.049$, $R_w = 0.045$, and at convergence, no peaks in the difference electron density synthesis were greater than 0.75 ε Å^{-3}. Final fractional coordinates for the atoms of the cation are given in Table 4.

Crystal structure determination of $[Ru_2(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)_2(OH)_3]Cl \cdot 3H_2O$ *(V)*

Crystal data: $C_{18}H_{33}ClO_6Ru_2$, $M = 583.0$, rhombohedral, a 14.675(3), c 9.630(2) Å, U 1796 Å^3, $Z = 3$, D_c 1.62 g cm^{-3}, μ(Mo-K_α 13.6 cm^{-1}), space group $R3m$ (by structure determination).

Intensities were collected on a CAD-4 diffractometer with monochromated Mo-K_α radiation for 978 reflections, θ_{max} 27°, yielding 494 independent data; the solution and refinement are based on 398 data with $I > 3\sigma(I)$. No absorption correction was made. The Patterson function gave Ru positions at (0,0,± 0.157) and those related by the rhombohedral lattice. These are compatible with the space groups $R32$, $R3m$ and $R\bar{3}m$. The last of these would not allow an ordered bridging of the ruthenium atoms by three hydroxyl groups. In $R32$, the oxygen atoms would have to occupy

TABLE 4

FRACTIONAL COORDINATES OF ATOMS IN III AND IV WITH STANDARD DEVIATIONS

Atom	x	y	z
Compound III			
Ru(1)	0.15357(21)	0.08108(25)	0.63246(6)
Ru(2)	0.36221(21)	0.0934(3)	0.61287(6)
Ru(3)	0.30011(20)	0.32971(24)	0.66051(5)
Ru(4)	0.20134(19)	0.33459(23)	0.59122(5)
O(1)	0.2174(16)	0.0392(17)	0.5907(4)
O(2)	0.2960(16)	0.0290(17)	0.6517(4)
O(3)	0.1628(15)	0.3780(18)	0.6351(5)
O(4)	0.3416(16)	0.3860(17)	0.6174(4)
O(5)	0.2552(17)	0.2097(12)	0.6260(4)
C(1)	0.080(3)	0.052(3)	0.6757(8)
C(2)	0.058(3)	0.162(3)	0.6654(8)
C(3)	0.0052(22)	0.178(3)	0.6306(7)
C(4)	−0.0096(23)	0.084(3)	0.6114(7)
C(5)	0.012(3)	−0.025(3)	0.6183(10)
C(6)	0.069(3)	−0.042(3)	0.6531(10)
C(7)	0.434(3)	0.082(3)	0.5690(8)
C(8)	0.454(3)	0.183(3)	0.5823(9)
C(9)	0.494(3)	0.201(3)	0.6128(10)
C(10)	0.518(3)	0.109(3)	0.6350(9)
C(11)	0.500(3)	−0.001(3)	0.6209(8)
C(12)	0.453(3)	−0.018(3)	0.5878(9)
C(13)	0.2575(25)	0.346(3)	0.7073(7)
C(14)	0.296(3)	0.243(3)	0.7046(9)
C(15)	0.393(3)	0.228(3)	0.6961(8)
C(16)	0.450(3)	0.309(3)	0.6900(8)
C(17)	0.414(3)	0.419(3)	0.6908(9)
C(18)	0.319(3)	0.444(3)	0.7011(9)
C(19)	0.2460(24)	0.376(3)	0.5443(7)
C(20)	0.212(3)	0.264(3)	0.5424(9)
C(21)	0.108(3)	0.239(3)	0.5533(10)
C(22)	0.050(3)	0.332(3)	0.5627(8)
C(23)	0.092(3)	0.439(3)	0.5628(7)
C(24)	0.185(3)	0.463(3)	0.5525(8)
Compound IV			
Os(1)	0.15170(13)	0.07838(17)	0.63263(4)
Os(2)	0.36585(13)	0.09119(18)	0.61266(3)
Os(3)	0.30100(12)	0.32636(16)	0.66118(3)
Os(4)	0.20073(12)	0.33143(16)	0.59015(3)
O(1)	0.2218(16)	0.0380(18)	0.5929(4)
O(2)	0.2983(17)	0.0301(19)	0.6520(5)
O(3)	0.1611(17)	0.3811(21)	0.6336(5)
O(4)	0.3375(17)	0.3783(21)	0.6169(4)
O(5)	0.2548(21)	0.2085(13)	0.6245(5)
C(1)	0.0801(18)	0.045(3)	0.6754(4)
C(2)	0.0558(18)	0.152(3)	0.6656(4)
C(3)	0.0134(18)	0.173(3)	0.6338(4)
C(4)	0.0047(18)	0.088(3)	0.6117(4)
C(5)	0.0196(18)	−0.019(3)	0.6214(4)
C(6)	0.0620(16)	−0.041(3)	0.6532(4)
C(7)	0.4352(16)	0.075(3)	0.5694(4)
C(8)	0.4546(16)	0.179(3)	0.5825(4)

Table 4 (continued)

Atom	x	y	z
C(9)	0.4985(16)	0.191(3)	0.6147(4)
C(10)	0.5231(16)	0.098(3)	0.6338(4)
C(11)	0.5037(16)	−0.006(3)	0.6207(4)
C(12)	0.4597(16)	−0.018(3)	0.5885(4)
C(13)	0.2570(14)	0.3485(22)	0.7084(5)
C(14)	0.2976(14)	0.2436(22)	0.7072(5)
C(15)	0.3940(14)	0.2290(22)	0.6983(5)
C(16)	0.4499(14)	0.3193(22)	0.6905(5)
C(17)	0.4094(14)	0.4243(22)	0.6916(5)
C(18)	0.3130(14)	0.4389(22)	0.7006(5)
C(19)	0.2395(20)	0.3728(16)	0.5447(5)
C(20)	0.2090(20)	0.2635(16)	0.5447(5)
C(21)	0.1147(20)	0.2362(16)	0.5535(5)
C(22)	0.0507(20)	0.3181(16)	0.5623(5)
C(23)	0.0812(20)	0.4273(16)	0.5623(5)
C(24)	0.1756(20)	0.4546(16)	0.5535(5)

sites of the type (x,O,O) and in $R3m$ sites of the type $(x,\bar{x},z)$ with z near O. A difference electron density map strongly favoured $R3m$. In this space group, the two Ru atoms are independent, but their z parameters were linked to fix the origin, which is otherwise undefined in this direction. One mesitylene ring could be located as three independent carbon atoms, all on mirror planes, 1.67 Å along z from Ru(2), but an ordered model for the other mesitylene moiety could not be found, difference maps strongly suggesting that it was disordered over two sites. Satisfactory refinement of the entire cation was achieved by constraining the ordered ring in terms of two positional parameters: C(4), $(x,\bar{x},z)$; C(5), $(\bar{x},x,z)$ and C(6), $(1.2x, -1.2x,z)$. The disordered ring was similarly defined in terms of three parameters: C(1), (x,y,z); C(2), $(\bar{x},\bar{y},z)$; C(3), $(1.2x, 1.2y,z)$, each atom being given a site occupancy of one half. The water molecules and the chloride ions could not be uniquely

TABLE 5

FRACTIONAL COORDINATES OF ATOMS IN V WITH STANDARD DEVIATIONS (Several parameters were linked in refinement; see text for further details)

Atom	Site symmetry		Site occupancy	x	y	z
Ru(1)	$3m$	C_{3v}	1	0	0	0.15525(15)
Ru(2)	$3m$	C_{3v}	1	0	0	−0.15525(15)
OH	m	C_s	1	0.0580(5)	−0.0580(5)	0.0012(14)
C(1)	1	C_1	0.5	−0.0271(10)	0.0810(10)	0.3239(16)
C(2)	1	C_1	0.5	0.0271(10)	−0.0810(10)	0.3239(16)
C(3)	1	C_1	0.5	−0.0569(21)	−0.1700(22)	0.3239(16)
C(4)	m	C_s	1	−0.0549(4)	0.0549(4)	−0.3282(17)
C(5)	m	C_s	1	0.0549(4)	−0.0549(4)	−0.3282(17)
C(6)	m	C_s	1	−0.1152(9)	0.1152(9)	−0.3282(17)
H_2O	1	C_1	0.5	−0.2821(17)	−0.0060(25)	0.0249(24)
Cl	1	C_1	1/6	−0.1990(22)	−0.0859(22)	0.0335(28)

assigned, but satisfactory convergence was achieved to the positions and site occupancies given in Table 5, these site occupancies being in agreement with the analytical composition. No attempt was made to include hydrogen atoms in the refinement. In the final cycles of refinement, the two ruthenium atoms were given independent, anisotropic thermal parameters; these were, however, strongly correlated. Unit weights were used throughout, and a final analysis of agreement showed poor agreement only for the lowest range of sinθ, as would be expected with so much disorder. At convergence, no shift in the 28 parameters refined was greater than 0.2 times an e.s.d., and a final difference Fourier synthesis showed no peaks above 0.7 ε Å^{-3}. At convergence, $R = 0.047$, $R_w = 0.055$. Final fractional coordinates are given in Table 5.

Crystallographic calculations not otherwise noted used the SHELX-76 program [15]. Tables of observed and calculated structure factors for all compounds, and a full list of positional and thermal parameters, including hydrogen atoms for III may be obtained on request from the authors.

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