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**PREPARATION, X-RAY CRYSTAL STRUCTURE ANALYSIS AND SOME REACTIONS OF THE HYDROXO-BRIDGED, TETRANUCLEAR,  $\eta$ -ARENE RUTHENIUM(II) QUADRIVALENT CATION  $[\{\text{Ru}(\eta\text{-C}_6\text{H}_6)(\text{OH})\}_4](\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$**

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**Summary**

Reaction of  $[\{\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{Cl}_2\}_2]$  with aqueous  $\text{Na}_2\text{CO}_3$  (1 : 2 molar ratio) in the presence of an excess of  $\text{Na}_2\text{SO}_4$  gives the cubane-like complex  $[\{\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{OH}\}_4](\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$  (A) whose structure has been determined by X-ray analysis. The crystals are cubic, space group  $Pm\bar{3}n$ , with  $a = 12.405(1) \text{ \AA}$ . A possible mechanism of formation of compound A and its reactions with  $\text{NaOH}$ ,  $\text{LiBr}$ ,  $\text{C}_5\text{H}_5\text{N}$ , 4-MeC<sub>5</sub>H<sub>4</sub>N and 1,10-phenanthroline are also described.

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Recently, we have presented the full results of our studies on the synthesis of binuclear hydroxo-bridged  $\eta$ -arene complexes of ruthenium(II) [1]. These complexes were prepared by the reaction of various  $[\{\text{Ru}(\eta\text{-arene})\text{Cl}_2\}_2]$  compounds (arene =  $\text{C}_6\text{H}_6$ , 1,3,5-C<sub>6</sub>H<sub>3</sub>Me<sub>3</sub>, C<sub>6</sub>Me<sub>6</sub>, *p*-MeC<sub>6</sub>H<sub>4</sub>CHMe<sub>2</sub>) with an excess of aqueous  $\text{NaOH}$  or  $\text{Na}_2\text{CO}_3$ , followed by precipitation with  $\text{NaBPh}_4$ . However, if  $[\{\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{Cl}_2\}_2]$  is treated with less  $\text{Na}_2\text{CO}_3$  ( $[\text{Ru}^{2+}] : [\text{CO}_3^{2-}]$  ca. 1 : 1 molar ratio) in the presence of a large excess of  $\text{Na}_2\text{SO}_4$ , the novel tetranuclear, hydroxo-bridged,  $\eta$ -arene ruthenium(II) complex  $[\{\text{Ru}(\eta\text{-C}_6\text{H}_6)(\text{OH})\}_4](\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$  can be isolated. The full details [2] of the preparation, X-ray analysis and some reactions of this compound are now presented in this paper.

**Results and discussion**

As discussed earlier [1], reaction of an aqueous solution of  $[\{\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{Cl}_2\}_2]$  with an excess of  $\text{NaOH}$  (or  $\text{Na}_2\text{CO}_3$ ) gave, on warming, a yellow solution from which a yellow solid could be precipitated by addition of  $\text{NaBPh}_4$ . On the basis of various physicochemical studies, this product was

shown to be a mixture of mainly  $[\eta\text{-C}_6\text{H}_6(\text{OH})\text{Ru}(\text{OH})_2\text{Ru}(\text{H}_2\text{O})(\eta\text{-C}_6\text{H}_6)]\text{BPh}_4$  together with some  $[\eta\text{-C}_6\text{H}_6\text{Ru}(\text{OH})_3\text{Ru}(\eta\text{-C}_6\text{H}_6)]\text{BPh}_4$ . Recrystallisation from acetone then gave pure samples of  $[\text{Ru}_2(\eta\text{-C}_6\text{H}_6)_2(\text{OH})_3]\text{BPh}_4\text{Me}_2\text{CO}$ .

If, however,  $[\{\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{Cl}_2\}_2]$  was dissolved in water and shaken with a large excess of  $\text{Na}_2\text{SO}_4$  for a short period and this solution then treated with  $\text{Na}_2\text{CO}_3$ , ( $[\text{Ru}^{2+}] : [\text{CO}_3^{2-}]$  ca. 1 : 1 molar ratio), an orange crystalline solid (A) was deposited in low yield. The same product was obtained if  $\text{Na}_2\text{HPO}_4$  ( $[\text{Ru}^{2+}] : [\text{HPO}_4^{2-}]$  ca. 1 : 1 molar ratio) was added but no solid was precipitated on shaking only  $\text{Na}_2\text{SO}_4$  with  $[\{\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{Cl}_2\}_2]$  for prolonged periods. The yield of compound A could be considerably increased by pretreating an aqueous solution of  $[\{\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{Cl}_2\}_2]$  with  $\text{AgNO}_3$  and, after filtering off the  $\text{AgCl}$ , shaking with an excess of  $\text{Na}_2\text{SO}_4$  followed by  $\text{Na}_2\text{CO}_3$  (1 : 2 molar ratio).

Unfortunately, compound A was too insoluble in organic solvents for  $^1\text{H}$  NMR studies and too involatile for mass spectral studies. The mull IR spectrum of A showed very broad bands at ca.  $3250$  and  $1640\text{ cm}^{-1}$  assigned to the  $\nu(\text{OH})$  and  $\delta(\text{HOH})$  vibrational modes of water and these of course obscured any  $\nu(\text{OH})$  bands arising from hydroxo groups (cf.  $[\text{Ru}_2(\eta\text{-C}_6\text{H}_3\text{Me}_3)_2(\text{OH})_3]\text{Cl} \cdot 3\text{H}_2\text{O}$  [1]). No bands due to  $\nu(\text{RuCl})$  vibrations were observed in the IR spectrum but bands at  $1060$ ,  $975$ ,  $610$  and  $478\text{ cm}^{-1}$  suggested the presence of sulphate ion [3] and a strong band at  $864\text{ cm}^{-1}$  indicated retention of the benzene ring.

The compound was very sparingly soluble in water and gave strongly conducting solutions. Furthermore, freeze-drying of an aqueous solution of A produced a solid with the same properties as A, indicating that dissociation of this complex to form ions was not caused by decomposition in water. A solid could be precipitated on addition of  $\text{NaBPh}_4$  to this aqueous solution but this rapidly decomposed on standing for short periods.

Elemental analyses on A confirmed the presence of C, H, O, and S and the absence of chlorine and suggested the empirical formula  $\text{C}_{12}\text{H}_{26}\text{O}_{12}\text{Ru}_4\text{S}$ , which, together with the information given above, suggested the molecular formula  $[\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{OH}]_{2n}(\text{SO}_4)_n \cdot 6n\text{H}_2\text{O}$ . Fortunately, the orange crystalline solid (A) was suitable for X-ray structural analysis (see below) and this showed it to be the unusual  $[\{\text{Ru}(\eta\text{-C}_6\text{H}_6)(\text{OH})\}_4](\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  complex containing  $\pi$ -bonded benzene groups and hydroxo bridges.

*Crystal Data for A.*  $[\text{Ru}_4(\text{C}_6\text{H}_6)_4(\text{OH})_4]^{4+}$ ,  $2\text{SO}_4^{2-}$ ,  $12\text{H}_2\text{O}$  ( $\text{C}_{24}\text{H}_{52}\text{O}_{24}\text{Ru}_4\text{S}_2$ ),  $M = 1193$ , dark red octahedra, cubic,  $a = 12.405(1)\text{ \AA}$ ,  $U = 1909\text{ \AA}^3$ ,  $D_m = 2.10$ ,  $Z = 2$ ,  $D_c = 2.08\text{ g cm}^{-3}$ ,  $\mu(\text{Mo-K}\alpha) = 17.1\text{ cm}^{-1}$ , space group  $Pn\bar{3}m$  (no 224), conditions for reflection,  $h k 0$ ,  $h 0 l$ ,  $0 k l$ ,  $h + k + l = 2n$ .

*Refinement of Crystal Structure of A.* Data collection is described in the Experimental section. The approximate parameters, reported previously, [2], were refined with careful constraints, in view of the extensive disorder. The final values, together with site symmetries and site occupancies, are given in Table 1.

In the cation, which is centred at  $1/4, 1/4, 1/4$  and has  $\bar{4}3m$  ( $T_d$ ) symmetry, the Ru and O atoms were refined anisotropically, (a total of 6 parameters). The coordinated benzene is disordered over two positions, related by a  $30^\circ$  rotation about a threefold axis. These rings were given fixed site occupancies of 0.5 and

TABLE 1

## CRYSTAL PARAMETERS FOR A.

See text for discussion of errors.

Atom	Site symmetry	Site occupancy	$10^4 X$	$10^4 Y$	$10^4 Z$	$10^4 U(\text{\AA}^2)$	$10^4 U_{ij}(\text{\AA}^2)$	
Ru	3m	$C_{3v}$	1.0	1558	1558	1558	246	-37
O(1)	3m	$C_{3v}$	1.0	3241	3241	3241	244	-32
C(1)	1	$C_1$	0.5	-2	803	1608	327	-
C(2)	m	$C_s$	0.5	338	338	1733	442	-
C(3)	m	$C_s$	0.5	1268	1268	-127	436	-
S	3m	$C_{3v}$	0.5	5092	5092	5092	1549	-972
O(2)	3m	$C_{3v}$	0.5	4405	4405	4405	546	-
O(3)	m	$C_s$	0.5	5783	5783	4405	3371	-
H <sub>2</sub> O(1)	222	$D_2$	0.5	0	2500	7500	2327	-
H <sub>2</sub> O(2)	m	$C_s$	0.5	1438	1438	7104	2610	-
H <sub>2</sub> O(3)	$\bar{4}2m$	$D_{2d}$	0.5	2500	2500	7500	3161	-

were constrained to be identical regular hexagons, normal to the threefold axis. One ring consists of 6 symmetry related atoms in general positions [C(1)] while the other has two groups of 3 symmetry related atoms on mirror planes [C(2) and C(3)]. The constraints for the carbon atoms may be expressed thus: C(1) at  $u - v, u, u + v$ ; C(2) at  $u - w, u - w, u + 2w$ ; C(3) at  $u + w, u + w, u - 2w$ . In the refined structure,  $u = 0.0803$ ,  $v = w/\sqrt{3} = 0.0805$ . Hydrogen atoms for the benzene ring and for the hydroxyl group were included in the refinement in fixed positions to give C-H = 1.10 Å, O-H = 1.02 Å. The standard deviations for the four positional parameters are:  $xyz$ [Ru]; 0.0008 Å,  $xyz$ [O(1)]: 0.007 Å,  $u$ : 0.006 Å,  $v$ : 0.006 Å.

The sulphate ions are disordered about  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$  with averaged symmetry  $3m(D_{3d})$ . The sulphur atom and the oxygen lying along the threefold axis have essentially twofold disorder, while the position of the other atoms is much less well defined. For refinement, the ions were constrained to be a set of interpenetrating regular tetrahedra with S-O fixed at 1.48 Å. The high temperature factor of O(3) and some residual electron density in the vicinity shows that the model is not entirely adequate. The standard deviation of  $xyz$ [S], the only positional parameter refined, is 0.013 Å.

The water molecules are very poorly defined. Their presence is indicated by elemental analysis and the X-ray molecular weight, but they only show on difference electron density syntheses as broad peaks in the channels intersecting at  $1/4, 1/4, 3/4$  and symmetry related positions, with  $\bar{4}2m(D_{2d})$  symmetry. Various positions were tried, but the best refinement occurred with half occupancy of three independent sites. This accounts for  $10\frac{1}{2}$  of the 12 water molecules required by the formula, but can only be taken as an approximate indication of the positions occupied by water molecules in the crystal. The root mean square standard deviation of H<sub>2</sub>O (2) is 0.06 Å.

A projection of one cation along a  $\bar{4}$  ( $S_4$ ) axis is shown in Fig. 1. The Ru-O distance in the "cube" is 2.117(7) Å, and the angles at Ru and O are 75.8(1)° and 102.6(2)°, respectively. The centres of the benzene rings are 1.622(8) Å from the ruthenium atoms, and the Ru-C distance is 2.151(8) Å. The C-C dis-

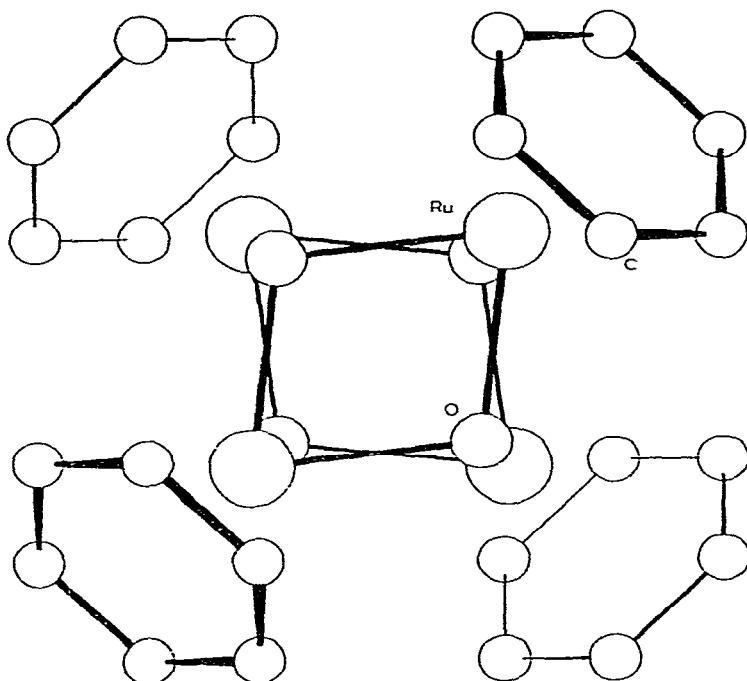


Fig. 1. Projection of  $[\{\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{OH}\}_4]^{4+}$  cation along a  $\bar{4}$  ( $S_4$ ) axis.

tance in the rings is 1.395(10) Å. This tetrameric cation is, to our knowledge, only the second ruthenium complex with this cubane stereochemistry ( $[\text{Ru}_4(\eta^5\text{-C}_5\text{H}_5)_4(\mu_3\text{-CO})_4]$  is the other [4]) and the first example of a cubane-like structure containing  $\pi$ -bonded arene rings. A large number of cubane clusters containing a wide range of elements, bridging and terminal groups have however been synthesised [5].

Unfortunately, attempts to synthesise other  $[\{\text{Ru}(\eta\text{-arene})\text{OH}\}_4]^{4+}$  cations by reaction of  $[\{\text{Ru}(\eta\text{-arene})\text{Cl}_2\}_2]$  (arene =  $\text{C}_6\text{Me}_6$ , 1,3,5- $\text{C}_6\text{H}_3\text{Me}_3$ ,  $p\text{-MeC}_6\text{H}_4\text{-CHMe}_2$ ) with stoichiometric amounts of  $\text{Na}_2\text{CO}_3$  in the presence of an excess of  $\text{Na}_2\text{SO}_4$  in water were unsuccessful since only unreacted starting materials and/or the triple hydroxo-bridged cations  $[\text{Ru}_2(\eta\text{-arene})_2(\text{OH})_3]^+$  were recovered on work-up. For example, treatment of either  $[\{\text{Ru}(\eta\text{-C}_6\text{H}_3\text{Me}_3)\text{Cl}_2\}_2]$  or  $[\{\text{Rh}(\eta\text{-C}_5\text{Me}_5)\text{Cl}_2\}_2]$  with aqueous  $\text{AgNO}_3$  followed by shaking with an excess of  $\text{Na}_2\text{SO}_4$  and then  $\text{Na}_2\text{CO}_3$  (1 : 2 molar ratio) for several hours gave on concentration, the triple hydroxo-bridged complexes  $[\text{Ru}_2(\eta\text{-C}_6\text{H}_3\text{Me}_3)_2(\text{OH})_3]\text{-NO}_3 \cdot \text{H}_2\text{O}$  and  $[\text{Rh}_2(\eta\text{-C}_5\text{Me}_5)_2(\text{OH})_3]\text{NO}_3 \cdot 2 \text{H}_2\text{O}$ , respectively.

The crystal structure gives an indication as to why arenes other than benzene do not form similar complexes. Each cation in A may be regarded as being bonded to eight others through the cube corners. At the vertices occupied by Ru, this is achieved by strong Van der Waals interactions between the benzene rings of adjacent cations. These lie in parallel planes separated by 3.45 Å (cf. 3.35 Å in graphite). This close approach implies that the rings are staggered with respect to one another ( $\text{C}\cdots\text{C} = 3.53$  Å) but such local ordering will have

no effect on the relative positions of pairs of benzene rings elsewhere in the structure. At the same time, the vertices of the cube occupied by OH are hydrogen bonded to the sulphate ion lying between them. In whichever way it is oriented, an atom of type O(2) will lie 2.50 Å from the O(1) of one cube, while the three atoms of type O(3) will be 3.38 Å from the O(1) of another. Thus the stability of the crystal, and probably of the cation, depends both on the arenes having no aliphatic substituents and the anions being of suitable size to bridge a gap between two OH groups for which O...O is 7.56 Å and H...H is about 5.50 Å.

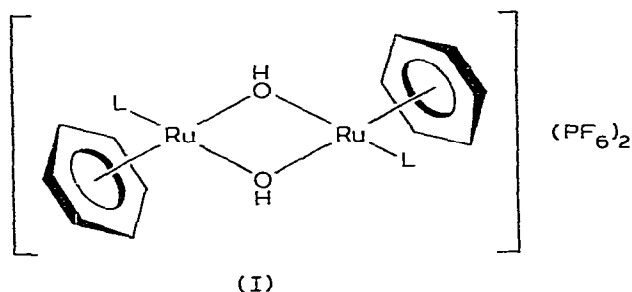
A possible mechanism of formation of compound A is via deprotonation of the trisaqua cation  $[\text{Ru}(\eta\text{-C}_6\text{H}_6)(\text{H}_2\text{O})_3]^{2+}$  (generated in situ in high yield by reaction of  $[\{\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{Cl}_2\}_2]$  with aqueous  $\text{AgNO}_3$  [6]) by equimolar amounts of  $\text{CO}_3^{2-}$  or  $\text{HPO}_4^{2-}$  to give the  $[\text{Ru}(\eta\text{-C}_6\text{H}_6)(\text{H}_2\text{O})_2\text{OH}]^+$  cation. The combination of the bridging propensity of hydroxo groups and the desire of ruthenium(II) to exhibit six coordination [7] could then lead to tetramerisation of the  $[\text{Ru}(\eta\text{-C}_6\text{H}_6)(\text{H}_2\text{O})_2\text{OH}]^+$  cation with concomitant elimination of water to form the  $[\{\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{OH}\}_4]^{4+}$  cubane cluster cation. This process is enhanced by the presence of an excess of sulphate ion which removes the tetrameric cation from solution. In fact, if an aqueous solution of  $[\{\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{Cl}_2\}_2]$  was treated with an equimolar amount of  $\text{Na}_2\text{CO}_3$  before addition of  $\text{Na}_2\text{SO}_4$ , then only binuclear hydroxo-bridged cations (see ref. [1]) could be isolated from the solution.

In support of this observation, treatment of compound A with either aqueous  $\text{Na}_2\text{CO}_3$  or  $\text{NaOH}$  followed by addition of  $\text{NaBPh}_4$  readily gave  $[\text{Ru}_2(\eta\text{-C}_6\text{H}_6)_2(\text{OH})_3]\text{BPh}_4 \cdot \text{H}_2\text{O}$ . The  $^1\text{H}$  NMR spectrum of this compound in  $(\text{CD}_3)_2\text{CO}$  at 298 K showed only one  $\eta\text{-C}_6\text{H}_6$  resonance at  $\delta$  5.60 ppm which indicated that no  $[\eta\text{-C}_6\text{H}_6(\text{OH})\text{Ru}(\text{OH})_2\text{Ru}(\text{H}_2\text{O})(\eta\text{-C}_6\text{H}_6)]\text{BPh}_4$  ( $[\delta$  5.33 ppm ( $^1\text{H}$  NMR)] [1]) had been formed by this route. Hence, the tetrameric  $[\{\text{Ru}(\eta\text{-C}_6\text{H}_6)(\text{OH})\}_4]^{4+}$  cation is readily cleaved by hydroxide ion to give the binuclear  $[\text{Ru}_2(\eta\text{-C}_6\text{H}_6)_2(\text{OH})_3]^+$  cation.

Similarly, treatment of compound A with aqueous  $\text{LiBr}$  (1 : 2 molar ratio) gave an orange solution from which orange-yellow solids could be precipitated by addition of either  $\text{NH}_4\text{PF}_6$  or  $\text{NaBPh}_4$ . These compounds analysed quite closely for “ $[\text{Ru}_2(\eta\text{-C}_6\text{H}_6)_2(\text{OH})_2\text{Br}]\text{Y}$ ” ( $\text{Y} = \text{PF}_6^-$ ,  $\text{BPh}_4^-$ ) but their  $^1\text{H}$  NMR spectra contained several  $\eta\text{-C}_6\text{H}_6$  resonances. A possible explanation of this observation is that in solution the  $(\mu\text{-OH})_2(\mu\text{-Br})$  cation rapidly rearranged to give a mixture containing the  $(\mu\text{-OH})_3$ ,  $(\mu\text{-OH})_2(\mu\text{-Br})$ ,  $(\mu\text{-OH})(\mu\text{-Br}_2)$  and  $(\mu\text{-Br})_3$  cations (cf. related studies on the “ $[\text{Ru}_2(\eta\text{-C}_6\text{H}_6)_2\text{Cl}_2\text{Br}]^+$ ” and “ $[\text{Ru}_2(\eta\text{-C}_6\text{H}_6)_2\text{ClBr}_2]^+$ ” cations [8]). The same species were obtained on mixing nitromethane solutions of  $[\text{Ru}_2(\eta\text{-C}_6\text{H}_6)_2(\text{OH})_3]^+$  and  $[\text{Ru}_2(\eta\text{-C}_6\text{H}_6)_2\text{Br}_3]^+$  cations. On leaving in solution the “ $[\text{Ru}_2(\eta\text{-C}_6\text{H}_6)_2(\text{OH})_2\text{Br}]^+$ ” cation slowly deposits some insoluble  $[\{\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{Br}_2\}_2]$  and this was the only product formed when compound A was treated with an excess of  $\text{LiBr}$ .

Similarly, compound A reacted in water with neutral Lewis bases such as pyridine and 4-methylpyridine (L) to give yellow solutions from which yellow solids were precipitated on addition of  $\text{NH}_4\text{PF}_6$ . These however were formulated as the dicationic, binuclear complexes  $[\{\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{OHL}\}_2](\text{PF}_6)_2$  (I) on the basis of elemental analyses,  $^1\text{H}$  NMR, IR and conductivity studies. Again,

cleavage of the tetramer has occurred but since pyridine and 4-methylpyridine do not act as bridging groups, the double hydroxo-bridged cation (I) was produced.



Finally, compound A reacted with an excess of 1,10-phenanthroline in water under reflux to give an orange solution from which an orange solid was precipitated by addition of  $\text{NH}_4\text{PF}_6$ . This did not contain any  $\eta$ -benzene or hydroxo groups and was formulated as the previously known  $[\text{Ru}(\text{phen})_3](\text{PF}_6)_2$  [9].

### Experimental

Microanalyses were by BMAC and the University of Edinburgh Chemistry Department. Infrared spectra were recorded in the region  $4000\text{--}250\text{ cm}^{-1}$  on a Perkin-Elmer 447 grating spectrometer using Nujol and hexachlorobutadiene mulls on caesium iodide plates. Hydrogen-1-NMR spectra were obtained on Varian Associates HA-100 and EM-360 spectrometers. Conductivity measurements were made at 303 K using a model 310 Portland Electronics conductivity bridge. Melting points were determined with a Köfler hot stage microscope and are uncorrected.

### Materials

Ruthenium trichloride trihydrate, rhodium trichloride and silver nitrate (Johnson Matthey Ltd),  $\text{CD}_3\text{NO}_2$ , cyclohexa-1,3-diene,  $\text{NH}_4\text{PF}_6$  (Aldrich Chemicals); pyridine (Fisons), 1,10-phenanthroline (BDH). The compounds  $[\{\text{Ru}(\eta\text{-arene})\text{Cl}_2\}_2]$  [8] and  $[\{\text{Rh}(\eta\text{-C}_5\text{H}_5)\text{Cl}_2\}_2]$  [10] were prepared as described elsewhere.

*Tetra- $\mu_3$ -hydroxotetrakis[( $\eta$ -benzene)ruthenium(II)] sulphate hydrate (1/12).* The complex  $[\{\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{Cl}_2\}_2]$  (0.20 g; 0.40 mmol) was dissolved in water ( $10\text{ cm}^3$ ) and the orange solution was filtered. An excess of  $\text{Na}_2\text{SO}_4$  (0.20 g, 1.50 mmol) was then added, the solution shaken vigorously for 10 minutes and then  $\text{Na}_2\text{CO}_3$  (0.08 g; 0.80 mmol) added. On further vigorous shaking for 24 hours, the orange crystalline solid was deposited from solution, m.p.  $200^\circ\text{C}$  (decomp) (0.07 g; 31%). Alternatively, an aqueous solution of  $[\{\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{Cl}_2\}_2]$  (0.20 g; 0.40 mmol) in water ( $10\text{ cm}^3$ ) was shaken with  $\text{AgNO}_3$  (0.27 g; 1.60 mmol). After filtering off the  $\text{AgCl}$ , the orange/yellow solution was treated as above with  $\text{Na}_2\text{SO}_4$  (0.20 g; 1.50 mmol) and then  $\text{Na}_2\text{CO}_3$  (0.08 g; 0.80 mmol) to give orange crystals (0.14 g; 60%)  $\nu(\text{OH})$   $3250\text{ cm}^{-1}$ ;  $\delta(\text{HOH})$   $1640\text{ cm}^{-1}$ ;  $\nu(\text{S-O})$   $1060, 610, 975$  and  $478\text{ cm}^{-1}$  Found: C, 24.4; H, 3.9; O, 30.4; S, 4.7. Calcd. for  $\text{C}_{24}\text{H}_{52}\text{O}_{24}\text{S}_2\text{Ru}_4$ : C, 24.2; H, 4.4; O,

32.2; S, 5.4%.  $\Lambda_m$  ( $10^{-3}$  mol dm $^{-3}$ ) in water = 198 S cm $^2$  mol $^{-1}$ .

The same compound was also prepared by using Na $_2$ HPO $_4$  (0.11 g; 0.80 mmol) instead of Na $_2$ CO $_3$ .

*Tri- $\mu$ -hydroxobis[( $\eta$ -mesitylene)ruthenium(II)] nitrate hydrate (1/1)*. The complex [ {Ru( $\eta$ -C $_6$ H $_3$ Me $_3$ )Cl $_2$  } $_2$ ] (0.23 g; 0.40 mmol) was dissolved in water (15 cm $^3$ ) by refluxing and AgNO $_3$  (0.27 g; 1.60 mmol) added. The AgCl precipitate was filtered off and the yellow filtrate was shaken with an excess of Na $_2$ SO $_4$  (0.20 g; 1.50 mmol) and then Na $_2$ CO $_3$  (0.08 g; 0.40 mmol) for ca. 2 hours. The solution was then concentrated under vacuo to give a yellow crystalline solid, m.p. 195°C (decomp) (0.06 g; 25%) [ $\nu$ (OH) 3250(br) cm $^{-1}$ ,  $\delta$ (HOH) 1650 cm $^{-1}$ ;  $\nu$ (NO) 1045, 830, 720 cm $^{-1}$ ] Found: C, 38.6, H, 4.8; N, 2.5. Calcd. for C $_{18}$ H $_{29}$ NO $_7$ Ru $_2$ : C, 37.7; H, 5.1; N, 2.4% [ $\Lambda_m$  ( $10^{-3}$  mol dm $^{-3}$ ) in water = 69 S cm $^2$  mol $^{-1}$ ]  $^1$ H NMR in D $_2$ O (external Me $_4$ Si capillary reference) at 298 K: 5.30 (s) (H); 2.50 (s) (Me).

Addition of NaBPh $_4$  to an aqueous solution of [Ru $_2$ ( $\eta$ -C $_6$ H $_3$ Me $_3$ ) $_2$ (OH) $_3$ ]-NO $_3$  · H $_2$ O gave [Ru $_2$ (C $_6$ H $_3$ Me $_3$ ) $_2$ (OH) $_3$ ]BPh $_4$ .

*Tri- $\mu$ -hydroxobis[pentamethyl(cyclopentadienyl)rhodium(III)] nitrate hydrate (1/2)*. This was prepared by the same method as [Ru $_2$ (C $_6$ H $_3$ Me $_3$ ) $_2$ (OH) $_3$ ]-NO $_3$  · H $_2$ O starting from [ {Rh( $\eta$ -C $_5$ Me $_5$ )Cl $_2$  } $_2$ ], m.p. 165°C (decomp) (60%) [ $\nu$ (OH) 3250 cm $^{-1}$ ;  $\delta$ (HOH) 1660 cm $^{-1}$ ;  $\nu$ (NO) 1030, 830, 720 cm $^{-1}$ ] Found: C, 38.3; H, 5.5; N, 2.2. Calcd. for C $_{20}$ H $_{37}$ NO $_8$ Rh $_2$ : C, 38.4, H, 5.9; N, 2.2%].

*Tri- $\mu$ -hydroxobis[( $\eta$ -benzene)ruthenium(II)] tetraphenylborate hydrate (1/1)*. The compound [ {Ru( $\eta$ -C $_6$ H $_6$ )OH } $_4$ ](SO $_4$ ) $_2$  · 12 H $_2$ O (0.10 g; 0.08 mmol) was added to NaOH (0.15 g; 4.0 mmol) dissolved in water (5 cm $^3$ ). The solution was warmed gently and an orange precipitate formed. This was filtered off, redissolved in water and addition of NaBPh $_4$  then gave an orange-yellow precipitate, m.p. 195°C (decomp) (0.04 g; 34%) [ $\nu$ (OH) 3620, 3500 cm $^{-1}$ ;  $\nu$ (OH)-(H $_2$ O) 3220 cm $^{-1}$ ;  $\delta$ (HOH) 1620 cm $^{-1}$ ] Found: C, 58.9; H, 4.8. Calcd. for C $_{36}$ H $_{37}$ BO $_4$ Ru $_2$ : C, 57.9, H, 5.0%]  $^1$ H NMR in (CD $_3$ ) $_2$ CO at 298 K: 5.60 (s) ( $\eta$ -C $_6$ H $_6$ ); 6.90–7.60 (m) (BPh $_4^-$ ).

*" $\mu$ -Bromo(di- $\mu$ -hydroxo)bis[( $\eta$ -benzene)ruthenium(II)] hexafluorophosphate hydrate (1/2)"*. The complex [ {Ru( $\eta$ -C $_6$ H $_6$ )OH } $_4$ ](SO $_4$ ) $_2$  · 12 H $_2$ O (0.10 g; 0.08 mmol) was suspended in water and LiBr (0.015 g; 0.16 mmol) was added giving an orange solution. Addition of NH $_4$ PF $_6$  (0.05 g; 0.40 mmol) gave an orange-yellow precipitate, m.p. 170°C (decomp) (0.05 g; 51%) [ $\nu$ (OH) 3640, 3580 cm $^{-1}$ ;  $\nu$ (OH)(H $_2$ O) 3300 cm $^{-1}$ ;  $\delta$ (HOH) 1630 cm $^{-1}$ ] Found: C, 21.6; H, 2.4; Br, 12.9. Calcd. for "C $_{12}$ H $_{18}$ BrF $_6$ O $_4$ PRu $_2$ ": C, 22.0; H, 2.7; Br, 12.3%.

*" $\mu$ -Bromo(di- $\mu$ -hydroxo)bis[( $\eta$ -benzene)ruthenium(II)] tetraphenylborate* was similarly prepared from [ {Ru( $\eta$ -C $_6$ H $_6$ )OH } $_4$ ](SO $_4$ ) $_2$  · 12 H $_2$ O, LiBr and NaBPh $_4$ . [Found: C, 54.8; H, 4.4. Calcd. for "C $_{36}$ H $_{34}$ BBro $_2$ Ru $_2$ ": C, 54.6; H, 4.3%]  $^1$ H NMR in (CD $_3$ ) $_2$ CO at 298 K: 5.92 (s) ( $-\mu$ -Br $_3^-$ ); 5.88 (s) ( $-(\mu$ -OH)-( $\mu$ -Br $_2^-)$ ); 5.70 (s) ( $-(\mu$ -OH $_2$ )( $\mu$ -Br)-); 5.52 (s) ( $-(\mu$ -OH) $_3$ ); 6.90–7.60 (m) (BPh $_4^-$ ).

*Di- $\mu$ -hydroxobis[( $\eta$ -benzene)pyridineruthenium(II)] hexafluorophosphate*. The complex [ {Ru( $\eta$ -C $_6$ H $_6$ )OH } $_4$ ](SO $_4$ ) $_2$  · 12 H $_2$ O (0.10 g; 0.08 mmol) was suspended in water and pyridine (0.50 cm $^3$ ) was added. The solution was gently warmed and addition of NH $_4$ PF $_6$  to the resulting yellow solution gave a yellow

precipitate, m.p. 205°C (decomp) (0.09 g; 68%) [ $\nu(\text{OH})$  3640, 3590  $\text{cm}^{-1}$ ] [Found: C, 31.4, H, 2.9; N, 3.5. Calcd: for  $\text{C}_{22}\text{H}_{24}\text{F}_6\text{N}_2\text{O}_2\text{PRu}_2$ : C, 31.4; H, 2.9; N, 3.3%.]  $\Lambda_m$  ( $10^{-3}$  mol  $\text{dm}^{-3}$ ) in  $\text{CH}_3\text{NO}_2 = 176 \text{ S cm}^2 \text{ mol}^{-1}$ .  $^1\text{H NMR}$  in  $(\text{CD}_3)_2\text{CO}$  at 298 K 2.05 (s) ( $\text{OH}^-$ ); 5.88 (s) ( $\eta\text{-C}_6\text{H}_6$ ), 7.10 (m), 8.30 (m) ( $\text{C}_5\text{H}_5\text{N}$ ). Similarly prepared was di- $\mu$ -hydroxobis[( $\eta$ -benzene)(4-methylpyridine)ruthenium(II)] hexafluorophosphate, m.p. 195°C (decomp.) (0.09 g, 65%) [ $\nu(\text{OH})$  3650, 3590  $\text{cm}^{-1}$ ]. [Found: C, 32.9; H, 3.2; N, 3.3. Calcd. for  $\text{C}_{24}\text{H}_{28}\text{F}_6\text{N}_2\text{O}_2\text{PRu}_2$ : C, 33.2; H, 3.2; N, 3.2%] [ $\Lambda_m$  ( $10^{-3}$  mol  $\text{dm}^{-3}$ ) in  $\text{CH}_3\text{NO}_2 = 150 \text{ S cm}^2 \text{ mol}^{-1}$ ].  $^1\text{H NMR}$  in  $(\text{CD}_3)_2\text{CO}$  at 298 K: 2.45 (s) ( $\text{OH}^-$ ); 5.88 (s) ( $\eta\text{-C}_6\text{H}_6$ ); 2.31 (s) (Me), 6.90 (d); 8.05 (d) ( $\text{MeC}_5\text{H}_4\text{N}$ ).

*Tris(1,10-phenanthroline)ruthenium(II) hexafluorophosphate diethyl-etherate (1/1)*. The complex [ $\{\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{OH}\}_4\text{(SO}_4)_2 \cdot 12 \text{ H}_2\text{O}$ ] (0.10 g; 0.08 mmol) was suspended in water (10  $\text{cm}^3$ ) and an excess of 1,10-phenanthroline (0.20 g; 2.0 mmol) added. The solution was refluxed for 30 min, filtered and addition of  $\text{NH}_4\text{PF}_6$  then gave an orange solid which was recrystallised from acetone/diethyl ether, m.p. >290°C (decomp.) (0.20 g, 70%) [Found: C, 45.6; H, 3.0; N, 7.9. Calcd. for  $\text{C}_{40}\text{H}_{34}\text{F}_{12}\text{N}_6\text{OP}_2\text{Ru}$ : C, 45.3; H, 3.2; N, 7.9%] [ $\Lambda_m$  ( $10^{-3}$  mol  $\text{dm}^{-3}$ ) in  $\text{CH}_3\text{NO}_2 = 161 \text{ S cm}^2 \text{ mol}^{-1}$ ].  $^1\text{H NMR}$  in  $(\text{CD}_3)_2\text{CO}$  at 298 K: 7.72 (m), 8.43 (m), 8.75 (m), 8.85 (m) (1,10-phen).

*Crystal structure determination of A*. Cell dimensions and intensity data were measured on an Enraf-Nonius CAD-4 diffractometer using monochromatised  $\text{Mo-K}_\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ). The cell was refined using 24 reflections equivalent to 1, 6, 11 ( $2\theta = 51.30^\circ$ ). In view of the extensive disorder reported previously [2], a more extensive data set was collected and the refinement reported here was based on it. Intensities were measured for 1741 reflections to  $2\theta = 70^\circ$ , and these were reduced to 416 independent data including 48 systematic absences. The merging gave an estimated  $R$ -factor of 0.043 and no indication of deviation from cubic symmetry. No absorption corrections were made; the crystal used for data collection was an octahedron of edge 0.05 mm. Refinement was based on the 245 reflections with  $I \geq 3\sigma(I)$ . To rule out the possibility of the space group being  $F43c$  (with  $a = 24.81 \text{ \AA}$ ) all reflections of type  $uuu$  in that cell with  $2\theta \leq 30^\circ$  were measured and none gave  $I > \sigma(I)$ . The refinement is described in the main part of the text. For the final cycles, a weighting scheme of  $W = 1.0$  for  $F_0$  100,  $W^{1/2} = 100/F_0$  otherwise was used. At convergence, based on 22 adjustable parameters,  $R = 0.048$ ,  $R_w = 0.058$ . An analysis of agreement showed good uniformity except for reflections with low  $\sin \theta$  values, where the poor modelling of the disordered water would be most serious. A table of observed and calculated structure factors may be obtained on request from the authors. Crystallographic calculations made use of the SHELX and XRAY program systems [11].

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