# Preparation, *X*-Ray Crystal Structure Analysis, and Reactions of a Novel, Hydroxo-Bridged, Tetranuclear, π-Arene Ruthenium(II) Quadrivalent Cation $[\{(\eta^6\text{-}C_6H_6)Ru(OH)\}_4](SO_4)_2\cdot 12H_2O$

By ROBERT O. GOULD,* C. LYNN JONES, DONALD R. ROBERTSON, and T. ANTHONY STEPHENSON*
(*Department of Chemistry, University of Edinburgh, Edinburgh* EH9 3JJ)

*Summary* Reaction of $[\{(\eta^6\text{-}C_6H_6)RuCl_2\}_2]$ with aqueous sodium carbonate (1 : 2 molar ratio) and excess of sodium sulphate gives the title compound (II) whose structure has been determined by *X*-ray diffraction; a mechanism of formation and some reactions of (II) are also outlined.

RECENTLY,[1] we reported that the reaction of $[\{(\eta^6\text{-}C_6H_6)RuCl_2\}_2]$ with an excess of aqueous sodium hydroxide gave the yellow triple hydroxy-bridged cation $[(\eta^6\text{-}C_6H_6)Ru(OH)_3Ru(\eta^6\text{-}C_6H_6)]Cl.3H_2O$ (I). The same compound is also formed using excess of aqueous sodium carbonate.

We now find that if $[\{(\eta^6\text{-}C_6H_6)RuCl_2\}_2]$ is treated with less sodium carbonate ($[Ru^{2+}] : [CO_3^{2-}]$ *ca.* 1 : 1 molar ratio) and the resulting solution treated with excess of sodium sulphate, orange crystals are precipitated in low yield (*ca.* 25%) and these have been shown by *X*-ray analysis to be the novel tetrameric complex (II) containing both π-bonded benzene groups and hydroxo bridges.

*Crystal data:* $C_{24}H_{52}O_{24}Ru_4S_2$, *M* 1192, cubic, $a = 12{\cdot}362(2)$ Å, $U = 1889$ Å$^3$, $Z = 2$, $D_m = 2{\cdot}10$, $D_c = 2{\cdot}14$ g cm$^{-3}$, space group *Pn*3*m* (no. 224). From precession photographs (Mo-$K_\alpha$ radiation) 204 independent intensities were obtained using a Saab Mark II film scanner linked to a PDP-15 computer. The structure was solved by Patterson and difference Fourier syntheses and has been refined to $R = 0{\cdot}11$ based on all non-hydrogen atoms except the water molecules and the three oxygen atoms of each sulphate ion which do not lie on a three-fold axis.†

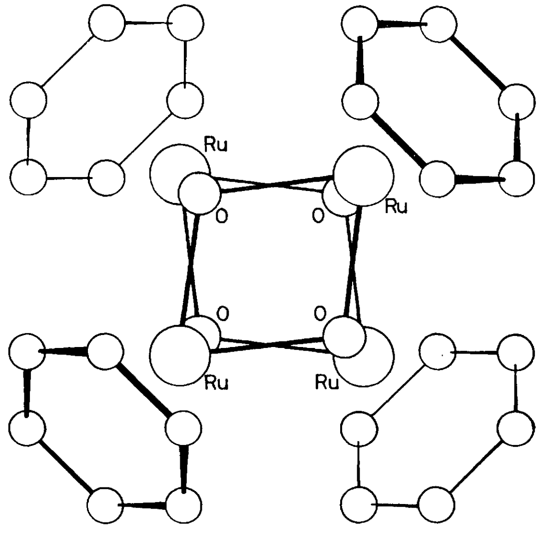
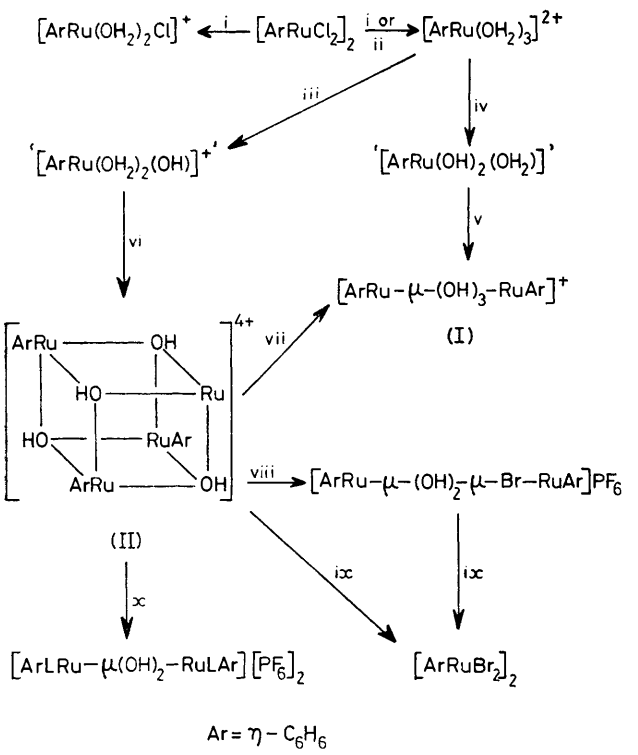


FIGURE. Structure of $[\{(\eta^6\text{-}C_6H_6)Ru(OH)\}_4]^{4+}$

---

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by a full literature citation for this communication.

The structure consists of discrete cations with the formula $[\{(\eta^6\text{-}C_6H_6)Ru(OH)\}_4]^{4+}$ and sulphate anions. The cations have crystallographic $\bar{4}3m$ ($T_d$) symmetry containing interpenetrating tetrahedra of ruthenium and oxygen atoms. Each ruthenium atom has bonds to three hydroxy groups of equal length (2·12 Å) and the O–Ru–O and Ru–O–Ru angles are 76·3 and 102·2° respectively. The arrangement of ruthenium and oxygen atoms may thus be described as a substantially distorted cube in which the Ru – – – Ru and O – – – O diagonals are 3·29 and 2·62 Å, respectively (see Figure) (*cf.* $[Me_3Pt(OH)]_4$[2]). The ruthenium atoms in (II) are also bound to benzene rings, located 1·74 Å further out along the three-fold axes (Ru–C = 2·23 Å). The rings are, however, disordered with essentially equal site occupancy over two locations related by a 30° rotation about the axis. The sulphate ions in (II) are disordered on sites of $\bar{3}m$ ($D_{3d}$) symmetry and only the half-occupied sites on the three-fold axes could be identified in the electron density maps.



SCHEME. i, $H_2O$; ii, $AgNO_3$ or $AgBF_4$; iii, $Na_2CO_3$ (1:1 molar ratio); iv, excess of $Na_2CO_3$ or NaOH; v, dimerisation; vi, excess of $Na_2SO_4$; vii, aqueous NaOH; viii, aqueous LiBr (1:2 molar ratio), then $NH_4PF_6$; ix, excess of aqueous LiBr; x, L = pyridine or γ-picoline, then $NH_4PF_6$.

The cations are centred at the points $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$ in the cell, and are each linked to four others by contacts of benzene rings (3·3 Å) and to a further four by hydrogen bonds to sulphate ions from the OH groups (O – – – O *ca.* 2·6 Å). The resulting structure is very open, and contains channels with van der Waals diameters of about 3·2 Å parallel to each of the three crystallographic axes, and intersecting in pairs at the points $\frac{1}{4}, \frac{1}{4}, \frac{3}{4}$, *etc.* Difference Fourier syntheses indicate broad, low regions of electron density in these channels and the water molecules are presumably randomly arranged there. Heating a powdered sample of (II) to 100 °C results in the reversible loss of water, also indicating that it is not tightly held in chemically discrete sites.‡

The probable mechanism of formation of (I) and (II) is shown in the Scheme. Thus, earlier[3] it was suggested that in aqueous solution $[\{(\eta^6\text{-}C_6H_6)RuCl_2\}_2]$ gave a mixture of $[(\eta^6\text{-}C_6H_6)RuCl(H_2O)_2]^+$ and $[(\eta^6\text{-}C_6H_6)Ru(H_2O)_3]^{2+}$ and therefore, in basic solution, successive deprotonation of the latter should give $[(\eta^6\text{-}C_6H_6)Ru(OH)(H_2O)_2]^+$ and $[(\eta^6\text{-}C_6H_6)Ru(OH)_2H_2O]$ respectively with the dihydroxo species favoured in strongly basic solutions. Because of the bridging propensity of hydroxo groups and the desire of ruthenium(II) to exhibit six-co-ordination,[4] it seems reasonable that $[(\eta^6\text{-}C_6H_6)Ru(OH)_2H_2O]$ will tend to dimerise with concomitant elimination of water to form (I) and similarly, $[(\eta^6\text{-}C_6H_6)Ru(OH)(H_2O)_2]^+$ will tetramerise to form (II). The latter process is enhanced by addition of sulphate ion which removes the tetrameric cation from solution.

Support for the correctness of this mechanism comes from the observation that reaction of $[\{(\eta^6\text{-}C_6H_6)RuCl_2\}_2]$ with either aqueous $AgNO_3$ or $AgBF_4$ {which produces the $[(\eta^6\text{-}C_6H_6)Ru(H_2O)_3]^{2+}$ cation in high yield} followed by addition of $Na_2CO_3$ (1:1 molar ratio) and excess of $Na_2SO_4$ gives (II) in much higher yields (*ca.* 60%).

Finally, preliminary work (see Scheme) shows that (II) undergoes some interesting reactions. For example, with hydroxide ion, (I) is formed whereas addition of LiBr (1:2 molar ratio) gives the mixed triple bridged $[(\eta^6\text{-}C_6H_6)Ru(OH)_2BrRu(\eta^6\text{-}C_6H_6)]^+$ cation; with excess of $Br^-$ the insoluble $[\{(\eta^6\text{-}C_6H_6)RuBr_2\}_2]$[3] is precipitated. In contrast, with neutral Lewis bases, *e.g.* pyridine or γ-picoline (L) the double hydroxo bridged cations $[(\eta^6\text{-}C_6H_6)LRu(OH)_2RuL(\eta^6\text{-}C_6H_6)](PF_6)_2$ can be isolated.

We thank the S.R.C. for financial support (to C.L.J. and D.R.R.) and Johnson-Matthey Ltd. for generous loans of hydrated ruthenium trichloride.

(*Received*, 15*th December* 1976; *Com.* 1365.)

---

‡ The presence of twelve water molecules of hydration is based upon full elemental analyses and the *X*-ray molecular weight determination.

[1] D. R. Robertson and T. A. Stephenson, *J. Organometallic Chem.*, 1976, **116**, C29.
[2] H. S. Preston, J. C. Mills, and C. H. L. Kennard, *J. Organometallic Chem.*, 1968, **14**, 447; T. C. Spiro, D. H. Templeton, and A. Zalkin, *Inorg. Chem.*, 1968, **7**, 2165.
[3] R. A. Zelonka and M. C. Baird, *Canad. J. Chem.*, 1972, **50**, 3063.
[4] See P. W. Armit, W. J. Sime, and T. A. Stephenson, *J.C.S. Dalton*, 1976, 2121.