Triple Halide-bridged Diruthenium Complexes in Higher Oxidation States

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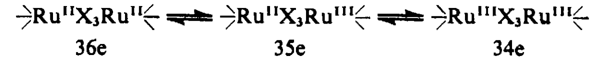
The $NBu^n{}_4{}^+$ salt of $[Ru_2{}^{III,III}Br_9]^{3-}$ is soluble in organic solvents and electrochemical studies in CH_2Cl_2–0.50 mol dm^{-3} $[NBu^n{}_4][BF_4]$ at 233 K show it to have three reversible, one-electron processes: namely oxidations at +0.83 and +1.36 V and a reduction at −0.60 V. Preparative-scale electrogeneration of the $[Ru_2{}^{III,IV}Br_9]^{2-}$ and $[Ru_2{}^{IV,IV}Br_9]^-$ ions has been achieved, and variable-temperature magnetic measurements on anolyte solutions of the former ($\mu_{eff.}$ = 4.40 μ_B per molecule at 273 K) indicate three unpaired electrons per molecule.

In recent publications [1] we have drawn attention to the occurrence in three distinct oxidation levels, ranging from $Ru_2{}^{II,II}$ to $Ru_2{}^{III,III}$, of various triple chloro-bridged binuclear complexes of general form $[L_{3-x}Cl_xRuCl_3RuCl_yL_{3-y}]^z$ where L are neutral ligands such as PR_3, AsR_3, CO, *etc.*[1] and NH_3 [2] and H_2O.[3] Furthermore, extensive voltammetric studies have established that the individual complexes generally display two reversible one-electron transfers to connect these oxidation levels (Scheme 1).[1]



$$\rightarrow Ru^{II}X_3Ru^{II}\leftarrow \rightleftharpoons \rightarrow Ru^{II}X_3Ru^{III}\leftarrow \rightleftharpoons \rightarrow Ru^{III}X_3Ru^{III}\leftarrow$$

Scheme 1.

Preparative-scale electrogeneration of a number of such triads of redox-related species has been achieved and variable-temperature magnetic measurements on the diruthenium(III) compounds, together with the intervalence charge-transfer bands of the ruthenium(II)ruthenium(III) compounds, reveal that the degree of metal–metal interaction in these confacial bioctahedral systems increases as the asymmetry in chloride ligation ($u = y - x$) in $[L_{3-x}Cl_xRuCl_3RuCl_yL_{3-y}]^z$ decreases.[1]

The pattern of electrode potentials is also largely determined by the level ($y + x$) and asymmetry ($y - x$) of terminal halide binding. For example, substitution of PMe_2Ph by chloride in $[(PMe_2Ph)_3RuCl_3Ru(PMe_2Ph)_3]^{3+}$ causes shifts in the first reduction potential of −0.75 V for each additional chloride at the redox-active centre and −0.25 V for attachment at the remote ruthenium.[1,4] Unrefined extrapolation to exhaustively substituted $[Ru_2X_9]^{3-}$ ions (X = Cl or Br) suggests that the $E_{\frac{1}{2}}(Ru_2{}^{III,III}–Ru_2{}^{II,III})$ couple could shift by a remarkable −3.0 V compared to $[(PMe_2Ph)_3RuCl_3Ru(PMe_2Ph)_3]^{3+/2+}$. From the limited number of analogues available, *e.g.* $[(PMe_2Ph)_3RuBr_3Ru(PMe_2Ph)_3]^{+/2+/3+}$, it appears that the corresponding bromo-systems have very similar electrochemical behaviour, in accord with Scheme 1.[4]

We now describe the electrochemical behaviour of the highly symmetrical $[Br_3Ru^{III}Br_3Ru^{III}Br_3]^{3-}$ ion and report the bulk electrogeneration of the new redox-related $[Ru_2Br_9]^{n-}$ ions (n = 2 or 1) which are respectively the first examples of diruthenium 33 and 32 valence-electron, triple halide-bridged systems.

Results and Discussion

The salt $K_3[Ru_2Br_9]$ was readily prepared by the method described by Fergusson and Greenaway,[5] namely reaction of '$RuCl_3 \cdot xH_2O$' with a concentrated HBr–ethanol mixture followed by addition of KBr. This material is freely soluble only in water (in which electrochemical studies are very limited). However, we find that treatment of the aqueous solution with $[NBu^n{}_4]Br$ induces precipitation of $[NBu^n{}_4]_3[Ru_2Br_9]$ which dissolves readily in organic solvents. The $PPh_3(CH_2Ph)^+$ salt was similarly prepared.

The constitution of these $M_3[Ru_2Br_9]$ compounds was confirmed by elemental analyses and conductivity measurements (see Experimental section).

Magnetochemistry of $[NBu^n{}_4]_3[Ru_2Br_9]$.—For $Cs_3[Ru_2Br_9]$ [5] the reported solid-state magnetic moment $\mu_{eff.}$ is 1.01 μ_B per Ru at 296 K. From susceptibility measurements by the Evans method [6] on $[NBu^n{}_4]_3[Ru_2Br_9]$ in CH_2Cl_2, we calculate $\mu_{eff.}$ = 1.19 μ_B per Ru at 299 K, confirming that the effective magnetic moment per ruthenium atom is depressed from that characterising monomeric ruthenium(III) complexes. This evidence establishes the presence of significant interactions between the paramagnetic centres within the symmetric binuclear complex, (*cf.* $[\{As(C_6H_4Me\text{-}p)_3\}_2ClRu^{III}Cl_3Ru^{III}Cl\{As(C_6H_4Me\text{-}p)_3\}_2]^+$ (u = 0) [1] where $\mu_{eff.}$ = 0.91 μ_B per Ru at 233 K). Comparison may be made with the lower symmetry $[\{As(C_6H_4Me\text{-}p)_3\}_2ClRu^{III}Cl_3Ru^{III}Cl_2\{As(C_6H_4Me\text{-}p)_3\}]$ (u = 1) [1] where $\mu_{eff.}$ = 1.45 μ_B per Ru at 229 K and 1.61 μ_B per Ru at 297 K, and $[\{As(C_6H_4Me\text{-}p)_3\}_3Ru^{III}Cl_3Ru^{III}Cl_2\{As(C_6H_4Me\text{-}p)_3\}]^+$ (u = 2) [1] where $\mu_{eff.}$ = 2.01 μ_B per Ru even at 233 K.

The measured Ru–Ru internuclear distances of 2.86 Å in $Cs_3[Ru_2Br_9]$ (powder diffraction data) [5] and 2.725 (3) Å in the recently reported $Cs_3[Ru_2Cl_9]$ (three-dimensional single-crystal diffraction data) [7] are in keeping with the magnetic data for these symmetric systems.

In the case of $[Ru_2Cl_9]^{3-}$, Cotton and co-workers [8] have calculated by the SCF-Xα-SW method that the ground-state valence-electron structure is $a_1'^2e'^4e''^4$. The reported magnetic moment of $Cs_3[Ru_2Cl_9]$ is particularly low ($\mu_{eff.}$ = 0.51 μ_B per Ru at 300 K) and indeed has been attributed to temperature-independent paramagnetism rather than to contributions from thermally accessible triplet states.[7]

Voltammetry of $[NBu^n{}_4]_3[Ru_2Br_9]$.—Cyclic voltammetry (c.v.) and linear stirred voltammetry (s.v.) together with a.c. voltammetry (a.c.v.) at platinum electrodes in CH_2Cl_2 establish that at 233 K $[NBu^n{}_4]_3[Ru_2Br_9]$ undergoes reversible, stepwise oxidations at +0.83 and +1.36 V and a quasi-reversible reduction at −0.60 V (Figure).† Unlike the two oxidations, the reduction step shows no c.v. return wave at room temperature due to rapid breakdown of $[Ru_2Br_9]^{4-}$.

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† All potentials are corrected to 293 K and were measured in CH_2Cl_2–0.50 mol dm^{-3} $[NBu^n{}_4][BF_4]$ *vs.* a Ag–AgCl reference at which ferrocene is oxidised at +0.55 V.

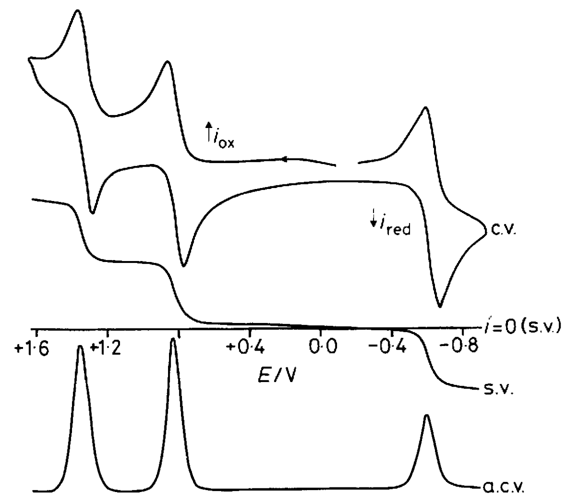

Figure. Voltammetry of $[NBu^n{}_4]_3[Ru_2Br_9]$ in CH_2Cl_2 at 233 K. Scan rates: 100 mV s^{-1} (c.v.); 10 mV s^{-1} (s.v. and a.c.v.). Potentials *vs.* Ag–AgCl reference (against which ferrocene is oxidised at +0.55 V)

The one-electron nature of these steps is indicated by the equal heights of the low-temperature s.v. waves, the a.c.v. peak widths at half-height at 233 K (72 mV, independent of the a.c. frequency (ω) in the range 40—400 Hz), the characteristic diffusion coefficient ($D = 4.73 \times 10^{-6}$ cm^2 s^{-1} at 285 K, measured at +1.0 V),[9] and finally by coulometric measurements which show that the first oxidation step corresponds to the loss of 1.0 electron per molecule of $[Ru_2Br_9]^{3-}$. These features have been separately confirmed for the $PPh_3(CH_2Ph)^+$ salt.

$$\underset{35e}{[Ru_2{}^{II,III}Br_9]^{4-}} \xrightleftharpoons{-0.60\,V} \underset{34e}{[Ru_2{}^{III,III}Br_9]^{3-}} \xrightleftharpoons{+0.83\,V}$$

$$\underset{33e}{[Ru_2{}^{III,IV}Br_9]^{2-}} \xrightleftharpoons{+1.36\,V} \underset{32e}{[Ru_2{}^{IV,IV}Br_9]^{-}}$$

Scheme 2.

Hence, these observations establish the sequence of metal-based redox interconversions shown in Scheme 2. The $[Ru_2Br_9]^{3-}$ ion is reported[5] to undergo chemical oxidation in solutions containing excess of bromide ion to form $[Ru^{IV}Br_6]^{2-}$ (*i.e.* $[Ru_2Br_9]^{3-} + Br^- + Br_2 \rightleftharpoons 2[RuBr_6]^{2-}$). Electrochemical studies on $[PPh_3(CH_2Ph)]_2[RuBr_6]$ in CH_2Cl_2–0.20 mol dm^{-3} $[NBu^n{}_4][BF_4]$ show a reduction wave at +0.20 V (irreversible at 300 K but reversible at 233 K) and an oxidation wave at +1.55 V (irreversible at all temperatures). Hence this species is clearly *absent* in the electrochemical oxidation of $[Ru_2Br_9]^{3-}$ described above.

It is interesting to note that the cumulative effect of exhaustive bromo-substitution has made the 33- and 32-electron species accessible while shifting the 34–35 electron couple *ca.* −2.5 V with respect to that of $[Ru_2Cl_3(PMe_2Ph)_6]^{3+/2+}$.

Magnetic Studies on Electrogenerated $[Ru_2Br_9]^{n-}$ *Ions.*—In order to explore further the structural and electronic changes which might accompany these stepwise electron-transfer processes in the $[Ru_2Br_9]^{3-}$ ions, we have sought to electrogenerate the $[Ru_2Br_9]^{n-}$ ions (n = 4, 2, or 1) on a preparative scale. Unfortunately, bulk electrosynthesis of the $[Ru_2Br_9]^{4-}$ ion has not been accomplished even at 200 K because of the very low stability of the material.

Table. Magnetic measurements on $[NBu^n{}_4]_2[Ru_2Br_9]$

T/K	$10^6\chi_M$(corr)	$1/\chi_M$(corr)	$\mu_{eff.}(\mu_B)$ per molecule
273	8 792	113.7	4.40
263	9 146	109.3	4.40
252	9 425	106.1	4.38
242	9 592	104.3	4.33
231	9 851	101.5	4.28
220	9 962	100.4	4.20
210	10 231	97.7	4.16
200	10 429	95.9	4.10
190	10 479	95.4	4.01

However, controlled-potential electrolysis in CH_2Cl_2–0.50 mol dm^{-3} $[NBu^n{}_4][BF_4]$ at +1.0 V and 223 K of $[NBu^n{}_4]_3[Ru_2Br_9]$ proceeds smoothly with the expected exponential decay of current. The percentage conversion was monitored by stirred voltammetry and essentially quantitative conversion into the $[Ru_2Br_9]^{2-}$ ion was achieved. This anion is quite stable in solution up to 273 K although ready decomposition occurs at higher temperatures. Magnetic studies were made on the anolyte solution between 190 and 273 K by the Evans method. From duplicate measurements on separately electrogenerated solutions, we calculate that for the $[Ru_2Br_9]^{2-}$ ion a plot of $1/\chi_M$(corr) *vs.* T is linear with intercept $\theta = -234$ K, and $\mu_{eff.} = 4.40\ \mu_B$ per molecule at 273 K decreasing to 4.01 μ_B at 190 K.

These results imply that $[Ru_2Br_9]^{2-}$ possesses *three* unpaired electrons per molecule (whereas one unpaired electron might have been anticipated following oxidation of either $a_1'^2e'^4e''^4$ or $a_1'^2e'^4e''^3a_2''^1$ states of $[Ru_2Br_9]^{3-}$). Thus, in contrast to $[Ru_2Br_9]^{3-}$, it appears that the oxidised complex contains only loosely coupled ruthenium(III) (d^5) and ruthenium(IV) (d^4) centres, having one and two unpaired electrons respectively. The striking possibility exists that the 33-electron complex $[Ru_2Br_9]^{2-}$ might have a flickering asymmetric geometry with ' trapped ' spin centres [as demonstrated for the related 35-electron ruthenium(II)ruthenium(III) complexes discussed earlier[1]].

In any event the much smaller Ru–Ru interaction in $[Ru_2Br_9]^{2-}$, compared to $[Ru_2Br_9]^{3-}$, is in accord with the decreased metal d-electron density in higher oxidation states. This view receives strong support from very recent structural studies by Cotton *et al.*[10] on the related $[W_2Cl_9]^{n-}$ ions (n = 2 or 3). They find that the internuclear distance in $[W_2Cl_9]^{2-}$ [2.540(1) Å] is 0.122(9) Å longer than in $[W_2Cl_9]^{3-}$, and attribute this effect largely to the increased mean oxidation state of the metal atoms, whereby the d orbitals contract leading to weaker σ bonding.

From a molecular orbital viewpoint, increased Ru–Ru separation due to such effects in $[Ru_2Br_9]^{2-}$ could result in near degeneracy in the valence-orbital manifold[11] and hence a readily accessible spin-quartet state $a_1'^2e'^4e''^2a_2''^1$. In the limit of negligible bonding, the two ruthenium centres could become almost independent as suggested above, although the orthodox molecular orbital description implies a symmetrical charge distribution for such binuclear complexes.

Electrogeneration of the diruthenium(IV) complex $[Ru_2Br_9]^-$ proceeds smoothly to *ca.* 80% conversion at 200 K and examination of the resulting solution by s.v. and c.v. establishes the formation of the stable monoanion. However the electrosynthesis appears to halt abruptly and reproducibly at this point. This is presumably due to the fact that the requisite oxidation potential is substantially more positive than that of free bromide and even 1% dissociation of the complex would make 80% electrolysis the thermodynamic limit. Magnetic measurements confirm the compound is less paramagnetic than the $[Ru_2Br_9]^{2-}$ precursor but, in the circumstances, quantitative discussion is unwarranted.

Studies in collaboration with Professor F. A. Cotton are now in hand to evaluate the alternative descriptions of these systems. These include further SCF-Xα-SW calculations on the $[Ru_2X_9]^{n-}$ ions, together with electrochemical examination of the chloride system and attempts to isolate single crystals for $n = 2$ or 1.* A detailed comparison of the electronic spectra of the various electrogenerated anions will also be described.

Experimental

Microanalyses were by the Butterworth Micro Analytical Consultancy and the University of Edinburgh Chemistry Department. Infrared spectra were recorded in the region 4 000—200 cm^{-1} on a Perkin-Elmer 557 grating spectrometer using Nujol mulls on caesium iodide plates. Solution magnetic measurements (Evans method) were obtained on a Varian HA 100 n.m.r. spectrometer equipped with a variable-temperature probe. Electronic spectra were obtained on a Pye-Unicam SP8-400 spectrophotometer. Conductivity measurements were made in CH_3NO_2 at 303 K using a model 310 Portland Electronics conductivity bridge. Melting points were determined with a Köfler hot-stage microscope and are uncorrected.

Investigative electrochemistry was performed using a PAR model 170 potentiostat and programmer and $[NBu^n_4][BF_4]$ solutions (0.50 mol dm^{-3}) in CH_2Cl_2 (293—200 K) with platinum working and auxiliary electrodes and an Ag–AgCl reference electrode (against which ferrocene is oxidised at $E_{\frac{1}{2}} = +0.55$ V, which is *ca.* 50 mV removed from the s.c.e. values). All electrosyntheses were carried out using a Hi-Tek type DT2101 potentiostat in conjunction with a Hi-Tek type PPR1 waveform generator and associated bipotentiostat module for voltammetric monitoring.

Potassium Tri-μ-bromo-hexabromodiruthenate(III).—The compound ' $RuCl_3 \cdot xH_2O$ ' (0.50 g) was dissolved in 100 cm^3 of a mixture (1 : 1 v/v) of concentrated HBr (48%) and ethanol and heated under reflux under a nitrogen atmosphere for 2 h. A stoicheiometric amount of KBr (0.34 g) was then added and on concentration and cooling of the solution the black microcrystalline product precipitated. This was filtered off, washed with ethanol and diethyl ether, and dried *in vacuo*, yield 0.80 g (81%). Electronic spectrum (in water) (40 000—10 000 cm^{-1}): 35 710 ($\varepsilon = 21\,090$), 32 050 (14 140), 24 390 (3 970), and 20 330 cm^{-1} (4 540 dm^3 mol^{-1} cm^{-1}).

Tetra-n-butylammonium Tri-μ-bromo-hexabromodiruthenate(III).—This was prepared from the potassium salt by treatment of an aqueous solution of the latter with an excess of $[NBu^n_4]Br$. The precipitated purple solid was washed with water and diethyl ether and dried *in vacuo* at 40 °C, m.p. 194 °C. The yield was almost quantitative (Found: C, 35.1; H, 6.6; N, 2.7. Calc. for $C_{48}H_{108}Br_9N_3Ru_2$: C, 34.9; H, 6.6; N, 2.6%); Λ (0.95×10^{-3} mol dm^{-3}) in CH_3NO_2 = 177 S cm^2 mol^{-1}. Electronic spectrum (in CH_2Cl_2) (40 000—10 000 cm^{-1}): 34 720 ($\varepsilon = 26\,740$), 30 960 (18 200), 23 360 (4 120), and 19 720 cm^{-1} (6 050 dm^3 mol^{-1} cm^{-1}).

Benzyltriphenylphosphonium Tri-μ-bromo-hexabromodiruthenate(III).—This was similarly prepared by treatment of aqueous solutions of $K_3[Ru_2Br_9]$ with an excess of $[PPh_3(CH_2Ph)]Cl$, m.p. 135—137 °C (decomp.) (Found: C, 44.3; H, 3.4; Br, 36.3; P, 4.4. Calc. for $C_{75}H_{66}Br_9P_3Ru_2$: C, 45.4; H, 3.3; Br, 36.3; P, 4.6%); Λ (1×10^{-3} mol dm^{-3}) in CH_3NO_2 = 232 S cm^2 mol^{-1}. Electronic spectrum (in CH_2Cl_2) (40 000—10 000 cm^{-1}): 34 970 cm^{-1} ($\varepsilon = 27\,460$), 31 250 (19 350), 23 470 (4 970), and 19 680 cm^{-1} (6 270 dm^3 mol^{-1} cm^{-1}).

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* *Note added at proof:* we have now prepared $[NBu^n_4]_3[Ru_2Cl_9]$ and shown that it has closely comparable redox behaviour, with E_{red} (1) = −0.57, E_{ox} (1) = +0.92, and E_{ox} (2) = +1.58 V, in CH_2Cl_2.