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# Preparation and Properties of some Nonachloro-*triangulo*-triruthenate(II) Salts and Related Species: Novel Trimeric and Dimeric Ruthenium(II) Complexes

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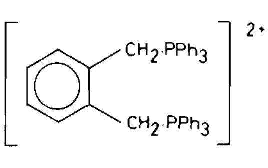
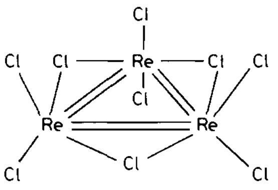
Charonnat, in 1931, reported the preparation of yellow-brown tetrachlorobis(pyridine)ruthenium(IV), $[RuCl_4(py)_2]$ (py = pyridine), by the oxidation of an aqueous solution of commercial '$RuCl_3 \cdot xH_2O$' with hydrogen peroxide, followed by the addition of a solution of pyridine in hydrochloric acid [1]. Despite the more recent preparations of the paramagnetic, black or dark-purple complexes $[RuCl_4(2,2'\text{-bipy})]$ [2, 3] and $[RuCl_4(phen)]$ [2, 3] (2,2'-bipy = 2,2'-bipyridine; phen = 1,10-phenanthroline), formed under vigorously oxidising conditions, the formation of $[RuCl_4(py)_2]$ under the conditions described [1] seemed open to doubt, and we indeed report here the non-repeatability of the preparation. The product of the reaction is a red-brown powder, of empirical formula $(pyH)[RuCl_3]$†. By the addition of a variety of monopositive (A) and dipositive (B) cations to a red-brown solution prepared by heating an aqueous solution of $RuCl_3 \cdot xH_2O$ with excess hydrogen peroxide (until the latter was completely decomposed), two series of red-brown complexes were isolated: $A[RuCl_3]$ {A = pyH, quinH (quin = quinoline), Cs, $Ph_4As$}† and $B_2[Ru_3Cl_{10}]$ {B = 2,2'-$bipyH_2$, 4,4'-$bipyH_2$(4,4'-bipy = 4,4'-bipyridine), cat [4]}†. Infrared and electronic spectral studies upon these complexes (*vide infra*) indicate that they all contain the same anion, and so the simplest formulations of these complexes (consistent with these data) are as $A_3[Ru_3Cl_9]$ and $B_2[Ru_3Cl_9]Cl$. The complex $[Ru(2,2'\text{-bipy})_3]_3[Ru_3Cl_9]_2$†was also prepared in a similar manner.



The formulation of the anion as $[Ru_3Cl_9]^{3-}$ invites a comparison with the complexes $[Re_3Cl_9]$, $[Re_3Cl_9L_3]$ (L = $H_2O$, py, *etc.*), $A[Re_3Cl_{10}]$, $A_2[Re_3Cl_{11}]$ and $A_3[Re_3Cl_{12}]$ [5]. If it is tentatively assumed that the $[Ru_3Cl_9]^{3-}$ anion is isostructural with an isolated $Re_3Cl_9$ unit (I), then it classifies as an eighteen electron species, containing formal double metal–metal bonds analogous to those found in $[Re_3Cl_9]$. Indeed, there is a remarkable similarity between the low-energy regions of the electronic spectra of $[Ru_3Cl_9]^{3-}$ and $[Re_3Cl_9]$ (Fig. 1), as might be expected in view of the occurrence of transitions associated with the double metal–metal bond which dominate this region [6]. The salts $A_3[Ru_3Cl_9]$ and $B_2[Ru_3Cl_9]Cl$ all contain bands at *ca.* 21000, *ca.* 14000 and *ca.* 7500 $cm^{-1}$ in their diffuse reflectance spectra. Typical of the spectra obtained in solution (in 2.4 *M* hydrochloric acid) is that of $(pyH)_3[Ru_3Cl_9]$: 21500 ($\epsilon$ = 11200), 14500 ($\epsilon$ = 150), 11500 (shoulder) and 8000 $cm^{-1}$ ($\epsilon$ = 60 l $mol^{-1}$ $cm^{-1}$). The room temperature magnetic moments of $Cs_3[Ru_3Cl_9]$ and $[Re_3Cl_9]$ are also



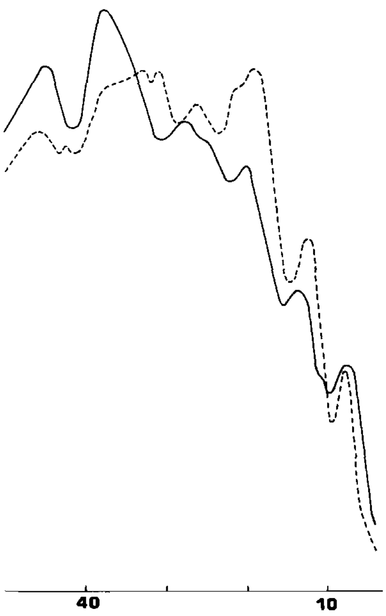


Fig. 1. Diffuse reflectance spectra of $Cs_3[Ru_3Cl_9]$ (——) and $Re_3Cl_9$ (---------). Ordinate: absorbance (arbitrary units); abscissa: $10^{-3}\,\tilde{\nu}/cm^{-1}$.

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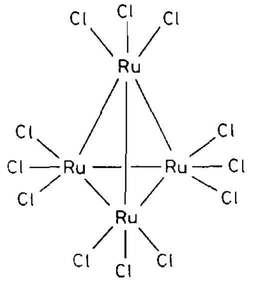
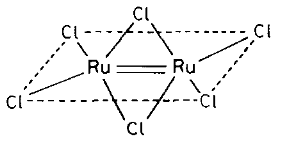
†All complexes reported in this communication give satisfactory elemental analyses.

similar: $\mu_{eff}$ being 0.97 $\mu_B$ and 1.12 $\mu_B$ [7], respectively (both values are quoted per 3 metal atoms). Octahedral ruthenium(II) in a conventional chloride environment would be expected to be diamagnetic, and show no bands in its electronic spectrum below *ca.* 13000 cm$^{-1}$ [8, 9]. The infrared spectra of the salts $A_3[Ru_3Cl_9]$ and $B_2[Ru_3Cl_9]Cl$ all show a strong broad band at *ca.* 325 cm$^{-1}$. This is assigned to the accidental coincidence of the terminal $\nu(RuCl_2)$ and bridging $\nu(Ru_2Cl)$ modes. Conductivity measurements upon $A_3[Ru_3Cl_9]$ (A = pyH, $Ph_4As$) in ethanenitrile (25 °C) give $(\Lambda_M)_\infty \sim 435\ \Omega^{-1}\ cm^2\ mol^{-1}$, typical of values found for 3:1 electrolytes [10] (although the assumption of monomeric or dimeric formulations, it should be emphasised, would equally well fit the ranges expected for 1:1 or 2:1 electrolytes). All attempts to grow crystals of these cluster complexes have, as yet, been unsuccessful.

Two examples of salts of empirical formulation $A[RuCl_3]$ have previously been reported [11]. These are the green salts $(pyH)[RuCl_3]$ and $(Et_4N)[RuCl_3]$, prepared by saturating the blue ruthenium(II) chloride solution [12] (prepared by reducing methanolic $RuCl_3 \cdot xH_2O$ with dihydrogen in the presence of trace amounts of $PtO_2$ [11]) with hydrogen chloride, and adding a similarly saturated solution of ACl in methanol. The green air-sensitive $(pyH)[RuCl_3]$ is isomeric with the red-brown air-stable $(pyH)_3[Ru_3Cl_9]$.

We have prepared green $(pyH)[RuCl_3]^\dagger$ (and also green $Cs[RuCl_3]^\dagger$) by Rose and Wilkinson's route [11], and confirm their empirical formulation. However, we do not agree with their proposed tetrameric structure (II), which was based on the two fallacious assumptions that (i) ruthenium(II) in a chloride complex must be in an octahedral environment (*cf.* the *pseudo*-tetrahedral environment found in $[Ru_2(S_2CNPr_2)_5]_2[Ru_2Cl_6]$ [13]) and that (ii) a band at 300 cm$^{-1}$ in the infrared spectrum is at too high an energy for $\nu(Ru_2Cl)$ (*cf.* $\nu(Ru_2Cl)$ occurs at 376 cm$^{-1}$ in $\beta$-$RuCl_3$ [14]). Instead, we propose that the cation has structure (III), which was found in a single-crystal X-ray structural determination upon $[Ru_2(S_2CNPr_2)_5]_2[Ru_2Cl_6] \cdot 2CHCl_3$ [13]. This material was a minor by-product in the preparation of $Ru(S_2CNPr_2)_3$, and has not been prepared in sufficient quantities to even permit microanalysis to be performed. The only data available upon the anion are its structure, (III), and the observation of a band in its electronic absorption spectrum at 4200 cm$^{-1}$ ($\epsilon$ = 224 l mol$^{-1}$ cm$^{-1}$). We find similar bands in the spectra of $(pyH)_2[Ru_2Cl_6]$ and $Cs_2[Ru_2Cl_6]$ at *ca.* 4200 cm$^{-1}$ ($\epsilon$ = 410 l mol$^{-1}$ cm$^{-1}$) (*n.b.* these bands are not present in the spectra of $(pyH)_3[Ru_3Cl_9]$ or $Cs_3[Ru_3Cl_9]$), along with characteristic bands at *ca.* 15500 cm$^{-1}$ ($\epsilon \sim 10^3$ l mol$^{-1}$ cm$^{-1}$). The conductivity of $(pyH)_2[Ru_2Cl_6]$ in ethanenitrile (25 °C) gives $(\Lambda_M)_\infty \sim 250\ \Omega^{-1}\ cm^{-1}$, typical of values found for 2:1 electrolytes [10] (but could equally well fit a more polymeric formulation, *vide supra*). The infrared spectra of $A_2[Ru_2Cl_6]$ (A = pyH, Cs) show bands at *ca.* 340 cm$^{-1}$ $\{\nu(RuCl_2)\}$ and at *ca.* 320 cm$^{-1}$ $\{\nu(Ru_2Cl_2)\}$ (*cf.* for $[Ru_3Cl_9]^{3-}$, the terminal and bridging modes are coincident at 325 cm$^{-1}$). Again, attempts to grow crystals of these green complexes have, as yet, been to no avail.





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