Preparation and Vibrational Spectra of $[OsX_6]^{3-}$ (X = Cl, Br, or I) and of Other Platinum-group Hexahalogeno-complexes†

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The preparation, Raman and infrared spectra of the new salts $[Co(NH_2CH_2CH_2NH_2)_3][OsX_6]$ (X = Cl, Br, or I) are reported together with vibrational spectra of $Cs_2[RhCl_6]$, $[RuX_6]^{2-}$ (X = Cl or Br), and $[RuBr_6]^{3-}$.

The only established osmium(III) hexahalogeno-complex is $K_3[OsBr_6]$, prepared by electrolytic reduction of $[OsBr_6]^{2-}$;[1] electronic spectra of solutions made by reduction of $[OsX_6]^{2-}$ with silver powder and believed to contain $[OsX_6]^{3-}$ (X = Cl, Br, or I) have been measured.[2] We report here the isolation and characterisation of the new salts $[Co(en)_3][OsX_6]$ (X = Cl, Br, or I; en = $NH_2CH_2CH_2NH_2$), their Raman and i.r. spectra, and the Raman spectra of $[OsX_6]^{3-}$ in acid (HX) solution. We also give Raman and i.r. data for those hexahalogeno-complexes of the platinum-group metals for which such data have not hitherto been reported or are incomplete.

Results and Discussion

Preparation and Spectra of $[OsX_6]^{3-}$ (X = Cl, Br *or* I).—We find that addition of $[Co(en)_3]X_3$ to solutions obtained by adding silver powder to $[OsX_6]^{2-}$ in concentrated HX under nitrogen gives brown microcrystalline precipitates of $[Co(en)_3][OsX_6]$; the $[Co(en)_3]^{3+}$ cation was used as it gives clean precipitates and its vibrational spectrum does not interfere with those of the $[OsX_6]^{3-}$ ions. These new salts are paramagnetic [$\mu_{eff.}$ 1.70 (Cl), 1.67 (Br), and 1.61 B.M. (I) at room temperature]. The electronic spectra of the solutions from which they were obtained are similar to those reported by Jørgensen[2] and ascribed by him to $[OsX_6]^{3-}$.

The Raman spectra of $[Co(en)_3][OsX_6]$, after subtraction of the few cation bands in the low-frequency region, show strong bands which we assign to the totally symmetric metal–halide stretch ν_1; weaker bands we assign to the non-totally symmetric stretch ν_2 and the deformation ν_5. The solutions of $[OsX_6]^{3-}$ from which these salts were obtained show polarised bands close to the ν_1 frequencies of the solids, but the depolarised ν_2 and ν_5 bands could not be observed for these solutions. Infrared spectra of solid $[Co(en)_3][OsX_6]$ provide the ν_3 (asymmetric metal–halide stretch) and ν_4 (asymmetric deformation) bands. For comparison in the Table we give the literature assignments for the corresponding modes of the appropriate $[OsX_6]^{2-}$ salts; frequencies are slightly lower for $[OsX_6]^{3-}$ than for $[OsX_6]^{2-}$, as would be expected in view of the lower oxidation state.

Vibrational Spectra of other Platinum-group Hexahalogeno-complexes.—Vibrational data are now available for most such complexes[3,4] but some gaps remain, and we give here data for some of the missing species.

$[RhCl_6]^{2-}$ *and* $[RuCl_6]^{2-}$. Although i.r. data for $Cs_2[RhCl_6]$, the only well characterised salt of $[RhCl_6]^{2-}$, are available[5,6] there are no Raman data. We find that the Raman spectrum of solid $Cs_2[RhCl_6]$ has bands at 322, 260, and 177 cm^{-1} which we assign to ν_1, ν_2, and ν_5 respectively. Although it has been claimed that $[RhCl_6]^{2-}$ is present in solutions of $[RhCl_6]^{3-}$ treated with chlorine[7] we find that the electronic and Raman spectra of solutions so treated show bands due to $[RhCl_6]^{3-}$ only.

Recent work has suggested that $[RuCl_6]^{2-}$ has only a fugitive existence in HCl solution and so its fundamental frequencies in solution have not been reported.[8] We find that $[RuCl_6]^{2-}$ in 6 mol dm^{-3} HCl saturated with chlorine exhibits bands at 337 and 256 cm^{-1}, which are assigned to ν_1 and ν_2 of $[RuCl_6]^{2-}$. In a paper which appeared during the course of this work the resonance-Raman spectrum of solid $[PPh_4]_2[RuCl_6]$[9] gave ν_1 326, ν_2 270, and ν_5 at 173 cm^{-1}, in agreement with our data from the ion in acid solution.

$[RuBr_6]^{2-}$ *and* $[RuBr_6]^{3-}$. Recent resonance-Raman data for solid $[NBu^n{}_4]_2[RuBr_6]$ give ν_1 200, ν_2 160, and ν_5 106 cm^{-1}.[9] This compares reasonably well with our Raman and i.r. data for solid $K_2[RuBr_6]$.

No vibrational data have hitherto been reported for $[RuBr_6]^{3-}$. It has been shown by *X*-ray studies that the anilinium salt '$[NH_3Ph]_6[RuBr_9]$' is in fact $[NH_3Ph]_3[RuBr_6]\cdot3[NH_3Ph]Br$[10] and so contains the $[RuBr_6]^{3-}$ ion. We report the Raman and i.r. spectra of this solid in the Table having subtracted bands due to the cation; again ν_1 and ν_3 are lower for this ruthenium(III) complex than for $[RuBr_6]^{2-}$. The values for the fundamentals are quite close to those for $[RhBr_6]^{3-}$[11,12] and $[OsI_6]^{3-}$.

Iodo-complexes. The only fully established hexaiodo-complexes of the platinum metals are $[OsI_6]^{2-}$ and $[PtI_6]^{2-}$. Raman data are available for the latter;[5] for the former, ν_1 is reported to lie at 128 cm^{-1} for $[OsI_6]^{2-}$ in a KI–$HClO_4$ solution.[13] However, we find a strong, polarised band at 152 cm^{-1} for $Na_2[OsI_6]$ in concentrated HI and prefer this value for ν_1; it agrees well with the ν_1 of 152 cm^{-1} reported for the resonance-Raman spectra of solid $[NBu^n{}_4]_2[OsI_6]$.[14] Both $K_2[IrI_6]$[15] and 'potassium iodorhodite',[16] presumably $K_3[RhI_6]$, make brief appearances in the literature but the salts have never been characterised, although there is a report of Raman and i.r. data for a 'commercial' sample of $K_2[IrI_6]$.[17] We find that both $IrCl_3{\cdot}nH_2O$ and $RhCl_3{\cdot}nH_2O$ dissolve in excess concentrated hydriodic acid and in aqueous potassium iodide respectively to give deep red solutions; caesium and potassium salts can be isolated from these but give variable analyses. Raman spectra of the iridium solution show a polarised band at 152 cm^{-1} and depolarised bands at 141 and 103 cm^{-1}, close to those reported[17] for commercial $K_2[IrI_6]$; we suggest that they could arise for ν_1, ν_2, and ν_5 of $[IrI_6]^{3-}$ [it is likely that iodide would be too reducing a ligand for iridium(IV), but $[IrI_6]^{3-}$ should exist]. Likewise the rhodium solution has a polarised Raman band at 148 cm^{-1} and a depolarised one at 130 cm^{-1}, which we tentatively assign to ν_1 and ν_2 of $[RhI_6]^{3-}$.

Experimental

Tris(ethylenediamine)cobalt(III) *Hexachloro-osmate*(III), $[Co(en)_3][OsCl_6]$.—Sodium hexachloro-osmate, Na_2-

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† *Non-S.I. unit employed:* B.M. = 0.927 × 10^{-23} A m^2.

Table. Vibrational spectra (cm^{-1}) of hexahalogeno-complexes

Complex	Spectrum	$\nu_1(A_{1g})$	$\nu_2(E_g)$	$\nu_3(F_{1u})$	$\nu_4(F_{1u})$	$\nu_5(F_{2g})$
$[Co(en)_3][OsCl_6]$	R*, i.r.[a]	313(10)		297vs, 290vs	185s	
$[OsCl_6]^{3-}$	R[a]	310 (p)				
$K_2[OsCl_6]$	R,[b] i.r.[c]	345.3	245.2	326	176	160
$[Co(en)_3][OsBr_6]$	R*, i.r.[a]	201(10)	180(4)	200vs	116w	94(5)
$[OsBr_6]^{3-}$	R[a]	189 (p)				
$K_2[OsBr_6]$	R,[b] i.r.[c]	210.6	169.2	227	122	100
$[Co(en)_3][OsI_6]$	R*, i.r.[a]	144(10)	113(3)	140s	111w	
$[OsI_6]^{3-}$	R[a]	140 (p)				
$Na_2[OsI_6]$	R[a]	152 (p)				
$[NBu^n{}_4]_2[OsI_6]$	R[a], i.r.[d]	152(10) (p)	121(2) (dp)	170	91	80(2) (dp)
$Cs_2[RhCl_6]$	R*, i.r.[a]	322(10)	260(4)	330s	184m	177(6)
$Cs_2[RuCl_6]$	R*, i.r.[a]	328(10)	253(5)	327vs	183m	
$[RuCl_6]^{2-}$	R[a]	337(10) (p)	256(4) (dp)			
$K_2[RuBr_6]$	R*, i.r.[a]	209(10)	178(5)	248s	123w	
$[NH_3Ph]_3[RuBr_6]\cdot3[NH_3Ph]Br$	R*, i.r.[a]	184		240s, 232s	141w	

Raman data on solutions in 6 mol dm^{-3} HX or as indicated with a asterisk in solid state (ν_1, ν_2, ν_5); all i.r. data on solids (ν_3, ν_4); dp = depolarised, p = polarised; relative intensities given in parentheses. [a] This work. [b] Ref. 3. [c] Ref. 17. [d] Ref. 14.

$[OsCl_6]\cdot nH_2O$ (1.0 g) was dissolved in 6 mol dm^{-3} HCl (20 cm^3) and shaken with powdered silver under nitrogen gas until the electronic spectrum agreed with that reported[2] for $[OsCl_6]^{3-}$. The yellow-green solution was filtered under nitrogen and transferred to a solution of $[Co(en)_3]$ Cl_3 in dilute HCl (stoicheiometric quantity in 100 cm^3) which was well stirred. A brownish precipitate formed which was filtered off under nitrogen and washed with degassed water, ethanol, and diethyl ether and dried *in vacuo* (Found: C, 11.1; H, 3.6; Cl, 32.5; N, 12.4. Calc. for $C_6H_{24}Cl_6CoN_6Os$: C, 11.2; H, 3.8; Cl, 33.1; N, 13.1%). Magnetic moment: $\mu_{eff.}$ = 1.70 B.M. at 298 K.

Tris(ethylenediamine)cobalt(III) *Hexabromo-osmate*(III), $[Co(en)_3][OsBr_6]$.—This was prepared in a similar fashion to that above using concentrated HBr. To obtain a pure product it was found necessary to use $[Co(en)_3]Br_3$ and then redissolve it in dilute HBr (Found: C, 7.9; H, 3.0; Br, 49.2; N, 9.2. Calc. for $C_6H_{24}Br_6CoN_6Os$: C, 7.9; H, 2.6; Br, 52.8; N, 9.2%). Magnetic moment: $\mu_{eff.}$ = 1.67 B.M. at 298 K.

Tris(ethylenediamine)cobalt(III) *Hexaiodo-osmate*(III), $[Co(en)_3][OsI_6]$.—This was prepared in a similar fashion to that above using concentrated HI. As with $[Co(en)_3][OsBr_6]$ it was found necessary to prepare $[Co(en)_3]I_3$ and then redissolve it in dilute HI (Found: C, 6.1; H, 1.9; N, 6.9. Calc. for $C_6H_{24}CoI_6N_6Os$: C, 6.05; H, 2.0; N, 7.1%). Magnetic moment: $\mu_{eff.}$ 1.61 B.M. at 298 K.

Tris(ethylenediamine)cobalt(III) *Tribromide and Tri-iodide*, $[Co(en)_3]Br_3$ *and* $[Co(en)_3]I_3$.—The addition of the respective dilute halogenic acid to a dilute solution of $[Co(en)_3]Cl_3$ in water resulted in the precipitation of $[Co(en)_3]Br_3$ and $[Co(en)_3]I_3$. These were washed with ethanol and air-dried.

Potassium and Caesium Hexachlororuthenate(IV), $K_2[RuCl_6]$ *and* $Cs_2[RuCl_6]\cdot2H_2O$.—Ruthenium trichloride, $RuCl_3\cdot nH_2O$, (0.7 g) was added to concentrated HCl (30 cm^3) and the mixture refluxed for 1 h. This solution was filtered and cooled in an ice-bath. Chlorine was bubbled through the cooled solution for 10 min, the ice removed, and chlorine bubbled through for a further 15 min. An excess of MCl (M = K or Cs) dissolved in a minimum of concentrated HCl and saturated with chlorine gas was then added and the solution cooled for several hours. A black powder of $K_2[RuCl_6]$ (or red-brown powder of $Cs_2[RuCl_6]$) formed and was separated out by centrifugation, washed with a little ice-cold water, and dried *in vacuo* (Found: Cl, 54.3; K, 19.9. Calc. for Cl_6K_2Ru: Cl, 54.3; K, 19.9%. Found: Cl, 34.4; Cs, 43.0. Calc. for $H_4Cl_6Cs_2O_2Ru$: Cl, 34.6; Cs, 43.2%).

Potassium Hexabromoruthenate(IV), $K_2[RuBr_6]$.—This was prepared in a similar way to that of $K_2[RuCl_6]$ using $RuCl_3\cdot nH_2O$ (0.5 g), concentrated HBr (30 cm^3), KBr (0.5 g), and saturating the solution with bromine vapour instead of chlorine gas (Found: Br, 72.1; K, 12.4. Calc. for Br_6K_2Ru: Br, 72.8; K, 11.8%).

Anilinium Hexabromoruthenate(III)–*Tris(anilinium bromide)*, $[NH_3Ph][RuBr_6]\cdot3[NH_3Ph]Br$.—This was prepared by the method of Drew *et al.*[10] Ruthenium trichloride, $RuCl_3\cdot nH_2O$, (0.5 g) was refluxed under nitrogen gas with HBr (60 cm^3) for 72 h. (The $RuCl_3\cdot nH_2O$ had been previously shaken with mercury to effect reduction of Ru^{IV} to Ru^{III}.) The hot solution was then saturated with anilinium bromide. Crystals of the salt separated out on cooling and were filtered off and dried *in vacuo* (Found: C, 30.5; H, 3.4; Br, 52.0; N, 5.9. Calc. for $C_{36}H_{48}Br_9N_6Ru$: C, 31.2; H, 3.5; Br, 52.0; N, 6.1%).

Caesium Hexachlororhodate(IV).—This was prepared by the literature procedure[18] (Found: H, 0.2; Cl, 34.6; Cs, 45.1. Calc. for $H_2Cl_6Cs_2RhO$: H, 0.33; Cl, 35.5; Cs, 44.1%).

Spectroscopy.—Raman spectra of solutions were measured in a spinning cell and of solids as pressed discs on KBr using a Spex Ramalog V instrument and a Coherent Radiation model 52 krypton-ion laser with excitation at 6 471, 5 682, or 5 309 Å. Infrared spectra (down to 250 cm^{-1}) were measured as Nujol mulls on a Perkin-Elmer 597 instrument, and far-i.r. spectra (60—250 cm^{-1}) on a Bruker IFS 113V Fourier-transform instrument, the latter at University College, London.

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