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Preparation and Raman Spectra of Some Tribromoselenium(IV) Cationic Complexes

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Complexes of the type $[SeCl_3]^+[MCl_{n+1}]^-$, where MCl_n = Lewis acid, are well-known and extensively characterised. In particular, X-ray [1] and Raman [2–4] studies have shown that the $SeCl_4 \cdot AlCl_3$ complex consists essentially of pyramidal $SeCl_3^+$ and tetrahedral $AlCl_4^-$ units. For the $SeCl_4 \cdot MCl_5$ (M = Sb, Nb, Ta) systems, however, the picture is less clear [3, 5]. Very recently the preparation of $SeBr_3^+MF_6^-$ (M = As, Sb) was briefly mentioned [6], although no details or spectroscopic data were given. We now report the preparation, analysis, and characterisation by Raman spectroscopy, of the complexes $SeBr_3AlX_4$ (X = Cl, Br).

Experimental

Tribromoselenium(IV) tetrabromoaluminate was prepared by addition of anhydrous aluminium tribromide (1.89 g, 0.0071 mol) to a suspension of selenium tetrabromide (2.86 g, 0.0072 mol) in dichloromethane (100 cm³) with stirring (2 h). The yellow product was filtered under dry nitrogen and dried *in vacuo*. Found: Br, 84.4%. Calc for $AlBr_7Se$: Br, 84.1%. Tribromoselenium tetrachloroaluminate was similarly prepared and isolated using aluminium trichloride (1.57 g, 0.011 mol) and monochloroselenium tribromide (3.15 g, 0.009 mol) in dichloromethane (100 cm³). Found: Br, 49.1; Cl, 29.2%. Calc. for $AlBr_3Cl_4Se$: Br, 49.2; Cl, 29.1%. Raman spectra were recorded on solid samples contained in dry melting-point capillaries using a Coderg pHO Raman spectrometer with exciting radiation of 647.1 nm (Coherent Radiation model 52 krypton laser).

Results and Discussion

Solid state Raman bands for the two compounds are listed in the Table. The spectra are consistent with ionic complexes involving pyramidal (C_{3v}) $SeBr_3^+$ ions although of the four AlX_4^- modes expected only one, the $\nu_1(A_1)$ symmetric stretch, is observed with significant intensity in each case. This is consistent with a significantly greater scattering power of $SeBr_3^+$ relative to AlX_4^-. The four Raman-active bands expected for $SeBr_3^+$ appear strongly and are assigned (Table) on the basis of (a) the expected pattern of relative intensities and splittings and (b) correspondence with the isoelectronic $AsBr_3$ [9]. The SeBr stretching modes at 282 cm^{-1} (ν_1, A_1) and the split $\nu_3(E)$ mode (295, 289 cm^{-1}) in $SeBr_3^+AlCl_4^-$ are both higher than in the $AlBr_4^-$ complex (271 (ν_1); 282, 277 (ν_3) cm^{-1}) reflecting the same pattern in the analogous SBr_3^+ complexes [10]. A Raman spectrum of the product from reaction of $SeClBr_3$ and $SbCl_5$ is more complex and, although the presence of SBr_3^+ is apparent, it is not explicable on the basis of a simple $SeBr_3^+SbCl_6^-$ formulation.

TABLE. Solid State Raman Bands (cm^{-1}) for $SeBr_3^+AlBr_4^-$ and $SeBr_3^+AlCl_4^-$.

$SeBr_3^+AlBr_4^-$ [a]	$SeBr_3^+AlCl_4^-$ [b]	$AsBr_3$ [c]	Assignment
	480(v.w, br)		$\nu_3(T_2)AlCl_4^-$
400(v.w, br)			$\nu_3(T_2)AlBr_4^-$
	400(w,br)		
	349(w)		$\nu_1(A_1)AlCl_4^-$
282(m) [d]	295(m) [d]	285 (ν_3,E)	$\nu_3(E)SeBr_3^+$
277(m)	289(m)	262	
271(vs)	282(vs)	272(ν_1,A_1)	$\nu_1(A_1)SeBr_3^+$
212(w)			$\nu_1(A_1)AlBr_4^-$
	180(vw)		$\nu_4(T_2)AlCl_4^-$
136(m)	139(m)	133(ν_2,A_1)	$\nu_2(A_1)SeBr_3^+$
	128(w,sh)		$\nu_2(E),AlCl_4^-$
118(vw)			$\nu_4(T_2),AlBr_4^-$
110(w)	112(m,sh)	106 (ν_4,E)	$\nu_4(E)SeBr_3^+$
101(w)	106(m)	96	

[a] $AlBr_4^-$ bands in $Et_4^+NAlBr_4^-$ [7] at 394 (ν_3, T_2), 212 (ν_1, A_1), 114 (ν_4, T_2) and 98 (ν_2, E) cm^{-1}. [b] $AlCl_4^-$ bands in $Cs^+AlCl_4^-$ [8] at 486–505 (ν_3, T_2), 356 (ν_1, A_1), 180–187 (ν_4, T_2) and 128 (ν_2, E) cm^{-1}. [c] Polycrystalline solid, ref. [9]. [d] Resolved at −196 °C.

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