The Vibrational Spectra of SbX_6^{3-} and TeX_6^{2-} Anions: New Observations on the Singular Properties of some Systems Related to XeF_6

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Summary New measurements of the vibrational spectra of the isoelectronic anions TeX_6^{2-} and SbX_6^{3-} (X = Cl, Br, or I), electronically related to XeF_6, reveal some remarkable deviations from the properties established for conventional octahedral systems.

REGARDING the stereochemical peculiarities of systems related to XeF_6,[1] we report some of our results for the anions TeX_6^{2-} and SbX_6^{3-} (X = Cl, Br, or I), i.r. and Raman spectra of which have been recorded in a wide variety of conditions. These results expose striking departures from the spectroscopic properties of normal octahedral species, and imply for the SbX_6^{3-} anions an unusual degree of stereochemical flexibility.

For the TeX_6^{2-} anions in non-aqueous solution the frequencies of the observed vibrational fundamentals are generally in good agreement with those reported elsewhere[2] for the anions in crystalline solids and in aqueous solution. Neither the patterns nor the frequencies of the bands are substantially dependent on the nature of the solvent or of the cation. The most noteworthy findings, seen to best effect for the $TeBr_6^{2-}$ ion, the spectra of which in dichloromethane solution are illustrated in the Figure, are as follows:

(i) The Raman lines due to $\nu_1(a_{1g})$ and $\nu_2(e_g)$ of the $TeCl_6^{2-}$ and $TeBr_6^{2-}$ ions are unusual in their relative intensities, $I(\nu_2)/I(\nu_1)$ being 0·5—1: for $SnCl_6^{2-}$ and $SnBr_6^{2-}$, octahedral species presumably representative of normal behaviour, $I(\nu_2)/I(\nu_1)$ is about 0·05—0·1. Because of the apparent coincidence of ν_1 and ν_2 the relative intensities cannot be assessed for TeI_6^{2-}. Among other octahedral anions behaviour comparable with that of $TeCl_6^{2-}$ and $TeBr_6^{2-}$ has been reported only for $PdCl_6^{2-}$, $PtCl_6^{2-}$, and $PtBr_6^{2-}$ for which $I(\nu_2)/I(\nu_1) > 1$.[3]

(ii) Contrary to the O_h selection rules the fundamental ν_3 (t_{1u}) is clearly perceptible in the Raman spectra of $TeBr_6^{2-}$ (in various solvents) and TeI_6^{2-} (in water[2]).

(iii) No feature attributable to the t_{1u} deformation ν_4 could be detected at frequencies above 70 cm^{-1}.

The spectroscopic distinctions between the $SnBr_6^{2-}$ and $TeBr_6^{2-}$ ions are evident in the Figure.

Subsequent to the formation of the ions SbX_4^- and SbX_5^{2-} in non-aqueous solution (X = F, Cl, Br, or I), the ions $SbBr_6^{3-}$ and SbI_6^{3-} have been identified as the ultimate complexes formed between the appropriate antimony trihalide and an excess of halide ions in the presence of the cations NEt_4^+ or $NBu^n{}_4^+$. In the i.r. and Raman spectra of the anions, essential features of which are summarised in the Table and illustrated for $SbBr_6^{3-}$ in the Figure, the frequencies, relative intensities and polarization properties

I.r. and Raman spectra of hexahalogenoantimonate(III) *anions*

	Solid $[Co(NH_3)_6]SbX_6$		SbX_6^{3-} in aq. HX	SbX_6^{3-} in CH_2Cl_2[a]	
Anion	Raman cm^{-1}	I.r. cm^{-1}	Raman cm^{-1}	Raman cm^{-1}	I.r. cm^{-1}
$SbCl_6^{3-}$			320 s,p		
	268 m		268 s,p(?)		
	218 w	215 sh			
		172 vs,vbr			
	124 m		140 w,dp		
	113 s				
$SbBr_6^{3-}$				229 s,p	229 w
			176 s,vbr[b]		
	159 m			156 s,br,p	*ca.* 150 vbr
		141 s,br			
	137 w			134 m,dp	
	81 s				
	67 w	69 m	60 w		
SbI_6^{3-}				183 w,p	183 w
			136 s,p		
		122 s			
	117 m				
	104 s		104 m,dp	105 s,p	100 w
				96 w,dp	
	79 w				
	61 mw				
	40 mw	39 ms			

s = strong; m = medium; w = weak; br = broad; sh = shoulder; v = very; p = polarized; dp = depolarized.
[a] Similar results obtained with MeCN, Me_2CO, or MeOH as solvent.
[b] Band polarized on the high-frequency side.

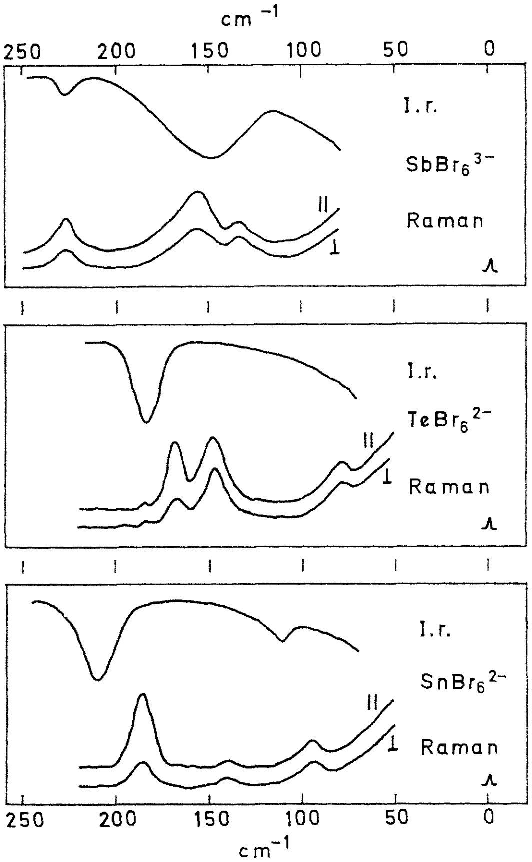

FIGURE. *Raman and far-i.r. spectra of some solutions of hexabromometallates in dichloromethane.*

of the bands are strikingly at variance with those of a conventional octahedral species like $SnBr_6^{2-}$. The region associated with Sb–X stretching modes of the anions contains no less than three Raman lines, two of which are polarized and coincident with absorptions in the i.r. Although manifestly incomplete, the spectra can be reconciled not with regular O_h symmetry for the SbX_6^{3-} anions but with a distorted octahedral unit belonging to the symmetry group C_{3v}. A similar structure is favoured[1] for the instantaneous configuration of gaseous XeF_6. For the solvents dichloromethane, acetonitrile, acetone, and methanol the results are found to be independent of the nature of the solvent. However, for aqueous solutions of the ions $SbBr_6^{3-}$ and SbI_6^{3-}, as well as for $SbCl_6^{3-}$ (not found in significant quantities in non-aqueous media), the Raman spectrum consists of two or three relatively broad bands; where comparison is possible, radically different frequencies, intensities and depolarization ratios are found for the ions in aqueous and non-aqueous solutions. In turn, the form of the vibrational features recorded for the hexahalogenoantimonate(III) ions in crystalline solids bears little resemblance to that found in the solution studies, and is moreover highly sensitive to the nature of the cation.

In their failure to conform with the vibrational behaviour of conventional octahedral systems the isoelectronic ions TeX_6^{2-} and SbX_6^{3-} are themselves dissimilar in their properties. We believe that TeX_6^{2-} has an O_h ground state the vibrational characteristics of which are perturbed by less symmetrical electronically excited states, leading to the breakdown of the O_h selection rules and giving rise possibly to a vibration of abnormally low frequency and large amplitude for the t_{1u} deformation ν_4.[4] However, except in the solid complexes $[Co(NH_3)_6]SbX_6$, SbX_6^{3-} appears to adopt a non-octahedral configuration highly susceptible to the influence of its environment.

We thank the S.R.C. (i) for grants for the purchase of the Beckman IR 11 and Cary 81 spectrometers and for the adaptation of the latter to excitation with an He–Ne laser, and (ii) for a research studentship (to C. J. A.)

(*Received, November 3rd,* 1970: *Com.* 1905.)

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[4] See for example I. D. Brown, *Canad. J. Chem.*, 1964, **42**, 2758; A. K. Das and I. D. Brown, *ibid.*, 1966, **44**, 939.