Resonance Raman Spectra of Some Mixed-valence Halogeno-compounds of Antimony and Lead

By **Robin J. H. Clark** * and **William R. Trumble**, Christopher Ingold Laboratories, University College London, London WC1H 0AJ

Resonance-Raman (r.r.) spectra are reported for a series of mixed-valence compounds of antimony. With $Cs_2[SbCl_6]$, $Rb_2[SbCl_6]$, or $Cs_4[SbBiCl_{12}]$, several overtone and combination tone progressions, in which the progressing fundamental is $\nu_1(a_{1g})$ of the $[SbCl_6]^-$ ion, have been observed on irradiation within the contour of the mixed-valence charge-transfer transition. The results are interpreted in terms of dimensional changes accompanying the transition. In view of the conflicting reports in the literature, the assignment of the Raman-active fundamental vibrations of the $[SbCl_6]^{3-}$ ion is discussed in the light of the r.r. results. Weak r.r. effects have also been observed for two related mixed-valence compounds of lead of composition $M^{III}[PbCl_6]$.

THE resonance-Raman (r.r.) spectra of many simple compounds,[1,2] and of biological materials,[1,3] have been extensively studied. Mixed-valence compounds of antimony [4] and of palladium and platinum [5] have also been shown to display striking r.r. effects. The results may have considerable bearing on the understanding of the electronic spectra of such materials,[5] in particular on the identification of the vibrations contributing to the (usually large) breadth of mixed-valence absorption bands.

Antimony forms many mixed-valence compounds,[6] in particular a series of solids of formula $M^I{}_2SbX_6$ (M = Cs, Rb, or NH_4; X = Cl or Br). These compounds contain antimony in the oxidation states III and V, in the forms of the octahedral anions $[SbX_6]^{3-}$ and $[SbX_6]^-$ respectively. The crystal structures are based on that of $K_2[PtCl_6]$, but with an ordered superlattice of Sb^{III} and Sb^V.[7,8] These substances are examples of Class II mixed-valence compounds.[6] They are all intensely coloured, the absorption having been attributed [9,10] to the mixed-valence $s \leftarrow s$ transition.

The preliminary study [4] of the r.r. spectrum of $Cs_2[SbCl_6]$ has now been extended to several other compounds of the same series, and also to some related compounds of lead.[6] These have the general formula $[M(NH_3)_6][PbCl_6]$ ($M = Co^{III}$ or Rh^{III}) and contain octahedral $[PbCl_6]^{4-}$ and $[PbCl_6]^{2-}$ ions in a lattice [11] based on that of sodium chloride. These compounds also show an intense absorption band in the visible region, ascribed, as in the case of the antimony compounds, to an $s \leftarrow s$ transition.[12,13]

The correct assignment of bands in the vibrational spectrum is a crucial part of the understanding of mixed-valence r.r. spectra. Since there is a considerable degree of confusion regarding the assignments for the fundamentals of the $[SbCl_6]^{3-}$ ion, we feel that it is necessary to review the situation. From a survey study of i.r. and Raman spectra of several salts of hexahalogeno-anions, in particular with the $[Co(NH_3)_6]^{3+}$ cation (and including some of the mixed-valence compounds studied here), Barrowcliffe *et al.*[14] proposed the following assignments for fundamentals of the $[SbCl_6]^{3-}$ ion: $\nu_1(a_{1g})$ 267; $\nu_2(e_g)$ 214; $\nu_3(t_{1u})$ 179; $\nu_5(t_{2g})$ 111 cm^{-1}; $\nu_4(t_{1u})$ (not located). The anion is known from *X*-ray studies to be octahedral in the $[Co(NH_3)_6]^{3+}$ salt,[15] and also in the mixed-valence compounds.[7,8]

This assignment has been challenged by Martineau and Milne.[16] Following a Raman study of several compounds of formula M_3SbCl_6 (M = K, Rb, Cs, or NH_4) they proposed that the $[SbCl_6]^{3-}$ ion was distorted from octahedral, not only in these materials but also in the $[Co(NH_3)_6]^{3+}$ salt, and that a strong Raman band in the 300—320 cm^{-1} region was characteristic of the anion. However, their attempt to reinterpret the Raman spectrum of the $[Co(NH_3)_6]^{3+}$ salt along these lines is seriously contradicted by deuteriation evidence (as has been pointed out previously),[17] and, moreover, the *X*-ray structure determination of this salt showed unambiguously the absence of distortion.[15] The alkali-metal salts studied by Martineau and Milne certainly showed more Raman bands than would be expected for an octahedral species; the quoted Raman frequencies are in fact very close to those reported [18] for the compound $[NBu^nH_3]_2[SbCl_5]\cdot[NBu^nH_3]Cl$, i.r. and Raman spectra of which show several coincidences where none would be expected for an octahedral anion. In fact the spectra of the M_3SbCl_6 salts are so dissimilar from those of compounds known to contain the regular octahedral $[SbCl_6]^{3-}$ anion as to suggest that either the ion present in these salts is seriously distorted from octahedral or that antimony is not six-co-ordinate at all (a possibility not eliminated by Martineau and Milne).

---

[1] J. Behringer, *Specialist Periodical Reports*, 'Molecular Spectroscopy,' eds. R. F. Barrow, D. A. Long, and D. J. Millen, The Chemical Society, London, 1975, vol. 3., p. 163.

[2] R. J. H. Clark, *Adv. Infrared Raman Spectroscopy*, 1975, **1**, 143.

[3] T. G. Spiro, *Adv. Infrared Raman Spectroscopy*, 1975, **1**, 98.

[4] R. J. H. Clark and W. R. Trumble, *J.C.S. Chem. Comm.*, 1975, 318.

[5] R. J. H. Clark and W. R. Trumble, *Inorg. Chem.*, in the press.

[6] M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247.

[7] A. T. Jensen and S. E. Rasmussen, *Acta Chem. Scand.*, 1955, **9**, 708.

[8] S. L. Lawton and R. A. Jacobson, *Inorg. Chem.*, 1966, **5**, 743.

[9] P. Day, *Inorg. Chem.*, 1963, **2**, 452.

[10] L. Atkinson and P. Day, *J. Chem. Soc.* (*A*), 1969, 2423.

[11] M. Atoji and T. Watanabe, *J. Chem. Phys.*, 1952, **20**, 1045.

[12] P. Day and I. D. Hall, *J. Chem. Soc.* (*A*), 1970, 2679.

[13] N. S. Hush, *Progr. Inorg. Chem.*, 1967, **8**, 391.

[14] T. Barrowcliffe, I. R. Beattie, P. Day, and K. Livingston, *J. Chem. Soc.* (*A*), 1967, 1810.

[15] D. R. Schroeder and R. A. Jacobson, *Inorg. Chem.*, 1973, **12**, 210.

[16] E. Martineau and J. B. Milne, *J. Chem. Soc.* (*A*), 1970, 2971.

[17] I. R. Beattie, F. C. Stokes, and L. E. Alexander, *J.C.S. Dalton*, 1973, 465.

[18] R. A. Walton, *Spectrochim. Acta*, 1968, **A24**, 1527.

Rather similar comments can be made concerning the spectra of HCl solutions of Sb^{III}. Here a value of 329 cm^{-1} was proposed [16] for ν_1 of the $[SbCl_6]^{3-}$ ion which was considered to be octahedral (a view slightly modified in more recent work [19]). This assignment is again very much at variance with the spectral evidence from compounds known to contain the octahedral anion (as Adams and Downs have pointed out [20]). The Raman spectra of the solutions consist of an ill defined system of very broad bands, and the species mainly responsible for the Raman scattering has not been clearly identified. Contrary to the author's assertion,[19] we feel that the spectra purporting to be those of the $[SbCl_6]^{3-}$ and $[SbCl_4]^{-}$ ions (Figures 3 and 4 of ref. 19) show very striking similarities to one another.

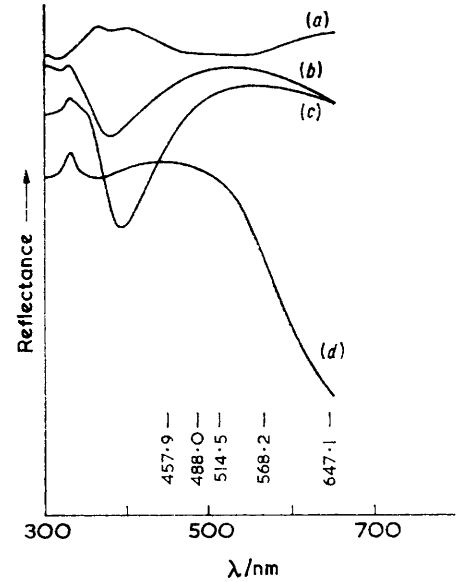

FIGURE 1 Diffuse-reflectance spectra of mixed-valence antimony compounds at room temperature. (Absolute values of the reflectance are not directly comparable as the spectra have been displaced for clarity.) (*a*), $[NH_4]_2[SbBr_6]$; (*b*), $Rb_2[SbCl_6]$; (*c*), $Cs_2[SbCl_6]$; (*d*), $Cs_4[SbBiCl_{12}]$

TABLE 1

Lowest electronic band maxima of mixed-valence compounds of antimony

Compound	$10^{-3}\ \tilde{\nu}_{max.}/cm^{-1}$	$\lambda_{max.}/nm$	Ref.
$Cs_2[SbCl_6]$	18.5	540.5	10
$Rb_2[SbCl_6]$	19.6	510.2	10
$Cs_4[SbBiCl_{12}]$	*ca.* 24	*ca.* 417	6
$[NH_4]_2[SbBr_6]$	9.5	1 053	9

To summarise, the assignments proposed by Milne are based on examples where the presence of antimony even approximately octahedrally co-ordinated is in considerable doubt, and are incompatible with cases where this stereochemistry has been verified. In the absence of single-crystal studies which could resolve this matter, we feel that the assignments of Barrowcliffe *et al.*,[14] regarding the Raman spectrum at least, are probably correct.

EXPERIMENTAL

The compounds $Cs_2[SbCl_6]$, $Rb_2[SbCl_6]$, and $Cs_4[Sb^VBi^{III}Cl_{12}]$ were prepared by slight variations of the method described by Weinland and Schmid,[21] using $SbCl_3$ rather than Sb_2O_3. Unless the correct conditions [22] are used, attempts to prepare $Rb_2[SbCl_6]$ yield $Rb[SbCl_6]$ or brown $Rb_2[SbCl_6]\cdot 2Rb_3[SbCl_6]$. Ammonium hexabromoantimonate was prepared by the method of Ephraim and Weinberg; [23] this compound loses bromine slowly in air but can be rebrominated in a desiccator under an atmosphere of bromine. Dicaesium hexabromoantimonate was also prepared [23] but lost bromine too rapidly in air for reliable spectra to be obtained. Samples of the mixed-valence lead compounds were kindly provided by Dr. P. Day of Oxford University. Their preparation is described in ref. 12.

Raman spectra were recorded with the rotating-sample technique [24] using a Spex 1401 spectrometer, in conjunction with Coherent Radiation Ar^+, Kr^+, and model 490 dye (rhodamine 6G) lasers. This system has been described elsewhere.[25] Electronic spectra, by diffuse reflectance, were recorded using a Cary 14 spectrometer.

RESULTS

Electronic Spectra.—Diffuse-reflectance spectra in the visible region of the mixed-valence antimony compounds are shown in Figure 1, together with the positions of several available exciting lines. Peak positions of the electronic band assigned to the $s\leftarrow s$ transition are listed in Table 1.

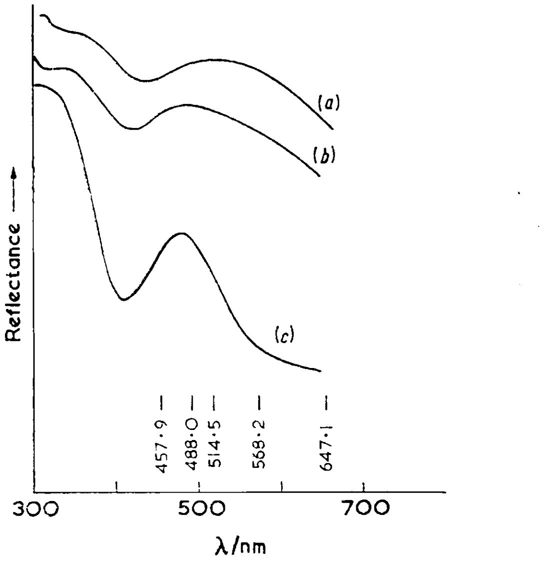

FIGURE 2 Diffuse-reflectance spectra of mixed-valence lead compounds at room temperature (see note to Figure 1). (*a*), $[Rh(NH_3)_6][PbCl_6]$; (*b*), $[Co(NH_3)_6][PbCl_6]$; (*c*), $[Co(NH_3)_6]_2[PbSnCl_{12}]$

Internal transitions of the anions do not occur below 36 900 cm^{-1} for the $[SbCl_6]^-$ ion,[10] 29 800 cm^{-1} for the

---

[19] J. Milne, *Canad. J. Chem.*, 1975, **53**, 888.

[20] C. J. Adams and A. J. Downs, *Chem. Comm.*, 1970, 1699.

[21] R. F. Weinland and H. Schmid, *Ber.*, 1905, **38**, 1080.

[22] L. Atkinson, D. Phil. Thesis, Oxford, 1968.

[23] F. Ephraim and S. Weinberg, *Ber.*, 1909, **42**, 4447.

[24] W. Kiefer and H. J. Bernstein, *Appl. Spectroscopy*, 1971, **25**, 501; R. J. H. Clark, *Spex Speaker*, 1973, **18**, 1.

[25] R. J. H. Clark and M. L. Franks, *J. Amer. Chem. Soc.*, 1975, **97**, 2691.

$[SbCl_6]^{3-}$ ion,[10] and 30 000 cm^{-1} for the $[BiCl_6]^{3-}$ ion.[26] The bromide spectrum was very ill defined in the visible region; the major contribution to the absorption may arise from a second mixed-valence transition (*cf.* a band at *ca.* 28 000 cm^{-1}, so assigned [9,10] in $Cs_2[SbCl_6]$) or from internal transitions of the $[SbBr_6]^{3-}$ ion (*cf.* the band at *ca.* 27 000 cm^{-1} [26]).

TABLE 2

Raman spectral data ($\bar{\nu}$/cm^{-1}) for several mixed-valence compounds of antimony

$Cs_2[SbCl_6]$ [a]	$Rb_2[SbCl_6]$	$Cs_4[SbBiCl_{12}]$	Assignment [b]	$[NH_4]_2[SbBr_6]$
175		174	ν_5^{V}, t_{2g}	
		215	ν_2^{III}, e_g	164(sh)
257	*ca.* 261br	255	ν_1^{III}, a_{1g}	188
286	289	286	ν_2^{V}, e_g	
324	334	326	ν_1^{V}, a_{1g}	214
351		351	ν_3^{V}, t_{1u}	
384	*ca.* 390br	387	$\nu_1^{V} + \nu_L$	*ca.* 250(?)
ca. 501		503	$\nu_1^{V} + \nu_5^{V}$	
			$2\nu_1^{III}$	374
584	590	578	$\nu_1^{V} + \nu_1^{III}$	
	620		$\nu_1^{V} + \nu_2^{V}$	
650	655	652	$2\nu_1^{V}$	
			$3\nu_1^{III}$	558
703		*ca.* 709	$2\nu_1^{V} + \nu_L$	
904		*ca.* 904	$2\nu_1^{V} + \nu_1^{III}$	
974		978	$3\nu_1^{V}$	
ca. 1 300			$4\nu_1^{V}$	

[a] From ref. 4. [b] *cf.* the following quoted values ($\bar{\nu}$/cm^{-1}) for Raman-active fundamentals (ν_1, ν_2, ν_5) of these anions: $[SbCl_6]^{3-}$, 267, 214, 111{$[Co(NH_3)_6]^{3+}$ salt,[14, 27]}; $[BiCl_6]^{3-}$, 259, 215, 115 ($[NMe_2H_2]^+$ salt [27]); $[SbBr_6]^{3-}$, 180, 153, 73($[NEt_2H_2]^+$ salt [27]); $[SbCl_6]^-$, 333, 291, 174 ($[AsCl_4]^+$ salt [28]). br = Broad, sh = shoulder.

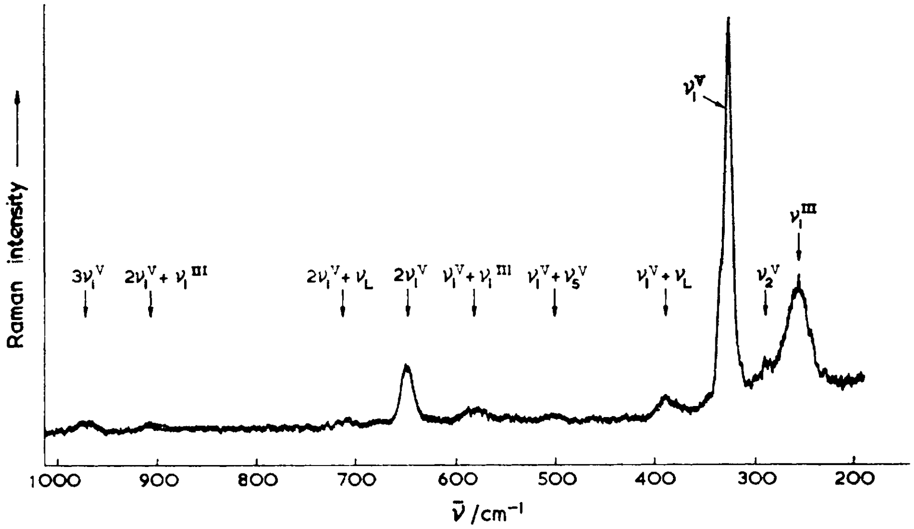

FIGURE 3 Raman spectrum of $Cs_2[SbCl_6]$ obtained with 514.5 nm excitation. Spectral slit width *ca.* 1.5 cm^{-1}

The corresponding spectra for three mixed-valence lead compounds are shown in Figure 2. The peak of the mixed-valence transition occurs at 19 350 and 20 080 cm^{-1} for the $[Co(NH_3)_6]^{3+}$ and $[Rh(NH_3)_6]^{3+}$ salts respectively.[13] In the case of the cobalt complex, this band overlaps with the $^1T_{1g} \leftarrow {}^1A_{1g}$ ligand-field transition of the cation (21 550 cm^{-1} in the $[InCl_6]^{3-}$ salt [12]), but there is no such complication in the case of rhodium (*ca.* 29 000 cm^{-1} for the lowest cation band [12]). In the case of the complex $[Co(NH_3)_6]_2$-$[Pb^{II}Sn^{IV}Cl_{12}]$, the band at 21 000 cm^{-1} is due to the cation. The mixed-valence transition is believed to occur [12] in the u.v. region, at *ca.* 29 000 cm^{-1}.

Raman Spectra.—Results for the antimony compounds are collected in Table 2. Assignments are based on comparison with those for other salts of these anions as discussed above and elsewhere.[27,28] Vibrational spectra of Class II mixed-valence compounds are characteristically approximate superpositions of those of the constituent species.[6] In the case of the crystal structure found for the complex $[NH_4]_2[SbBr_6]$,[8] both site- and factor-group effects may cause splitting of vibrational bands and relaxation of the selection rules for the free octahedral species. The primitive cell (D_{4h} symmetry) contains four antimony atoms, two of each oxidation state, on sites of D_{2d} symmetry. Furthermore, the quinquevalent anions may be distorted slightly.[8] However, the spectra show no evidence of any significant site- or factor-group effects, except for the weak appearance of the formally Raman-forbidden $\nu_3(t_{1u})$ mode of the $[SbCl_6]^-$ ion, for which this distortion is presumably responsible.

Our previous report [4] indicated that the compound

---

[26] R. A. Walton, R. W. Matthews, and C. K. Jørgensen, *Inorg. Chim. Acta*, 1967, **1**, 355.

[27] M. A. Hooper and D. W. James, *Austral. J. Chem.*, 1973, **26**, 1401.

[28] I. R. Beattie, T. Gilson, K. Livingston, V. Fawcett, and G. A. Ozin, *J. Chem. Soc.* (*A*), 1967, 712.

$Cs_2[SbCl_6]$ exhibited a r.r. spectrum (Figure 3) with several exciting lines covering the visible region. Several higher-order progressions appeared, in which the progressing fundamental was $\nu_1(a_{1g})$ of the $[SbCl_6]^-$ ion, *viz.* $n\nu_1$ for n up to 4, $n\nu_1 + \nu_1([SbCl_6]^{3-})$ ($n \leqslant 2$), $n\nu_1 + \nu_5([SbCl_6]^-)$ for $n = 1$, and $n\nu_1 + \nu_L$ ($n \leqslant 2$) where ν_L is a lattice mode deduced to occur at 60 cm^{-1}. The position of maximum resonance enhancement, measured by the ratio of the intensities of certain higher-order bands to that of the progressing fundamental, was found to coincide roughly with the peak of the mixed-valence transition.

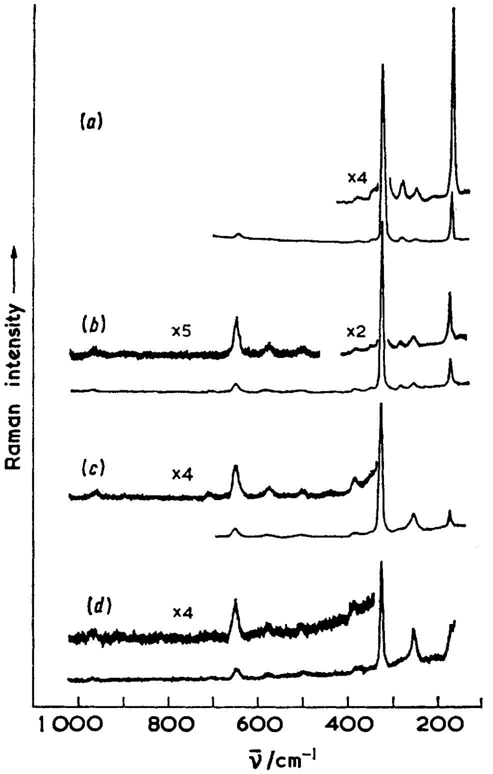

FIGURE 4 Raman spectra of $Cs_4[SbBiCl_{12}]$ obtained with various exciting lines: (*a*) 647.1, (*b*) 568.2, (*c*) 514.5, and (d) 457.9 nm. Spectral slit width *ca.* 2 cm^{-1}

TABLE 3

Raman spectral data ($\bar{\nu}/cm^{-1}$) for mixed-valence compounds of lead

$[Co(NH_3)_6][PbCl_6]$	$[Rh(NH_3)_6][PbCl_6]$	$[Co(NH_3)_6][PbSnCl_{12}]$	Assignment *
210br	*ca.* 200br		$\nu_2(?)\ M(^{IV})$
		ca. 242	$\nu_2(e_g)\ Sn^{IV}$
250	243		$\nu_1(a_{1g})\ M^{II}$, $\nu_5\{[Rh(NH_3)_6]^{3+}\}(t_{2g})$
285	287	313	$\nu_1(a_{1g})\ M^{IV}$
ca. 310br			$\nu_5\{[Co(NH_3)_6]^{3+}\}$
440	481	437	$\nu(M{-}NH_3)$
481	505		
493	515	485	
ca. 570	572		$2\nu_1\ M^{IV}$
	ca. 850		$3\nu_1\ M^{IV}$

* *cf.* the following values ($\bar{\nu}/cm^{-1}$) for the wavenumbers of the fundamentals of the ions (ν_1, ν_2, ν_5): $[PbCl_6]^{2-}$, 285,215, 137 (HCl solution [29]); $[SnCl_6]^{2-}$, 315, 246, *ca.* 163 {$[Ni(OH_2)_6]^{2+}$ salt [30]}, 309, 232, 159 ($[NEt_4]^+$ salt [31]); $[Rh(NH_3)_6]^{3+}$, 514, 483, 240 (Cl^- salt [32]); $[Co(NH_3)_6]^{3+}$, 495, 440 (Cl^- salt [33]), $\nu_5 \approx 308$ (various salts [14]). br = Broad.

The compound $Cs_4[SbBiCl_{12}]$, in which Bi^{III} replaces Sb^{III}, exhibited an almost exactly similar spectrum (Figure 4) containing the same higher-order features. In fact, because of the near coincidence of the fundamentals of the $[SbCl_6]^{3-}$ and $[BiCl_6]^{3-}$ ions, the r.r. spectra of $Cs_2[SbCl_6]$ and $Cs_4[SbBiCl_{12}]$ appear almost identical. In the latter case, however, the maximum in the electronic spectrum is at *ca.* 24 000 cm^{-1} and resonance enhancement increases slowly with decreasing exciting wavelength across the visible region. With red (647.1-nm) excitation we observed what is virtually an off-resonance (*i.e.* normal) spectrum, in which five of the six Raman-active vibrations of the two octahedral anions, *viz.* ν_1, ν_2, and ν_5 of the $[SbCl_6]^-$ ion and ν_1 and ν_2 of the $[BiCl_6]^{3-}$ ion, were clearly observed at positions very close to those found in other work. This provides very strong support for the assignments proposed by Barrowcliffe *et al.*[14] The $\nu_2(e_g)$ modes appear not to participate in resonance effects.

The compound $Rb_2[SbCl_6]$ is black and consequently a rather weak scatterer of light. The r.r. spectrum of this compound was different from those of $Cs_2[SbCl_6]$ and $Cs_4[SbBiCl_{12}]$ in that ν_2 of the $[SbCl_6]^-$ ion was more prominent, and the combination band $\nu_1^V + \nu_2^V$ was observed. This may indicate a small difference between these compounds in the geometry of the $[SbCl_6]^-$ ion in the excited state. A weak broad shoulder on the high-frequency side of the $\nu_1([SbCl_6]^-)$ band is assigned to a lattice-mode combination, but unfortunately its position could not be determined very accurately.

The spectrum of $[NH_4]_2[SbBr_6]$ showed essentially the two totally symmetric modes of the anions. In contrast to the chloro-complexes, two overtones of ν_1 of the tervalent anion were observed. Little difference was observed between spectra obtained with different exciting lines.

Raman spectra of the two mixed-valence lead compounds $[Co(NH_3)_6][PbCl_6]$ and $[Rh(NH_3)_6][PbCl_6]$ showed a weak overtone progression based on ν_1 of the $[PbCl_6]^{2-}$ anion. Results are listed in Table 3. Assignments are based on comparison with the spectra of other salts of these ions.[29–33] The frequency ν_1 of the $[PbCl_6]^{4-}$ ion, which is not well characterised by vibrational spectroscopy, was assigned in the 240—250 cm^{-1} region, since the band in question did not appear to correspond with fundamentals of the other ions. Barrowcliffe *et al.*[14] reported that $Cs_4[PbCl_6]$ gave Raman bands at 202m and 119s cm^{-1}.

Off-resonance (*i.e.* with red 647.1-nm excitation) the

---

[29] J. A. Creighton and L. A. Woodward, *Trans. Faraday Soc.*, 1962, **58**, 1077.

[30] D. M. Adams and W. R. Trumble, *Inorg. Chim. Acta*, 1974, **10**, 235.

[31] R. J. H. Clark, L. Maresca, and R. J. Puddephatt, *Inorg. Chem.*, 1968, **7**, 1603.

[32] W. P. Griffith, *J. Chem. Soc.* (*A*), 1966, 899.

[33] T. E. Haas and J. R. Hall, *Spectrochim. Acta*, 1966, **22**, 988.

bands due to the $[PbCl_6]^{2-}$ ion dominated the spectrum, but as the exciting wavelength was reduced across the visible region the bands due to the other ions increased in intensity relative to those of the $[PbCl_6]^{2-}$ ion. The 200—285 cm^{-1} region of the spectrum, especially with the cobalt salt, became very poorly resolved. Attempts to measure the variation of intensities more accurately were frustrated by rapid decomposition of the dark samples in the laser beam, which made measurements non-reproducible.

When Pb^{IV} was replaced by Sn^{IV} no r.r. effects were observed. The spectrum consisted chiefly of the fundamentals of $[SnCl_6]^{2-}$, superimposed on a high fluorescence background.

DISCUSSION

The spectra of the antimony compounds show certain features not previously observed in r.r. spectroscopy. In particular the lattice-mode combination progression is a novel feature. Atkinson and Day [10] suggested that several vibrational quanta were excited in the mixed-valence transition, and the r.r. spectra appear to demonstrate that the breadth of the electronic absorption band arises from coupling to lattice phonons as well as to internal vibrations of the anions. The participation of the lattice mode in resonance effects implies that the potential surface associated with this mode is displaced in the electronic transition, *i.e.* a distortion of the lattice accompanies the mixed-valence charge-transfer transition. The lattice mode has virtually the same frequency in $Cs_2[SbCl_6]$ and $Cs_4[SbBiCl_{12}]$, but was unfortunately not clearly observed with $Rb_2[SbCl_6]$. It thus appears to be insensitive to the nature of the $[MCl_6]^{3-}$ ion, and may therefore be primarily associated with displacements of the cations.* The situation is quite similar to that known in the electronic spectroscopy of transition-metal complexes, in which local lattice displacements can cause the appearance of lattice phonons in the vibrational fine structure of high-resolution luminescence spectra.[34]

A further new feature is the observation of a progression in ν_1 of the $[SbCl_6]^-$ ion based on one quantum of ν_1 of the $[MCl_6]^{3-}$ ion. Such an effect, which would only be expected to occur in the case of resonance with a mixed-valence transition, may imply an increased electronic overlap between the two anions in the excited state of the transition.

Donaldson *et al.*[35] recently published i.r. results for several of these mixed-valence antimony compounds, which were used to support the contention that the pair of 5*s* electrons on Sb^{III} were delocalised in a conduction band throughout the lattice so that at room temperature all antimony in the crystal was present at Sb^{V}. The authors suggested that the i.r. spectra only showed bands due to the $[SbCl_6]^-$ ion. However, the Raman spectra clearly show bands due to hexahalogeno-anions of Sb^{III}, and the suggestion that all antimony is effectively present in the quinquevalent state appears to us to be completely untenable. These authors also appear to have ignored *X*-ray [8] and Mössbauer data [36,37] showing two distinct types of antimony ion in the crystal. Certain of the compounds also showed [35] an i.r. absorption at *ca.* 245 cm^{-1} (*e.g.* $Cs_2[SbCl_6]$ and $Rb_2[SbCl_6]$) which is far removed from any fundamental of the $[SbCl_6]^-$ ion, and is presumably to be associated with Sb^{III}.†

In conclusion, the results confirm that r.r. spectroscopy can successfully complement other spectroscopic techniques in the study of mixed-valence compounds. In the case of the antimony compounds, the spectra confirm the mixed-valence charge-transfer nature of the electronic transition, in that r.r. effects involve fundamentals of both $[SbCl_6]^-$ and $[MCl_6]^{3-}$ species. The effects provide evidence as to dimensional changes occurring in the lattice on excitation of the mixed-valence transition, and point to differences between compounds otherwise thought to be very similar (*e.g.* $Cs_2[SbCl_6]$ and $Rb_2[SbCl_6]$). The r.r. spectra also exhibit special features (exemplified by the $n\nu_1^{V} + \nu_L$ and $n\nu_1^{V} + \nu_1^{III}$ combination band progressions observed for the antimony compounds) not observed in the r.r. spectra of comparable single-valence systems. The r.r. effects are, nevertheless, less spectacular than those observed for many single-valence inorganic compounds.[2,39] This is partly because the intensity of the colour of the mixed-valence compounds derives more from high chromophore concentrations in the solid state than from high absorption coefficients (*e.g.* that for $[NMeH_3]_2[SbCl_6]$ is *ca.* 110 dm^3 mol^{-1} cm^{-1}) [10] and partly because of the broadness of the mixed-valence transition, which militates against the appearance of very long r.r. progressions.[1]

We thank Dr. P. Day, Oxford University, for some of the samples and for helpful comments, and the S.R.C., the University of London Intercollegiate Research Service, and the University of London Central Research Fund for support.

[5/2282 *Received*, 21*st November*, 1975]

---

* A full factor-group analysis for the crystal structure predicts only one lattice mode of a_{1g} symmetry, primarily a translatory mode of the cations. In view of the general preponderance of totally symmetric modes in r.r. spectra, it is tempting to identify this a_{1g} mode with the lattice mode at 60 cm^{-1}. However, since for combination tones there is no restriction to zero values of the wave vector for component phonons, factor-group symmetry labels are probably not very meaningful in the case of lattice modes under resonance conditions.

† The band at 245 cm^{-1}, if genuine, may resolve a problem in the i.r. spectrum of $[SbCl_6]^{3-}$. The frequency ν_3 has previously been reported at *ca.* 178 cm^{-1}, which as Hooper and James [27] have pointed out, appears anomalously low, *cf.*, for example, $[SbBr_6]^{3-}$ (ν_3 at *ca.* 180 cm^{-1}). A value of 245 cm^{-1} for ν_3 of the $[SbCl_6]^{3-}$ ion, with ν_4 (previously not located) being a major contributor to the band at 178 cm^{-1}, appears more reasonable. I.r. spectra of octahedral species where the central atom has an inert pair of *s* electrons are known frequently to be unusual in respect of the intensities and band widths of the fundamentals (see *e.g.* ref. 38).

[34] C. D. Flint, *Adv. Infrared Raman Spectroscopy*, 1976, **2**, to be published.

[35] J. D. Donaldson, J. Silver, S. Hadjiminolis, and S. D. Ross, *J.C.S. Dalton*, 1975, 1500.

[36] T. Birchall, B. Della Valle, E. Martineau, and J. B. Milne, *J. Chem. Soc.* (*A*), 1971, 1855.

[37] J. D. Donaldson, M. J. Tricker, and B. W. Dale, *J.C.S. Dalton*, 1972, 893.

[38] D. M. Adams and S. J. Payne, *J.C.S. Dalton*, 1974, 407.

[39] R. J. H. Clark and M. L. Franks, *J. Amer. Chem. Soc.*, in the press.