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# Preparation of $[IBr_2][Sb_2F_{11}]$ and $[IBr_{0.75}Cl_{1.25}][SbCl_6]$ and Their Characterization by X-ray Crystallography and Raman Spectroscopy

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The X-ray crystal structures of $[IBr_2][Sb_2F_{11}]$ and $[IBr_{0.75}Cl_{1.25}][SbCl_6]$ have been determined from diffractometer data by the heavy-atom method. Crystals of $[IBr_2][Sb_2F_{11}]$ are orthorhombic, space group *Pbca*, with $a = 14.445$ (7) Å, $b = 14.034$ (5) Å, $c = 12.725$ (3) Å, $V = 2580$ (1) Å$^3$, and $d_{calcd} = 3.81$ g cm$^{-3}$ for $Z = 8$. Crystals of $[IBr_{0.75}Cl_{1.25}][SbCl_6]$ are triclinic, space group $P\bar{1}$, with $a = 7.084$ (1) Å, $b = 6.299$ (1) Å, $c = 13.511$ (3) Å, $\alpha = 94.50$ (2)°, $\beta = 100.32$ (2)°, $\gamma = 92.56$ (2)°, $V = 590.3$ (2) Å$^3$, and $d_{calcd} = 3.18$ g cm$^{-3}$ for $Z = 2$. The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares to $R_1 = 0.065$ and $R_2 = 0.064$ for 1390 observed ($I > 2\sigma(I)$) reflections for $[IBr_2][Sb_2F_{11}]$ and $R_1 = 0.061$ and $R_2 = 0.075$ for 2360 observed ($I > 2\sigma(I)$) reflections for $[IBr_{0.75}Cl_{1.25}][SbCl_6]$. Both structures consist of infinite chains of cations and anions such that the iodine in each cation achieves a trapezoidal four-coordination via cis bridges to the anions. In $[IBr_2][Sb_2F_{11}]$ the I–Br distances average 2.423 (3) Å and the bridging I–F distances are 2.845 (12) and 2.782 (12) Å. The disordered cation $[IBr_{0.75}Cl_{1.25}]^+$ has one terminal interaction at 2.427 (2) Å, very close to the I–Br distance in $[IBr_2]^+$, while the other terminal distance is 2.373 (3) Å, much longer than the I–Cl distance (2.268 (2) Å) in the $[ICl_2]^+$ cation. The bridging I–Cl distances in the disordered cation average 2.952 (2) Å. The Raman data are interpreted in terms of these structures and are compared to related literature data.

## Introduction

The reaction of $I_2Cl_6$ with Lewis acids results in the formation of salts of the $[ICl_2]^+$ cation,[1–4] some of which have been characterized by X-ray crystallography.[4,5] These compounds contain iodine in a trapezoidal-planar environment having two short I–Cl bonds and two much longer I···X (X = Cl, F) interactions. Passmore et al.[6] have reported the structure of $[I_3][AsF_6]$, in which the central portion of the $[I_3]^+$ cation also has this trapezoidal-planar arrangement. Vibrational spectroscopy has also been used to identify $IBr_2SO_3F$[7,8] and $[IBr_2][Sb_2F_{11}]$.[3] By reacting equimolar quantities of $IBr_2SO_3F$ and $ICl_2SO_3F$, Aubke and co-workers[3] obtained a compound of stoichiometry $BrIClSO_3F$, which was characterized by its Raman spectrum. Shamir and Lustig[9] have also identified the $[BrICl]^+$ cation by Raman spectroscopy. These bend cations probably also contain the central iodine in a trapezoidal coordination and fill in the gap between the $[ICl_2]^+$ and $[I_3]^+$ cations whose structures are well established. Here we report the X-ray crystal structures of $[IBr_2][Sb_2F_{11}]$ and $[IBr_{0.75}Cl_{1.25}][SbCl_6]$ and compare their vibrational spectra with the earlier data for the $[IBr_2]^+$ and $[BrICl]^+$ cations.

## Experimental Section

$[IBr_2][Sb_2F_{11}]$ was prepared as follows: A 6.5057-g quantity (30.014 mmol) of $SbF_5$ was added to one side of a Dean reaction vessel.[10] Then 2.4630 g (11.904 mmol) of IBr was prepared from $I_2$ and $Br_2$, by using the method described by Brauer,[11] in the other side of the vessel. $SO_2$ was distilled onto the $SbF_5$ and the $SbF_5/SO_2$ solution was poured through the frit, onto the IBr. After the mixture was stirred for 1 week, a very dark green, clear solution remained, which contained a fine white precipitate of $SbF_3$. The solution was filtered to the other side of the vessel, and the $SO_2$ was slowly removed in an attempt to induce crystallization. A dark thick paste remained, which, when $SO_2ClF$ was added, produced a dark green, clear solution. When the $SO_2ClF$ was removed by slow distillation, shiny, dark, needlelike crystals of $[IBr_2][Sb_2F_{11}]$ formed. The melting point of a single crystal is 139 °C.

$[IBr_{0.75}Cl_{1.25}][SbCl_6]$ was prepared in a Dean reaction vessel comprising two 100-mL Pyrex round-bottom flasks. A 12.0629-g quantity (40.34 mmol) of $SbCl_5$ was added to one side of the reaction vessel. Then 8.2915 g (40.07 mmol) of IBr was added to the $SbCl_5$. Following this, 2.8050 g (39.56 mmol) of dry $Cl_2$ was distilled onto the mixture at −196 °C. The reaction mixture was allowed to warm to room temperature over a period of several hours. $SO_2$ solvent was then introduced into the vessel, and the reaction product was stirred and then carried over to the other side of the vessel. After the $SO_2$ was removed by slow distillation, a very dark red-brown crystalline solid remained. The melting point of a single crystal is 50 °C.

**Crystal Data.** Crystal data for both compounds are found in Table I. Intensity measurements were made on a Nicolet P3 diffractometer. Lorentz and polarization correlations were applied to all the data. The two structures were solved by using conventional heavy-atom methods to locate the iodine and/or antimony atoms in the Patterson maps. Subsequent Fourier maps revealed the positions of the remaining atoms and confirmed the positional assignments of the heavy atoms. The details concerning the final stages of refinement are also found in Table I. Complete listings of observed and calculated structure factor amplitudes for the two structures are found in the supplementary material.

**Structure of $[IBr_2][Sb_2F_{11}]$.** The final atomic positional coordinates for $[IBr_2][Sb_2F_{11}]$ are given in Table II, and the thermal parameters are found in the supplementary material. The bond lengths of the molecules are given in Table III, and bond angles are found in the supplementary material. The atomic arrangement in the molecule is illustrated in Figure 1, and a stereoscopic view of the packing in the unit cell, along the *c* axis, is shown in Figure 2.

**Structure of $[IBr_{0.75}Cl_{1.25}][SbCl_6]$.** The X-ray structure analysis of this material revealed chlorine/bromine disorder in the cation, which has the approximate stoichiometry $[IBr_{0.75}Cl_{1.25}]^+$. In the early stages of the structure determination the atoms, which were later designated as XA and XB, were refined as bromines. However, the isotropic temperature factors for these two atoms were 0.080 (14) and 0.092 (18) Å$^2$, both of which were much too high for bromine, thereby indicating that there was less electron density at these positions than had been assigned. At the same stage of refinement the isotropic thermal parameter for the iodine atom was 0.0288 (4) Å$^2$. Varying the temperature factors of all the atoms in the structure anisotropically resulted in $R_1$ refining to 0.075. The population parameters of the two atoms initially assigned as bromines were then varied, and these refined to 0.70 and 0.60 for the disordered atoms XA and XB, respectively, and gave an improved $R_1$ of 0.049. A similar result was obtained when the two atoms were initially assigned as chlorines; the

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**Table I.** Crystal, Acquisition, and Refinement Data for $[IBr_2][Sb_2F_{11}]$ and $[IBr_{0.75}Cl_{1.25}][SbCl_6]$

| | $[IBr_2][Sb_2F_{11}]$ | $[IBr_{0.75}Cl_{1.25}]$-$[SbCl_6]$ |
|---|---|---|
| | Crystal Data | |
| system | orthorhombic | triclinic |
| $a$, Å | 14.445 (3) | 7.084 (1) |
| $b$, Å | 14.034 (5) | 6.299 (1) |
| $c$, Å | 12.725 (3) | 13.511 (3) |
| $\alpha$, deg | 90 | 94.50 (2) |
| $\beta$, deg | 90 | 100.32 (2) |
| $\gamma$, deg | 90 | 92.56 (2) |
| $V$, Å$^3$ | 2580 (1) | 590.3 (2) |
| $D_{calcd}$, g cm$^{-3}$ | 3.81 | 3.18 |
| reflcns used in cell determination, no./$2\theta$ range | $15/18° \leqslant 2\theta \leqslant 28°$ | $15/20° \leqslant 2\theta \leqslant 29°$ |
| $Z$ | 8 | 2 |
| fw | 739.3 | 565.7 |
| $F$(000) | 2592 | 506 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 123.2 | 88.5 |
| space group | *Pbca* | $P\bar{1}$ or $P1$ |
| systematic absences | $hkl$, no conditions; $0kl$, $k = 2n$; $h0l$, $l = 2n$; $hk0$, $h = 2n$; $h00$ ($h = 2n$); $0k0$, ($k = 2n$); $00l$ ($l = 2n$) | no conditions |
| mode | $\theta$:$2\theta$ | |
| wavelength | Mo K$\alpha$ radiation ($\lambda$ = 0.710 69 Å) | |
| stds | (4,−1,−1), (4,−1,1) | (−1,1,3), (−1,−1,7) |
| no./interval[a] | 2/48 | 2/48 |
| scan range, deg | K$\alpha_1$ − 1.2 to K$\alpha_2$ + 1.2 | K$\alpha_1$ − 1.2 to K$\alpha_2$ + 1.2 |
| scan speeds,[b] deg min$^{-1}$ | 4.0–29.3 | 4.0–29.3 |
| max $2\theta$, deg/quadrant | 45/$hkl$ | 55/$h{\pm}k{\pm}l$ |
| | Details of Refinements | |
| abs cor | spherical<br>$\mu r = 1.90$<br>($r$ = 0.015 cm)<br>$A^*$: 5.25–12.50 | none |
| no. of nonzero data | 1668 | 2738 |
| no. of data with $F \geqslant 2.0\sigma(F)$ | 1390 | 2360 |
| no. of data with $F \geqslant 6.0\sigma(F)$ | 1009 | 1917 |
| $R$ factors ($2\sigma$): $R_1$[c] | 0.065 | 0.061 |
| $R_2$[d] | 0.064 | 0.075 |
| $R$ factors ($6\sigma$): $R_1$ | 0.042 | 0.048 |
| $R_2$ | 0.050 | 0.063 |
| max shift/error | 0.001 | 0.002 |
| weighting scheme[e,f] | $w = 1.0/(\sigma(F_0)^2 + 0.001F_0^2)$ | $w = 1.0/(\sigma(F_0)^2 + 0.0023F_0^2)$ |
| highest peak in final diff map,[g] e/Å$^3$ | +1.3 | +3.6 |
| lowest valley in final diff map, e/Å$^3$ | −1.2 | −1.1 |

[a] No systematic trends in the intensities of the standards were observed. [b] Dependent on prescan. [c] $R_1 = (\Sigma ||F_o| - |F_c||/\Sigma |F_o|)$. [d] $R_2 = [\Sigma w ||F_o| - |F_c||^2/\Sigma w |F_o|^2]^{1/2}$. [e] In each case the final comparison of the average $w ||F_o| - |F_c||^2$ as a function of $F_o$ and $\sin\theta$ after the use of these schemes showed no systematic trends. [f] The weighting scheme used was $w = XY$, where (1) $X = (\sin\theta)/0.37$ if $\sin\theta < 0.37$, $X = 0.40/\sin\theta$ if $\sin\theta > 0.40$, or $X = 1$ otherwise and (2) $Y = 70.0/F$ if $F > 70.0$, $Y = F/50.0$ if $F < 50.0$, or $Y$ = 1.0 otherwise. [g] In all cases the final difference Fourier map was featureless with the maximum peaks and minimum valleys found around heavy atoms.

**Table II.** Atomic Coordinates (×10$^4$) for $[IBr_2][Sb_2F_{11}]$[a]

| | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| I(1) | 3611 (1) | 7370 (1) | 955 (1) |
| Br(1) | 2680 (2) | 8213 (2) | −329 (2) |
| Br(2) | 4526 (2) | 6375 (2) | −203 (2) |
| Sb(1) | −522 (1) | 10853 (1) | 3284 (1) |
| Sb(2) | 1640 (1) | 9162 (1) | 2883 (1) |
| F(1) | −1195 (8) | 9880 (9) | 3875 (10) |
| F(2) | −104 (9) | 11231 (9) | 4582 (9) |
| F(3) | 553 (8) | 9925 (9) | 3382 (9) |
| F(4) | 347 (8) | 11681 (8) | 2694 (10) |
| F(5) | −1488 (9) | 11711 (9) | 3243 (11) |
| F(6) | −734 (11) | 10362 (12) | 1960 (9) |
| F(7) | 2646 (8) | 8441 (8) | 2432 (10) |
| F(8) | 1093 (9) | 9125 (13) | 1592 (10) |
| F(9) | 2153 (11) | 10319 (10) | 2558 (15) |
| F(10) | 945 (11) | 8133 (10) | 3306 (12) |
| F(11) | 2101 (10) | 9250 (12) | 4218 (10) |

[a] Estimated standard deviations are in parentheses.

**Table III.** Bond Lengths (Å) for $[IBr_2][Sb_2F_{11}]$[a]

| | | | |
|---|---|---|---|
| I(1)–Br(1) | 2.424 (3) | Sb(1)–F(5) | 1.844 (13) |
| I(1)–Br(2) | 2.422 (3) | Sb(1)–F(6) | 1.846 (13) |
| I(1)–F(4) | 2.845 (12) | Sb(2)–F(3) | 2.003 (12) |
| I(1)–F(7) | 2.782 (12) | Sb(2)–F(7) | 1.862 (12) |
| Sb(1)–F(1) | 1.838 (12) | Sb(2)–F(8) | 1.823 (13) |
| Sb(1)–F(2) | 1.837 (12) | Sb(2)–F(9) | 1.832 (14) |
| Sb(1)–F(3) | 2.030 (13) | Sb(2)–F(10) | 1.840 (15) |
| Sb(1)–F(4) | 1.868 (12) | Sb(2)–F(11) | 1.829 (13) |

[a] Estimated standard deviations are in parentheses.

**Table IV.** Atomic Coordinates (×10$^4$) for $[IBr_{0.75}Cl_{1.25}][SbCl_6]$[a]

| | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| I(1) | 3088 (1) | 5347 (1) | 3485 (1) |
| Sb(1) | 0 | 0 | 0 |
| Sb(2) | 0 | 5000 | 5000 |
| XA | 4913 (3) | 8618 (3) | 3223 (2) |
| XB | 5441 (3) | 3886 (4) | 1627 (2) |
| Cl(1) | 1391 (5) | 2008 (5) | 4379 (2) |
| Cl(2) | 3077 (4) | 6714 (5) | 5539 (2) |
| Cl(3) | −208 (4) | 6530 (5) | 3398 (2) |
| Cl(4) | 6984 (4) | 1452 (5) | 9689 (2) |
| Cl(5) | 8572 (5) | 6971 (4) | 515 (2) |
| Cl(6) | 478 (5) | 1502 (5) | 1734 (2) |

[a] Estimated standard deviations are in parentheses.

**Table V.** Bond Lengths (Å) for $[IBr_{0.75}Cl_{1.25}][SbCl_6]$[a]

| | | | |
|---|---|---|---|
| I(1)–XA | 2.427 (2) | Sb(1)–Cl(5) | 2.332 (3) |
| I(1)–XB | 2.373 (3) | Sb(1)–Cl(6) | 2.416 (3) |
| I(1)–Cl(3) | 2.927 (3) | Sb(2)–Cl(1) | 2.333 (3) |
| I(1)–Cl(6) | 2.976 (3) | Sb(2)–Cl(2) | 2.354 (3) |
| Sb(1)–Cl(4) | 2.343 (3) | Sb(2)–Cl(3) | 2.422 (3) |

[a] Estimated standard deviations are in parentheses.

population parameters refined to 1.54 and 1.38 for the disordered atoms XA and XB, respectively. Thus if atom XA is assigned as a bromine, the population parameter refines to 0.70, corresponding to a 24-electron scatterer, while, if it is assigned as chlorine, the population parameter refines to 1.54, corresponding to a 26-electron scatterer. Atom XA then behaves, on average, as a 25-electron scatterer, consistent with a composition comprising about 0.45 Br and 0.55 Cl. Assignment of the disordered atom XB as bromine results in a population parameter of 0.60 (ca. 21 electrons) while refinement as chlorine results in a population parameter of 1.38 (ca. 23 electrons). Thus an average 22-electron scatterer would comprise about 0.30 Br and 0.70 Cl. These values result in a cation with an overall stoichiometry that is approximately $[IBr_{0.75}Cl_{1.25}]^+$. In the subsequent stages of the refinement the scattering factor curves for atoms XA and XB were calculated by using the curves for chlorine and bromine[12] and the above ratios for each atom. The scattering factor curve for XA as a function of $(\sin\theta)/\lambda$ was constructed by taking $0.45(\mathrm{sfac_{Br}}) + 0.55(\mathrm{sfac_{Cl}})$ for each of the given values for $(\sin\theta)/\lambda$. In the final stages of the least-squares refinement the population parameters of XA and XB were varied and both refined to a value of 1, and the thermal parameters for these disordered atoms were reasonable, indicating that the calculated

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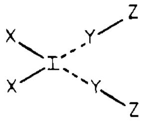
[12] "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1962.

**Table VI.** Geometry around Iodine in $[IX_2][ZY_6]$ and Related Compounds[a]



| | I–X, A | I···Y, A | X–I–X, deg | Y···I···Y, deg | I–Y–Z, deg | $[IX_2Y_2]$,[b] deg |
|---|---|---|---|---|---|---|
| $[ICl_2][SbF_6]$[4] | 2.268 (2) | 2.650 (6) | 97.2 (1) | 91.2 (2) | 155.3 (3) | 13.9 |
| $[ICl_2][SbCl_6]$[5] | 2.33 (4) | 2.85 (4) | 92.5 (14) | 85.0 (14) | 116.8 | 7.9[c] |
| | 2.29 (4) | 3.00 (4) | | | 114.8 | |
| $[ICl_2][AlCl_4]$[5] | 2.29 (4) | 2.86 (4) | 96.7 (14) | 85.3 (14) | 116 | 4.1[c] |
| | 2.26 (4) | 2.88 (4) | | | 108 | |
| $I_2Cl_6$[19] | 2.38 (3) | 2.72 (3) | 94 (1) | 86 (1) | | 0 |
| | 2.39 (3) | 2.68 (3) | | | | |
| $[IBr_{0.75}Cl_{1.25}][SbCl_6]$ | 2.427 (2) | 2.927 (3) | 97.67 (9) | 81.11 (9) | 109.3 (1) | 0.9 |
| | 2.373 (3) | 2.976 (3) | | | 122.1 (1) | |
| $[IBr_2][Sb_2F_{11}]$ | 2.424 (3) | 2.845 (12) | 100.0 (1) | 85.6 (3) | 151.6 (6) | 4.7 |
| | 2.422 (3) | 2.782 (12) | | | 153.3 (6) | |
| $[I_3][AsF_6]$ | 2.660 (2) | 3.01 (1) | 101.75 (6) | 101.58[d] | 124.42[d] | 11.1[d] |
| | 2.669 (2) | 3.07 (1) | | | 118.94[d] | |

[a] Estimated standard deviations are in parentheses. [b] $[IX_2Y_2]$ represents the angle in degrees between the two planes defined by $IX_2$ and $IY_2$. [c] Calculated here from atomic positions in ref 5. [d] Calculated here from atomic positions in ref 6.

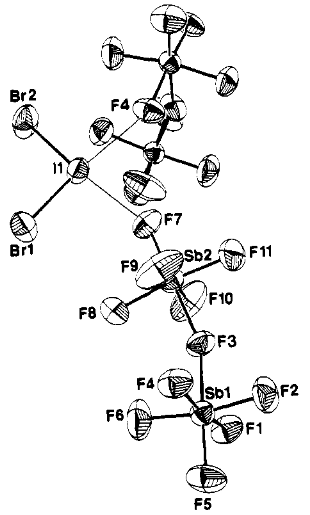


**Figure 1.** Structure of $[IBr_2][Sb_2F_{11}]$ showing the coordination around iodine and antimony.

scattering factor curves for the disordered atoms XA and XB were good models of their scattering power.

A structure solution was also attempted in the acentric space group $P1$ to test whether the observed disorder in space group $P\bar{1}$ was due to a crystallographically imposed center of symmetry. Refinement in space group $P1$ did not remove the disorder problem, and the overall agreement was not improved despite the fact that the number of refined parameters was nearly doubled.

The final atomic positional coordinates and the thermal parameters for $[IBr_{0.75}Cl_{1.25}][SbCl_6]$ are given in Table IV and the supplementary material, respectively. The bond lengths of the molecule are found in Table V, and bond angles are given in the supplementary material. The atomic arrangement in the molecule is illustrated in Figure 3, and a stereoscopic view of the packing in the unit cell along the *b* axis is shown in Figure 4.

**Laser Raman Spectroscopy.** Raman spectra of powdered samples were obtained with either a Spectra-Physics Model 164 argon ion laser, which gives up to 900 mW at 5145 Å, or a Spectra-Physics 250 helium/neon laser, which gives up to 70 mW at 6328 Å. The spectrometer was a Spex Industries Model 14018 double monochromator equipped with 1800 grooves/mm holographic gratings. An RCA C31034 phototube detector in conjunction with a pulse count system consisting of pulse amplifier, analyzer, and rate meter (Hamner NA-11, NC-11, and N-780A, respectively) and a Texas Instruments FSOZWBA strip chart recorder were used to record the spectra. The Raman shifts quoted are estimated to be accurate to ±1 $cm^{-1}$. The slit width used depended on the scattering efficiency of the sample, laser power, etc., with 100 μm being typical.

Cylindrical sample tubes were mounted vertically so that the angle between the incident laser beam and the sample tube was 45°, and Raman-scattered radiation was observed at 45° to the laser beam or 90° to the sample tube direction. We recorded the spectra while spinning the sample tube, which was cooled to −196 °C by mounting it vertically in an unsilvered Pyrex glass Dewar filled with liquid nitrogen.

## Results and Discussion

The X-ray crystal structure of $[IBr_2][Sb_2F_{11}]$ consists of infinite chains of $[IBr_2]^+$ cations, each of which has the trapezoidal geometry around iodine completed by bridging interactions to fluorine atoms of two separate $[Sb_2F_{11}]^-$ anions. These $[Sb_2F_{11}]^-$ anions have terminal Sb–F bonds averaging 1.84 Å, while the cation bridging Sb–F distances are 1.868

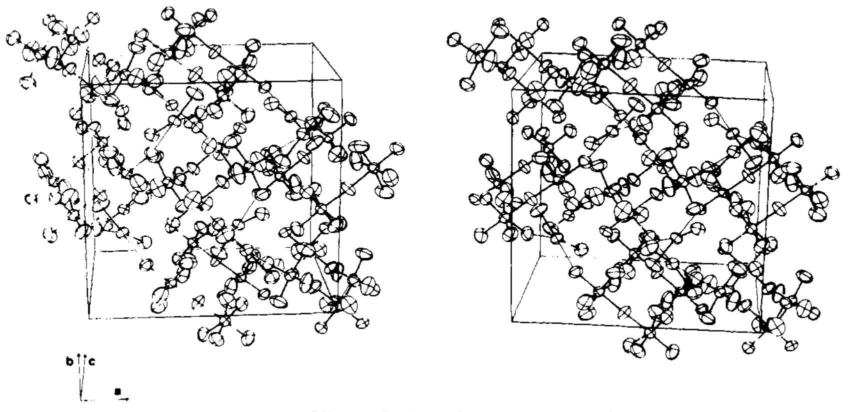


**Figure 2.** Stereoscopic drawing of the unit cell of $[IBr_2][Sb_2F_{11}]$ viewed along the *c* axis.

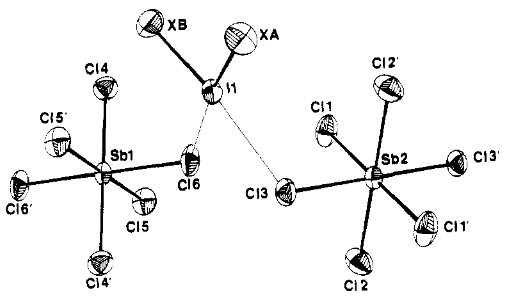


**Figure 3.** Structure of $[IBr_{0.75}Cl_{1.25}][SbCl_6]$ showing the coordination about iodine and antimony.

(12) and 1.862 (12) Å, respectively. The bridging Sb–F distances in the anion are 2.030 (13) and 2.003 (12) Å, and the Sb–F–Sb bond angle is 157.3 (6)°. The geometry of the $[Sb_2F_{11}]^-$ anion in $[IBr_2][Sb_2F_{11}]$ is very similar to that which is found in $[I_2][Sb_2F_{11}]$.[13]

The structure of $[IBr_{0.75}Cl_{1.25}][SbCl_3]$ is similar in that it consists of infinite chains of two crystallographically unique alternating $[SbCl_6]^-$ anions trans bridged through chlorine to the disordered cations. The two crystallographically discrete $[SbCl_6]^-$ anions are similar to each other and not unusual in their geometries. Each $[SbCl_6]^-$ anion possesses crystallographic symmetry in the form of an inversion center since Sb(1) is found at the special position (0, 0, 0) and Sb(2) is located at the special position $(0, {}^1/_2, {}^1/_2)$. As a result of the trans-bridged chlorine interaction to the cations, the anions are distorted from regular $O_h$ symmetry to $D_{4h}$ symmetry. In the Sb(1) octahedron the average Sb–Cl terminal bond distance is 2.338 Å while in the Sb(2) octahedron the terminal Sb–Cl distances average 2.344 Å. The Sb–Cl bridging bond lengths are elongated in these two octahedra to 2.416 (3) and 2.422 (3) Å, respectively. The Cl–Sb–Cl bond angles in both $[SbCl_6]^-$ anions remain close to 90°.

Table VI summarizes the geometry about the iodine atoms in these compounds and in related molecules. The data for $[IBr_2][Sb_2F_{11}]$ are the first reported X-ray crystal structure for a compound containing the $[IBr_2]^+$ cation. The I–Br bond distances are 2.424 (3) and 2.422 (3) Å, which can be compared to the I–Br distance in gaseous IBr (2.470 (5) Å) as determined by vibrational spectroscopy[14] and to the sum of the covalent radii of bromine and iodine, which is 2.48 Å.[15] Bridging I···Br interactions in diphenyliodonium bromide[16] are substantially longer and average 3.250 Å. The I···F secondary interactions in $[IBr_2][Sb_2F_{11}]$ are 2.845 (12) and 2.782 (12) Å, both of which are significantly longer than the same interaction in $[ICl_2][SbF_6]$ (2.650 (6) Å[4]) but similar to other I···F secondary interactions that have been reported.[13,17,18] From the relationship of Wiebenga and Kracht,[15] these bridging I···F interactions in $[IBr_2][Sb_2F_{11}]$ have bond orders of ca. 0.35.

The disordered cation $[IBr_{0.75}Cl_{1.25}]^+$ ($[IX_AX_B]^+$) has the iodine in a similar environment with two short contacts and two much longer ones. The I–XA and I–XB bond lengths are 2.427 (2) and 2.373 (3) Å, respectively. These bond distances may be compared to the I–Cl terminal bond distances found in the $[SbCl_6]^-$,[5] $[AlCl_4]^-$,[5] and $[SbF_6]^-$ [4] analogues of $[ICl_2]^+$ and the I–Br terminal bond distances in $[IBr_2][Sb_2F_{11}]$ (Table VI). The I–Cl bond distances in the $[ICl_2]^+$ cations average 2.29 Å while the I–Br bond distances in $[IBr_2][Sb_2F_{11}]$ average 2.423 Å. The I–XA(XB) bond lengths are consistent with the disordered atom XA having a higher percentage of bromine than the disordered atom XB. The I–XA distance is almost the same as the I–Br distance in $[IBr_2]^+$ whereas the I(1)–XB bond distance is roughly midway between the average of the I–Cl and I–Br terminal bond lengths. Although the formulation $[IBr_{0.75}Cl_{1.25}]^+$ could be accommodated by a disordered mixture of the $[IBr_2]^+$ and $[ICl_2]^+$ cations, the bond lengths cannot be rationalized on this basis, and it is necessary to have some contribution from the $[BrICl]^+$ cation to satisfy the observed atomic distances. It must be kept in mind that the final bond distance between the I atom and one of the disordered atoms, e.g. XA, is the average distance between all pairs of these two atoms found at these particular positions in the crystal structure.

The bridging contacts from the cation to the anion are through chlorine rather than through fluorine as in $[IBr_2][Sb_2F_{11}]$ and $[ICl_2][SbF_6]$;[4] these distances are I(1)···Cl(3) = 2.927 (3) Å and I(1)···Cl(6) = 2.976 (3) Å. The corresponding secondary interactions in $[ICl_2][SbCl_6]$[5] and $[ICl_2][AlCl_4]$[5] average 2.90 Å while in $I_2Cl_6$,[19] a more covalent type of compound, the bridging bond is much shorter at 2.70 Å. From the relationship of Wiebenga and Kracht,[15] these bridging I···Cl interactions have a bond order of ca. 0.45, similar to that which is found for the bridging I···F interaction in $[ICl_2][SbF_6]$.[4]

As is found for the $[ICl_2]^+$ cation,[4,5] there is significant deviation of the X–I–X bond angle from 90° in $[IBr_2]^+$ and $[IBr_{0.75}Cl_{1.25}]^+$. In compounds of $[ICl_2]^+$ the Cl–I–Cl angle was found to open up as the size of the anion decreased. In the case of $[IBr_2]^+$ the larger size of bromine, compared to chlorine, seems to be the most important factor, and the Br–I–Br bond angle is 100.0 (1)°. The influence of the larger bromine is evident in a comparison of the X–I–X angle in $[IBr_{0.75}Cl_{1.25}][SbCl_6]$ with that in $[ICl_2][SbCl_6]$ where the anion is common and the former cation has the large bond angle by 5°. In $[I_3][AsF_6]$[6] the I–I–I angle is even larger.

Another feature of interest in Table VI is the angle at the halogen that bridges cation to anion. For the I–F–Sb angle a value of ~153° appears to be normal, but when the bridging halogen is chlorine, the value drops to ~115°. One might be tempted to say that for a small bridging atom like fluorine, the angle at the bridging atom needs to be quite large, whereas for a larger bridging atom such as chlorine this constraint is not as critical and the angle can be smaller. However, it should be noted that the corresponding fluorine bridging angle in $[I_3][AsF_6]$ is only ~122°. It seems likely that factors such as packing of the ions in the crystal will also play a significant role in determining this angle.

The $[IBr_2][Sb_2F_{11}]$ is very similar to both $[ICl_2][SbCl_6]$ and $[ICl_2][AlCl_4]$ in terms of the degree of deviation from planarity of the $[IX_2Y_2]$ unit. A least-squares mean-plane analysis of the $[IBr_2F_2]$ fragment in $[IBr_2][Sb_2F_{11}]$ shows that one fluorine atom lies +0.23 Å out of the plane defined by the iodine and two bromine atoms, while the other fluorine atom remains in the $[IBr_2]$ plane. The angle between the two planes defined by Br(1)–I–Br(2) and F(4)–I–F(7) is 4.7°. The analogous two planes in $[ICl_2][SbF_6]$ have an angle between them of 13.9°. Thus in $[ICl_2][SbF_6]$ where the secondary interactions between cation and anion are strong, the $[IX_2Y_2]$ unit is distorted from planarity more severely than in $[ICl_2][SbCl_6]$,[5] $[ICl_2][AlCl_4]$,[5] and $[IBr_2][Sb_2F_{11}]$ where the longer, weaker, secondary interactions allow the $[IX_2Y_2]$ moiety to be less distorted.

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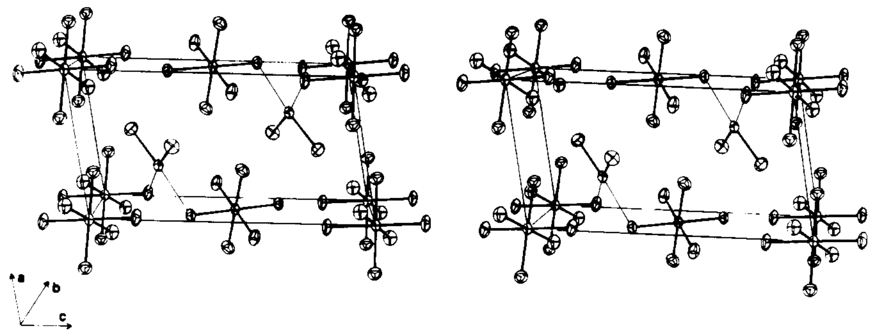


**Figure 4.** Stereoscopic drawing of the unit cell of [$IBr_{0.75}Cl_{1.25}$][$SbCl_6$] viewed along the *b* axis.

**Table VII.** Raman Frequencies of Iodine(III)–Halogen Cations, $\Delta\nu$ (cm$^{-1}$)

| [$ICl_2$]-[$SbCl_6$][20] | [$ICl_2$]-[$SbF_6$][4] | [$IBr_2$]-[$SO_3F$][21] | [$IBr_2$]-[$Sb_2F_{11}$] | [BrICl]-[$SbCl_6$][9] | [$IBr_{0.75}Cl_{1.25}$]-[$SbCl_6$] | assignt |
|---|---|---|---|---|---|---|
| 371 (100) | 393 (100) | | | 370 (100) | 362 (62) | $\nu_1(A_1)$ I–Cl str |
| 364 (66) | 387 (45) | | | 362 (sh) | 356 (58) | $\nu_3(B_1)$ |
| | | | | 323 (47) | 336 (60) | $\nu_1(A_{1g})$ [$SbCl_6$]$^-$ |
| | | | | 268 (22) | 296 (13) | $\nu_2(E_g)$ [$SbCl_6$]$^-$ |
| | | | | | 258 (13) | |
| | | 256 | 257 (63) | | 250 (62) | $\nu_3(B_1)$ I–Br str |
| | | 256 | 232 (100) | 255 (37) | 242 (100) | $\nu_1(A_1)$ |
| | 291 (9) | | | 177 (16) | 174 (13) | $\nu_5(T_{2g})$ [$SbCl_6$]$^-$ |
| | | | | 170 (19) | | |
| | | | 197 (34) | | | |
| 147 (10) | 142 (35) | 124 | 123 (12) | 149 (16) | 129 (33) | $\nu_2(A_1)$ bend |
| | 55 (57) | | | 125 | | lattice |
| | | | | 70 | | |

A least-squares mean-plane analysis of the [$IXAXBCl_2$] fragment of [$IBr_{0.75}Cl_{1.25}$][$SbCl_6$] shows that Cl(3) and Cl(6) lie −0.02 and +0.04 Å, respectively, out of the plane defined by XA–I–XB and that the angle between the planes XA–I–XB and Cl(3)–I–Cl(6) is 0.9°. This cation is the most planar of the cations whose structures have been reported so far. The long secondary interactions from cation to anion coupled with the larger bridging halogen (chlorine) allow the cation to adopt a nearly perfectly planar arrangement, though once again these distortions must be strongly influenced by the packing arrangements.

**Raman Spectroscopy.** The Raman spectra of these cations are summarized in Table VII together with literature data for related compounds for comparison. Raman data for the [$IBr_2$]$^+$ cation have been reported by Wilson and Aubke[7] but only two of the three Raman-active modes for this cation were observed. The two stretching modes, $\nu_1$ and $\nu_3$, were assigned as being coincident at 256 cm$^{-1}$, while $\nu_2$ was assigned at 124 cm$^{-1}$. Wilson and Aubke[7] predicted that the [$IBr_2$]$^+$ cation would be bent, and we have shown this to be the case by our X-ray analysis of the [$Sb_2F_{11}$]$^-$ analogue. Our results for [$IBr_2$][$Sb_2F_{11}$] are in substantial agreement with those of the earlier workers although we find all three vibrational modes for the [$IBr_2$]$^+$ cation. The strongest band at 232 cm$^{-1}$ is assigned to $\nu_1$, the totally symmetric stretch, while the other strong band at 257 cm$^{-1}$ is assigned as $\nu_3$, the antisymmetric stretch. The third cation band, the $\nu_2$ band, is at 123 cm$^{-1}$. The only other band in this region, at 197 cm$^{-1}$, is attributed to the anion. Differences between our results and those of Wilson and Aubke[7] probably arise from the different degrees of cation–anion interaction in the two compounds.

Since both the [$I_2$]$^+$ and [$Br_2$]$^+$ species have been characterized by X-ray crystallography,[13,21] it seemed reasonable that the mixed dihalogen cation should also exist. However, the [IBr]$^+$ cation has so far eluded isolation. The preparation described here, which produced [$IBr_2$][$Sb_2F_{11}$], was one such attempt to obtain [IBr]$^+$. Recently we have obtained $^{127}$I Mössbauer evidence for the dimerization of [$I_2$]$^+$ in solution to give the [$I_4$]$^{2+}$ cation,[22] and Gillespie et al.[23] have shown by X-ray crystallography that the [$I_4$]$^{2+}$ cation has a rectangular arrangement of the iodine atoms. There does not appear to be any reason to suppose that a similar dimerization of [IBr]$^+$, if formed, could not also occur to give **1**. We suggest

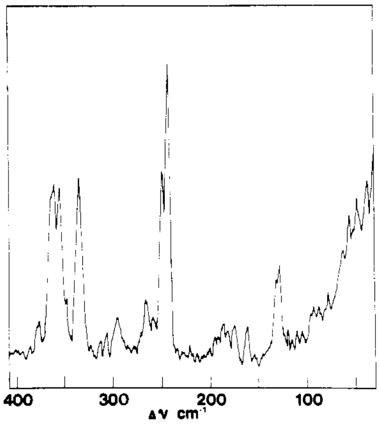
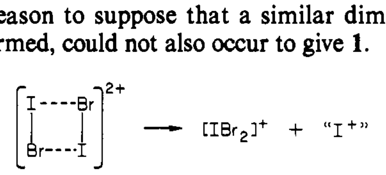


**Figure 5.** Raman spectrum of [$IBr_{0.75}Cl_{1.25}$][$SbCl_6$] taken at 77 K with 5145-Å excitation.



**1**

that this would be unstable with respect to decomposition to the [$IBr_2$]$^+$ cation and the elusive "I$^+$" cation. This latter species would be an extremely strong Lewis acid and pick up IBr molecules to form [$I_3Br_2$]$^+$, a species that is known.[24] We

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have previously suggested that the transient generation of "$I^+$" in the presence of ICl leads to the formation of the $[I_3Cl_2]^+$ cation.[25] If $[IBr]^+$ is produced in the oxidation of IBr, our inability to obtain $[IBr][Sb_2F_{11}]$ or similar salts is most likely due to the greater stability of its decomposition products under the conditions prevailing in our preparation.

We also attempted to prepare $[IBrCl][SbCl_6]$ according to the method of Shamir and Lustig.[9] However, the material that we obtained has the composition $[IBr_{0.75}Cl_{1.25}][SbCl_6]$ as we have established X-ray crystallography. The Raman spectrum of this material is shown in Figure 5 and the principal bands are given in Table VII. After assignment of the anion bands, the number of bands remaining is too great for the presence of only the simple $[IBrCl]^+$ cation, which should have only three bands. Indeed X-ray crystallography shows the cation composition to be $[IBr_{0.75}Cl_{1.25}]^+$, i.e., is a disordered mixture of probably all of the following cations: $[IBr_2]^+$, $[ICl_2]^+$, and $[IBrCl]^+$. Two I–Cl and two I–Br vibrations are clearly visible in our spectrum, which can be assigned to the appropriate modes of the $[ICl_2]^+$ and $[IBr_2]^+$ cations, respectively. We are unable to uniquely assign any bands to the $[IBrCl]^+$ cation, but these would occur in the same regions of the spectrum as the other cations and be obscured by these bands. The similarity between our spectrum and that of Shamir and Lustig,[9] whose preparation we followed, is close, although the relative intensities of the bands in the two spectra are not the same. It is not clear why we were unable to obtain pure $[IBrCl][SbCl_6]$ or even to change the composition of our disordered cation by repeated sublimation. Other workers[3] who isolated $[IBrCl][SO_3F]$ from the reaction between $[IBr_2][SO_3F]$ and $[ICl_2][SO_3F]$ were unable to decide unequivocally that they had prepared a true compound of $[IBrCl]^+$. Their reaction also could have resulted in a disordered bent cation as we have found.

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**Registry No.** $[IBr_2][Sb_2F_{11}]$, 56664-97-2; $[IBr_{0.75}Cl_{1.25}][SbCl_6]$, 85421-80-3; $[ICl_2][SbCl_6]$, 38656-81-4; $[ICl_2][AlCl_4]$, 42813-30-9; $[I_3][AsF_6]$, 59555-19-0.

**Supplementary Material Available:** A plot of scattering factor curves and listings of observed and calculated structure factor amplitudes, bond angles, and anisotropic thermal parameters (49 pages). Ordering information is given on any current masthead page.

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Contribution from the Molecular Structure Center and the Department of Chemistry,
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# Addition of Carboxylic Acids to $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2P(OC_2H_5)_2)]_4$ and the Molecular Structure of $[Mo(NC_6H_4CH_3)(S_2P(OC_2H_5)_2)]_2(\mu\text{-}S)(\mu\text{-}SH)(\mu\text{-}O_2CCF_3)$

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The addition of $CF_3CO_2H$ to solutions of $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2P(OC_2H_5)_2)]_4$ in $CH_2Cl_2$ results in $[Mo(NC_6H_4CH_3)(S_2OC_2H_5)_2)]_2(\mu\text{-}S)(\mu\text{-}SH)(\mu\text{-}O_2CCF_3)$, which crystallizes in the monoclinic space group $P2_1/a$, with $a = 23.569$ (9) Å, $b = 17.162$ (6) Å, $c = 10.050$ (3) Å, $\beta = 111.88$ (1)°, and $Z = 4$ at −165 °C. The bridging sulfhydryl ligand is bent away from the terminal, multiply bound arylimido ligands. A comparison with other carboxylic acids indicates that the equilibrium constants for the addition of the acids follows the order $CF_3CO_2H \sim CCl_3CO_2H > CHCl_2CO_2H > CH_2ClCO_2H > CH_3CO_2H$. In contrast, no reaction was observed between $[MoO(\mu\text{-}S)(S_2P(OC_2H_5)_2)]_2$ and $CF_3CO_2H$. Evidence for the existence of the conjugate bases, $[Mo(NC_6H_4CH_3)(S_2P(OC_2H_5)_2)]_2(\mu\text{-}S)_2(\mu\text{-}O_2CR)^-$, has also been accumulated.

## Introduction

The existing analogy between the structures of mononuclear oxo and arylimido compounds of molybdenum[1] suggests the likelihood of a similar analogy with certain dinuclear compounds. Thus, the authenticated structure[2] of $[MoO(\mu\text{-}S)(S_2P(O\text{-}i\text{-}C_3H_7)_2)]_2$ would suggest the existence of a similar compound with terminal arylimido ligands. The isolation[3] of the structurally characterized,[4] cubane-like tetranuclear compound $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2P(OC_2H_5)_2)]_4$ (**T**) was then totally unexpected. The formation of this compound from the expected dinuclear fragments of $[Mo(NC_6H_4CH_3)(\mu\text{-}S)(S_2P(OC_2H_5)_2)]_2$ (**D**), as shown by the equilibrium in eq 1, was recognized and verified experimentally. The equilibrium

$$2\mathbf{D} \rightleftarrows \mathbf{T} \tag{1}$$

constant for this reaction was found to be about $10^4$ in $CH_2Cl_2$. Clearly, substitution of arylimido ligands for oxo ligands has caused either enhanced Lewis acidities for the metal atoms (possibly due to a lessened trans effect), enhanced Lewis basicities for the bridging sulfur atoms, or both.

Although an enhanced Lewis basicity for a bridging sulfur atom will not necessarily be accompanied by an enhanced susceptibility to protonation, we elected to examine the reactions of **T** with a series of substituted acetic acids. The goals of this study were to delineate the site of protonation (if, indeed, protonation occurs), to determine if the apparent basicity of this site is in qualitative agreement with the acidities of the carboxylic acids, and to compare the ease of protonation of **T** with that of $[MoO(\mu\text{-}S)(S_2P(OC_2H_5)_2)]_2$.

## Experimental Section

**Reagents and Procedures.** Manipulations performed under nitrogen were done by using standard vacuum-line techniques and solvents that

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