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Contribution from the Department of Chemistry and Institute for Materials Research,
McMaster University, Hamilton, Ontario, Canada, L8S 4M1

Preparation of $[I_3Cl_2]^+[SbCl_6]^-$ and Its Characterization by X-ray Crystallography and Raman Spectroscopy

THOMAS BIRCHALL* and RONALD D. MYERS

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The X-ray crystal structure of I_3SbCl_8 has been determined from diffractometer data by the heavy-atom method. Crystals of I_3SbCl_8 are triclinic, space group $P\bar{1}$, with $a = 7.090$ (1) Å, $b = 11.591$ (2) Å, $c = 7.126$ (1) Å, $\alpha = 122.29$ (1)°, $\beta = 98.85$ (1)°, $\gamma = 115.86$ (1)°, $V = 383.5$ (1) Å^3, and $d_{calcd} = 3.404$ g cm^{-3} for $Z = 1$. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares to $R_1 = 0.032$ and $R_2 = 0.040$ for 1545 observed ($I > 3\sigma(I)$) reflections. In an ionic approximation, the structure consists of planar centrosymmetric $(C_{2h})[I_3Cl_2]^+$ cations and slightly distorted octahedral $[SbCl_6]^-$ anions. A reasonably strong cation–anion interaction does exist however in the form of an iodine–chlorine bridging contact of 2.941 (1) Å. The I–I and I–Cl bond distances in the novel $[I_3Cl_2]^+$ cation are 2.9057 (6) and 2.333 (1) Å, respectively. The Raman and visible absorption spectra of $[I_3Cl_2]^+[SbCl_6]^-$ are nearly identical with those which have been reported previously for $[I_2Cl]^+[SbCl_6]^-$. The unit cell parameters of crystals obtained from the reaction reported to produce $[I_2Cl]^+[SbCl_6]^-$ have been determined from diffractometer measurements and were found to be the same as those which we report here for $[I_3Cl_2]^+[SbCl_6]^-$. These findings cast considerable doubt on the existence of the previously reported $[I_2X]^+$ (X = Cl, Br) cations.

Introduction

The reactions of I_2Cl_6 with a number of Lewis acids such as $SbCl_5$,[1] $AlCl_3$,[1] SbF_5,[2,3] and SO_3[4] have been thoroughly studied. The hexachloroantimonate,[5] tetrachloroaluminate,[5] and more recently the hexafluoroantimonate[3] salts of $[ICl_2]^+$ have all been well established by X-ray crystallographic studies.

In an effort to further our studies of the reactions of I_2Cl_6 with potential Lewis acid acceptors and synthesize new polyhalogen cations of iodine, we have investigated the reaction of I_2Cl_6 with antimony(III) chloride. This reaction produced a highly crystalline material whose ^{121}Sb Mössbauer spectrum indicated the presence of Sb(V) rather than Sb(III).

It has been reported[6-8] that under suitable conditions iodine monochloride combines with antimony pentachloride to produce compounds with the general formulas $I[SbCl_6]\cdot nICl$ (n = 2–4), i.e., containing the cations $[I_3Cl_2]^+$, $[I_4Cl_3]^+$, and $[I_5Cl_4]^+$. The existence of any of these higher polyatomic cations of iodine has not been verified until now.[27]

We report here the X-ray crystal structure of $[I_3Cl_2]^+$-$[SbCl_6]^-$, the first structure of an interhalogen compound of iodine containing a cation of the general type $[I_nCl_{n-1}]^+$. The laser Raman spectrum and visible absorption spectrum of $[I_3Cl_2]^+[SbCl_6]^-$ are very similar to the corresponding spectra previously reported for $[I_2Cl]^+[SbCl_6]^-$.[9] We have shown that a single crystal, sublimed from the product of the reaction reported to produce $[I_2Cl]^+[SbCl_6]^-$, has the same unit cell parameters as $[I_3Cl_2]^+[SbCl_6]^-$.

Experimental Section

$[I_3Cl_2]^+[SbCl_6]^-$ was prepared as follows: 3.4303 g (15.03 mmol) of resublimed $SbCl_3$ was added to one side of a glass, Dean-type reaction vessel[10] under a dry-nitrogen atmosphere in a glovebox. Then 3.4134 g (7.31 mmol) of I_2Cl_6, prepared by direct oxidation of resublimed I_2 with dry Cl_2, was added to the other side of the vessel by vacuum sublimation from a preweighed glass vessel. SO_2 was then distilled onto the $SbCl_3$, and when the latter had dissolved the $SbCl_3/SO_2$ solution was poured onto the I_2Cl_6 through the sintered glass frit. After overnight stirring, a fine, brown precipitate was formed which after repeated washing to the other side of the vessel remained as dark brown crystals. After the solution was cooled to 0 °C to ensure maximum crystal formation, the SO_2 was decanted to the other side of the vessel, which was then sealed under vacuum.

$[I_3Cl_2]^+[SbCl_6]^-$ is highly moisture sensitive, and attempts to mount crystals in rigorously dried Lindemann capillaries inside a glovebox containing an atmosphere consisting of less than 2–3 ppm of moisture resulted in rapid crystal decomposition. Part of the driving force of this decomposition is thought to be the loss of the partial vapor pressure of the volatile crystals when the glass vessel is opened. So that this problem could be overcome, a sample of the material was placed in a sublimation vessel to which fine (0.2–0.3 mm) quartz capillaries had been attached. When a small temperature gradient was applied across the vessel, crystals were eventually sublimed into the capillaries without decomposition. The melting point of a single crystal of $[I_3Cl_2]^+[SbCl_6]^-$ under its own vapor pressure is 47 °C, giving a brown liquid with no decomposition. $[I_3Cl_2]^+[SbCl_6]^-$ gave satisfactory gravimetric analysis for total halide present by precipitation of AgI and AgCl.

The method of Shamir and Lustig[9] was followed in an attempt to prepare $[I_2Cl]^+[SbCl_6]^-$, and crystals were grown as described above.

Crystal Data. I_3SbCl_8: fw = 786.35; triclinic, $P\bar{1}$; $a = 7.090$ (1), $b = 11.591$ (2), $c = 7.126$ (1) Å; $\alpha = 122.29$ (1), $\beta = 98.85$ (1), $\gamma = 115.86$ (1)°; $V = 383.5$ (1) Å^3; $d_{calcd} = 3.404$ g cm^{-3} for $Z = 1$; Mo Kα radiation; $\lambda = 0.71069$ Å; μ(Mo Kα) = 92.63 cm^{-1}; $F(000) = 346.0$. The Delauney reduced primitive triclinic cell for this compound has $a' = 9.842$ Å, $b' = 7.126$ Å, $c' = 7.739$ Å, $\alpha' = 91.17°$, $\beta' = 134.35°$, $\gamma' = 95.44°$. It is related to the above cell by the transformation $(011)/(00\bar{1})/(\bar{1}\bar{1}\bar{1})$.

Intensity measurements were made on a Syntex P2$_1$ diffractometer using graphite-monochromated Mo Kα radiation. A nearly oval-shaped crystal of size 0.24 × 0.21 × 0.24 mm was selected for intensity measurements. The unit cell parameters were obtained from the least-squares refinement of the diffracting positions of 10 ($17° \leq 2\theta \leq 31°$) high-angle reflections. Reflections were measured with θ–2θ scans over a scan range Kα_1 − 1.0° to Kα_2 + 1.0°, with a variable scan rate of 4.0–29.3°/min depending on the intensity of a preliminary count. The intensities of two standard reflections were measured every 50 reflections, and these showed no significant variation during data collection. Reflections were eventually collected in the hemisphere with $0 \leq h \leq 9$, $-13 \leq k \leq 13$, and $-9 \leq l \leq 8$ for $5° \leq 2\theta \leq 55°$.

Lorentz and polarization corrections were applied to the data. Due to the shape of the crystal it was not possible to identify crystal faces and apply an adequate absorption correction. A spherical absorption correction was attempted and this resulted in no improvement to the data. Thus, although μR for the selected crystal was about 1.38, the data were not corrected for absorption. A total of 1711 unique reflections were collected of which 1545 were considered observed ($I \geq 3\sigma(I)$), and 1667 ($I \geq \sigma(I)$) were retained for refinement.

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Table I. Atomic Coordinates ($\times 10^4$)

	x/a	y/b	z/c
I(1)	1765.8 (6)	8336.3 (5)	682.0 (7)
I(2)	0	0	0
Sb(1)	5000	5000	0
Cl(1)	3269 (3)	4901 (2)	2627 (3)
Cl(2)	6918 (3)	7979 (2)	2661 (3)
Cl(3)	5817 (3)	833 (2)	3254 (3)
Cl(4)	8420 (3)	5637 (2)	2661 (3)

Table II. Bond Lengths (Å) and Bond Angles (Deg) for $[I_3Cl_2]^+[SbCl_6]^-$ [a] with Estimated Standard Deviations in Parentheses

I(1)-I(2)	2.9057 (6)	Sb(1)-Cl(1)	2.416 (2)
I(1)-Cl(3)	2.333 (1)	Sb(1)-Cl(2)	2.341 (2)
I(1)-Cl(1)	2.941 (1)	Sb(1)-Cl(4)	2.355 (2)
I(1)-I(2)-I(1′)	180.000 (7)	Cl(1)-Sb(1)-Cl(4)	89.56 (8)
Cl(3)-I(1)-I(2)	92.62 (7)	Cl(1″)-Sb(1)-Cl(4)	90.44 (8)
Cl(3)-I(1)-Cl(1)	177.56 (8)	Cl(2)-Sb(1)-Cl(4)	89.98 (8)
Cl(1)-I(1)-I(2)	89.55 (5)	Cl(2″)-Sb(1)-Cl(4)	90.02 (8)
I(1)-Cl(1)-Sb(1)	109.75 (5)	Cl(1)-Sb(1)-Cl(1″)	180.00 (4)
Cl(1)-Sb(1)-Cl(2)	89.71 (7)	Cl(2)-Sb(1)-Cl(2″)	180.00 (7)
Cl(1)-Sb(1)-Cl(2″)	90.29 (7)	Cl(4)-Sb(1)-Cl(4″)	180.00 (8)

[a] Symmetry transformations are (′) $-x, -y, -z$ and (″) $1-x, 1-y, -z$.

Structure Determination and Refinement. The structure was solved with conventional heavy-atom techniques in the centric space group $P\bar{1}$. The iodine atoms and antimony atom were located with a Patterson map; one iodine was placed on the special position (0, 0, 0) with $\bar{1}$ symmetry, and the antimony atom was placed on the special position ($^1/_2$, $^1/_2$, 0) also with $\bar{1}$ symmetry. Subsequent Fourier maps revealed the positions of the remaining chlorine atoms and confirmed the positional assignments of the heavy atoms. Full-matrix least-squares refinement in the space group $P\bar{1}$ converged to R_1 ($=\sum||F_o| - |F_c||/\sum|F_o|$) of 0.059 using anisotropic temperature factors for all atoms. It was evident that an extinction and/or absorption problem existed and subsequent to the application of a secondary extinction correction there was much better agreement between F_o and F_c found at low angles and high intensities. The extinction correction used followed the method of Larson[11] and calculated $g = 2.44 \times 10^{-3}$. In the final cycles of least-squares refinement, weights were calculated with the expression $w = 1.0/(\sigma(F_o)^2 + 1.1 \times 10^{-5}F_o^3 + 0.5 \sin \theta)$. Several cycles of full-matrix least squares using this weighting scheme and correcting for extinction converged to $R_1 = 0.032$ and $R_2 = 0.040$ ($R_2 = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$). In the final cycle of refinement, no parameter shift was greater than 9.1% of its standard error. A final difference Fourier showed a maximum peak and a minimum trough of +4.1 and −2.0 e/Å^3 around the antimony atom and the iodine atom at the origin, respectively. These values are somewhat large due to the lack of an adequate absorption correction for the data.

All calculations were performed on a Cyber 170/730 computer using the program SHELX-76[12a] in the initial stages, while the final refinement was completed with the series of programs in the XRAY 71 package.[12b] Atomic scattering factors corrected for anomalous dispersion were taken from ref 13. The final atomic positional coordinates are given in Table I. The bond lengths and bond angles of the molecule are given in Table II. Anisotropic thermal parameters and a listing of observed and calculated structure factor amplitudes may be found in the supplementary material.

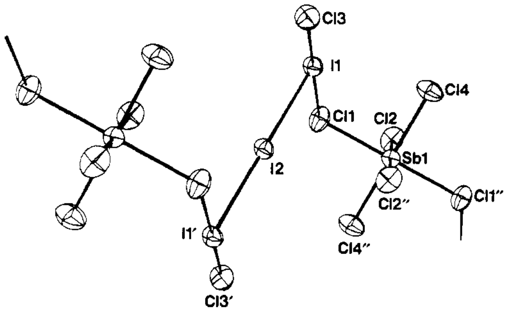

Figure 1. Molecular geometry of $[I_3Cl_2]^+[SbCl_6]^-$ showing the trans-bridged configuration of cation and anion. Symmetry transformations are (′) $-x, -y, -z$ and (″) $1 - x, 1 - y, -z$.

Laser Raman Spectroscopy. Raman spectra were obtained with either a 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. Spectra were recorded while spinning the sample tube and at −196 °C by mounting the sample tube vertically in an unsilvered Pyrex-glass Dewar filled with liquid nitrogen.

Visible Absorption Spectroscopy. The visible absorption spectrum of $[I_3Cl_2]^+[SbCl_6]^-$ was obtained with a Cary Model 14 spectrophotometer. The spectrum was recorded on a very dilute solution of $[I_3Cl_2]^+[SbCl_6]^-$ in SO_2 solvent with quartz cells with a sample thickness of 1 cm.

Results and Discussion

Structure of $[I_3Cl_2]^+[SbCl_6]^-$. The crystal structure consists of $[I_3Cl_2]^+$ cations and $[SbCl_6]^-$ anions which form infinite zigzag chains as a result of a secondary cation–anion interaction which occurs via a bridging chlorine atom. The atomic arrangement is illustrated in Figure 1, and a stereoscopic view of the packing in the unit cell is shown in Figure 2. The central iodine atom of the $[I_3Cl_2]^+$ cation lies on a crystallographic center of symmetry such that the cation is planar, and it possesses C_{2h} symmetry. The $[SbCl_6]^-$ anion is a very slightly distorted octahedron with the terminal Sb–Cl distances averaging 2.348 Å, while the bridging Sb···Cl(1) distance is somewhat longer at 2.416 (2) Å. The I(1)–I(2) bond distance in $[I_3Cl_2]^+[SbCl_6]^-$ is 2.9057 (6) Å. This may be compared to the analogous I–I bond distance found in the structurally related $[I_5]^+$ cation[14] and the average I–I distance observed in various symmetric and asymmetric $[I_3]^-$ ions.[15] The terminal I(1)–Cl(3) bond distance in the $[I_3Cl_2]^+$ cation is 2.333 (1) Å as compared to the I–Cl bond distance[16] in β-ICl which is 2.351 (14) Å. In β-ICl, in addition to the short I–Cl bond (2.351 Å) there is another longer I···Cl interaction at 2.939 (12) Å which is almost colinear (175°) with the primary bond. A similar interaction is present in $[I_3Cl_2]^+$ in the form of a secondary or bridging I(1)···Cl(1) contact at 2.941 (1) Å so that the Cl(3)–I(1)···Cl(1) angle is 177.56 (8)°. These terminal and bridging iodine–chlorine interactions are similar to those which occur in salts of $[ICl_2]^+$.[5]

The Cl(3)–I(1)–I(2) and Cl(1)···I(1)–I(2) bond angles found in $[I_3Cl_2]^+[SbCl_6]^-$ are 92.62 (7) and 89.55 (5)°, respectively. These values are very similar to those found for the analogous angles in $[I_5]^+$.

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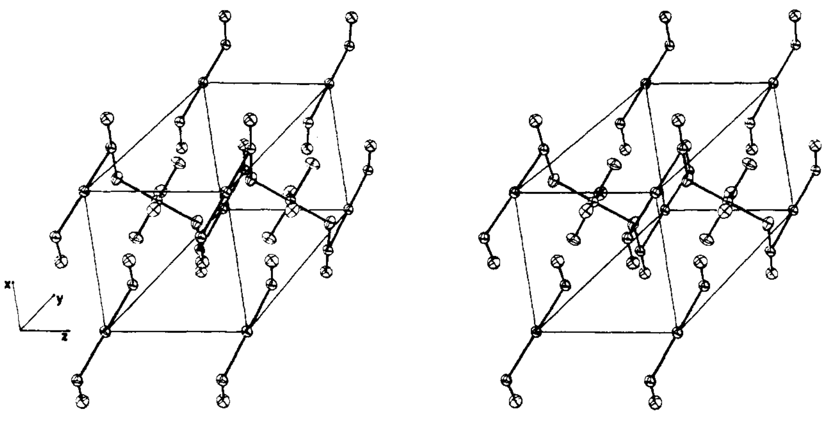
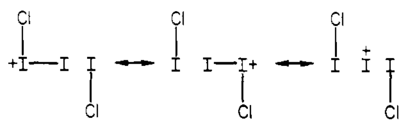


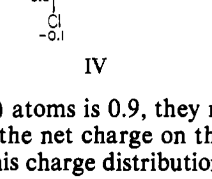
Figure 2. Stereoscopic drawing of the unit cell of $[I_3Cl_2]^+[SbCl_6]^-$ viewed along the y axis.

The bond orders of the bonding interactions found in $[I_3Cl_2]^+[SbCl_6]^-$ may be estimated by using the relationship between electrostatically corrected experimental bond lengths and calculated bond orders established for a series of interhalogen compounds by Wiebenga and Kracht.[17] According to this method, the I(1)–I(2) bond distance found in $[I_3Cl_2]^+[SbCl_6]^-$ corresponds to a bond order of ca. 0.6. The terminal I(1)–Cl(3) bond has an estimated bond order of 0.9. The analogous terminal I–I distances in the $[I_{15}]^{3+}$ cation[14] have an average bond order of 0.85. It appears then that the I(1)–Cl(3) interaction in $[I_3Cl_2]^+[SbCl_6]^-$ is of comparable strength to the corresponding I–I interactions in $[I_{15}]^{3+}$.

The variation in bond lengths present in the $[I_3Cl_2]^+$ cation suggests that it may be described by the valence bond structures I–III. Structures I and II imply formal bond orders of 1.0 and 0.5 for terminal and central bonds, respectively, while structure III, a minor contributor to the bonding description, would have a formal bond order of 1.0 for terminal bonds and 0 for the central bonds. An alternative charge distribution in $[I_3Cl_2]^+$ may be obtained by using the above bond orders and a bond valence type formalism similar to that of Brown.[18] According to this method, the sum of the bond orders to a particular atom must be equal to the sum of that atom's valency plus its charge. Since in $[I_3Cl_2]^+$ the I(1)–I(2) bond has an estimated bond order of 0.6 and the I(1)–Cl(3) estimated bond order is 0.9, the central I(2) atom must have a charge of +0.2, while the I(1) atoms much each have a charge of +0.5. This is shown in structure IV. Since the bond order of the terminal Cl(3) atoms is 0.9, they must bear a charge of −0.1 each so that the net charge on the $[I_3Cl_2]$ moiety is +1.0. Considering this charge distribution it is reasonable to assume that there is a secondary interaction between the I(1) atoms of the cation which possess the highest formal positive charge and the Cl(1) atoms of the $[SbCl_6]^-$ anions, whereas the less positive, central I(2) atom shows no such interaction. The formalism employed above to arrive at this model is, of course, semiempirical, depending to a large extent on the method used to obtain bond orders, and in neglecting the I(1)···Cl(1) secondary interaction, assumes some degree of ionicity in the molecule.



I II III



IV

Raman Spectroscopy. The laser Raman spectrum of a large crystal of $[I_3Cl_2]^+[SbCl_6]^-$ obtained at liquid-nitrogen tem-

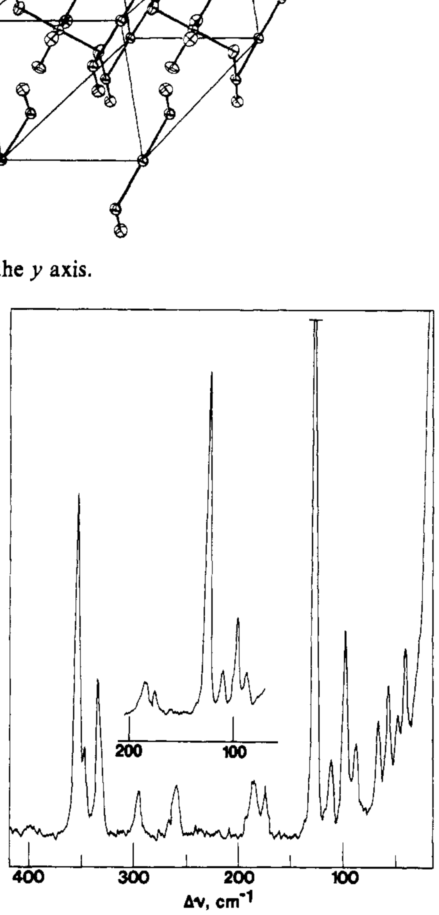


Figure 3. Raman spectrum of $[I_3Cl_2]^+[SbCl_6]^-$ at −196 °C with 6328-Å excitation.

Table III. Raman Frequencies and Assignments for $[I_3Cl_2]^+[SbCl_6]^-$

	freq shift,	assignts	
intens	cm⁻¹	$[I_3Cl_2]^+$ (C_{2h})	$[SbCl_6]^-$ (O_h)
	40	lattice	
	48		
	57		
	66		
	88		
	97		
	112		
100	126	$\nu_3(A_g)$ I-I-Cl bend	
6	174		ν_5 (T_{2g})
9	184	$\nu_2(A_g)$ I-I str	
8	259		ν_2 ($E_g \rightarrow A_{1g} + B_{1g}$)
10	296		
25	334		ν_1 (A_{1g})
16	348	$\nu_1(A_g)$ I-^{37}Cl str,	
52	354	$\nu_1(A_g)$ I-^{35}Cl str	

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perature with 6328-Å excitation is shown in Figure 3; the observed frequencies and their relative intensities are given in Table III. The spectrum shows the three characteristic Raman-active fundamentals (one of which is split) of the $[SbCl_6]^-$ anion. The measured frequencies are 334 (ν_1, A_{1g}), 296, 259 (ν_2, E_g), and 174 cm^{-1} (ν_5, T_{2g}) and are in good agreement with those of other salts containing the hexachloroantimonate anion.[19] The splitting of ν_2 is consistent with an effective lowering of symmetry in the anion, from O_h to D_{4h} ($E_g \rightarrow A_{1g} + B_{1g}$) due to the interaction of the anion with the cation via the bridging Cl(1) atom, which distorts the Sb–Cl(1) bond. This effect has also been observed in the Raman spectra of hexafluoroantimonate and hexafluoroarsenate salts.[20,21] The remaining lines in the spectrum apart from the low-frequency lattice modes are due to the vibrations of the cation. There are $3n - 6 = 9$ vibrational modes expected, and since $[I_3Cl_2]^+$ is centrosymmetric (C_{2h} symmetry), six are infrared active, and three modes of A_g symmetry are Raman active. The band at 354 cm^{-1} with a shoulder at 348 cm^{-1} is assigned to the I–Cl stretching mode of $[I_3Cl_2]^+$. This splitting results from the isotope effect of ^{35}Cl and ^{37}Cl, and the intensities of the peaks are in the expected 3:1 ratio. The most intense band at 126 cm^{-1} is the I(2)–I(1)–Cl(3) bend, while the remaining line at 184 cm^{-1} is assigned to the I–I stretch. Both stretching modes of $[I_3Cl_2]^+$ occur at a frequency lower than that which is observed for free ICl and I_2 molecules (381 and 213 cm^{-1}, respectively[22]) due to a weakening of the bond as a result of additional interactions.

The Raman spectrum of $[I_2Cl]^+[SbCl_6]^-$ has been reported,[9,23] and although the relative intensities of the lines vary, the frequency shifts are nearly the same as those reported here for $[I_3Cl_2]^+[SbCl_6]^-$. It has been proposed that the structure of $[I_2Cl]^+$ is that of a bent, asymmetric $[I_2X]^+$ cation which would have C_s symmetry and therefore exhibit three Raman-active modes of vibration, as does $[I_3Cl_2]^+$. However, as previously mentioned, $[I_3Cl_2]^+$ would have six infrared-active modes while $[I_2Cl]^+$ would have only three infrared-active modes whose frequencies would be coincident with those observed in the Raman spectrum. While these authors report a satisfactory chemical analysis for $[I_2Cl]^+[SbCl_6]^-$, they do not provide any infrared data, which is critical to an unambiguous structural assignment based upon vibrational spectroscopy. Unfortunately this is not a trivial matter, and attempts by us to do this have so far been unsuccessful for several reasons. In spite of the availability of FT infrared spectrophotometers equipped with far-infrared capabilities, the efficiency and quality of the experiment decreases rapidly at low energies, usually resulting in very broad lines compared to those observed in the Raman spectra. $[I_3Cl_2]^+[SbCl_6]^-$ and $[I_2Cl]^+[SbCl_6]^-$ as prepared by Shamir and Lustig[9] are both very moisture-sensitive compounds and strong oxidants, reacting very quickly with hydrocarbon mulling agents such as Nujol and with polyethylene when the latter material is used as a sample holder for neat solids. The fluorine-containing polymer FEP (copolymer of perfluoropolypropylene and perfluoropolyethylene) is inert to the above compounds; however, it transmits the light poorly, absorbing strongly from about 1600 to 450 cm^{-1}, and exhibits a broad band at about 205 cm^{-1}.

In view of the difficulties encountered with the infrared experiment, we followed the procedure of Shamir and Lustig in an attempt to prepare $[I_2Cl]^+[SbCl_6]^-$ and succeeded in subliming crystals into quartz capillaries by the method described for $[I_3Cl_2]^+[SbCl_6]^-$. A single crystal suitable for diffractometer measurements was obtained, and it was found to have the same unit cell parameters[24] as $[I_3Cl_2]^+[SbCl_6]^-$. This was verified by examining a number of crystals. A large crystal of this material exhibited a Raman spectrum identical with that of $[I_3Cl_2]^+[SbCl_6]^-$.

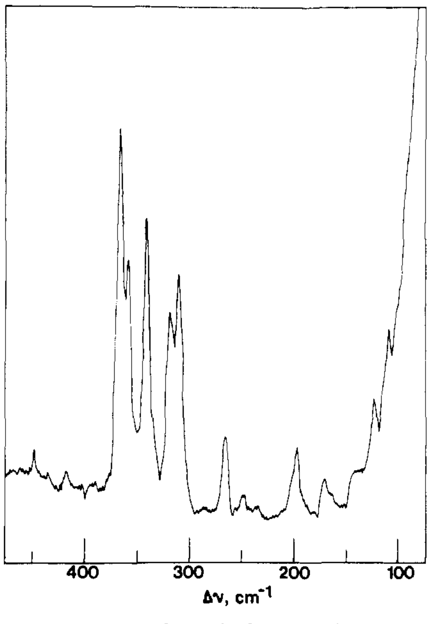

Figure 4. Raman spectrum of $I_2 + SbCl_5 + Cl_2$ (after removing excess liquid Cl_2) at −196 °C with 5145-Å excitation.

The preparation of $[I_3Cl_2]^+[SbCl_6]^-$ was effected by the reaction of I_2Cl_6 with $SbCl_3$ in SO_2 solvent. Thus the antimony(III) undergoes oxidation to antimony(V), while iodine(III) has formally been reduced to iodine(I) according to eq 1. We suggest that subsequent to this, chloride is removed

$$I_2Cl_6 + 2SbCl_3 \rightarrow 2ICl + 2SbCl_5 \qquad (1)$$

from ICl by $SbCl_5$ to produce $[I]^+$ and $[SbCl_6]^-$. The $[I]^+$ is an extremely strong Lewis acid and requires stabilization by 2 mol of ICl, thereby producing $[I_3Cl_2]^+[SbCl_6]^-$ (eq 2 and 3). Since the preparation was initially carried out using the

$$3ICl + SbCl_5 \rightarrow [I]^+{\cdot}2ICl[SbCl_6]^- \qquad (2)$$

$$[I]^+{\cdot}2ICl[SbCl_6]^- \rightarrow [I_3Cl_2]^+[SbCl_6]^- \qquad (3)$$

stoichiometry shown in eq 1, there is only 1 mol of ICl available per mole of $SbCl_5$, and not 3 mol, as the stoichiometry of eq 2 requires. Thus the $[I_3Cl_2]^+$ cation forms despite a shortage of ICl. These are just the conditions under which the $[I_2Cl]^+$ cation might have been expected to have been produced. It therefore seems unlikely that the formation of $[I_2Cl]^+[SbCl_6]^-$ would result from the reaction of ICl with an excess of $SbCl_5$, as has been reported.[23] It is interesting to note that the Raman spectrum of the material produced from the reaction of ICl with excess $SbCl_5$ is the same as that which we report for $[I_3Cl_2]^+[SbCl_6]^-$. In a separate experiment, we have shown that the reaction of ICl with $SbCl_5$ in a 3:1 ratio also produces $[I_3Cl_2]^+[SbCl_6]^-$.

The reaction of I_2 with $SbCl_5$ in excess Cl_2 at −78 °C reported to produce $[I_2Cl]^+[SbCl_6]^-$[9] is very complex. In light of the information obtained from single-crystal X-ray mea-

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(24) Unit cell parameters for $[I_2Cl]^+[SbCl_6]^-$ obtained from diffracting positions of 11 high-angle ($17° \leq 2\theta \leq 35°$) reflections: triclinic, $P\bar{1}$, $a = 9.839$ (4) Å, $b = 7.119$ (3) Å, $c = 7.732$ (2) Å, $\alpha = 91.15$ (3)°, $\beta = 134.31$ (2)°, $\gamma = 95.47$ (3)°, $V = 382.9$ (2) Å^3.

surements, it appears that the material is in fact $[I_3Cl_2]^+$-$[SbCl_6]^-$. When this particular reaction was repeated, it was noted that a yellow solid remained behind when the excess liquid Cl_2 was removed at −78 °C. After warming to room temperature, this solid quickly turned black. Also, while it was reported that the reaction was nearly quantitative, we have found that the $I_2/SbCl_5$ mixture had to be treated with liquid Cl_2 at least three times in order to ensure complete reaction. So that this yellow solid, which is formed at low temperature, could be identified, the Raman spectrum was measured of a reaction mixture at −196 °C, immediately after the Cl_2 had been removed at −78 °C. This is shown in Figure 4. There is evidence for the presence of I_2Cl_6 since the lines at 342, 312, and 197 cm^{-1} are very close to the frequencies of the three most intense bands of I_2Cl_6[25] (344, 314, and 198 cm^{-1}). The lines at 367, 360, 266, and 170 cm^{-1} are also observed in the Raman spectrum of $SbCl_5$ at −196 °C.[26] Thus at low temperature the sample appears essentially to be a mixture of I_2Cl_6 and $SbCl_5$. If a small amount of $[I_3Cl_2]^+[SbCl_6]^-$ has formed, the lines of its spectrum are masked by those of the former two constituents. After warming to room temperature for a few hours, the same sample exhibits a Raman spectrum identical with that of $[I_3Cl_2]^+[SbCl_6]^-$. There is no evidence for the formation of $[ICl_2]^+[SbCl_6]^-$ which is usually produced by the reaction of I_2Cl_6 with excess $SbCl_5$.[1] Had there been evidence in the Raman spectrum of the reaction mixture for the formation of ICl (ν(I–Cl), 384 cm^{-1}), the subsequent formation of $[I_3Cl_2]^+[SbCl_6]^-$ could be envisioned to occur by the same mechanism as suggested previously. Also, since there is no $[ICl_2]^+[SbCl_6]^-$ formed, one possible explanation for the formation of the observed product is that as the reaction mixture begins to warm the I_2Cl_6 formed at low temperature dissociates. The I_2 and Cl_2 may recombine to form ICl, ultimately producing $[I_3Cl_2]^+$ by interacting with $SbCl_5$ as discussed above.

Visible Absorption Spectroscopy. The visible absorption spectrum of $[I_3Cl_2]^+[SbCl_6]^-$ in SO_2 was recorded and found to have a band maximum at 440 nm. $[I_2Cl]^+[SbCl_6]^-$ is reported to have a band maximum at 450 nm.[9]

Conclusions

Single-crystal X-ray crystallographic studies on the product of the reaction between I_2Cl_6 and $SbCl_3$ have shown it to contain the novel $[I_3Cl_2]^+$ cation. The Raman spectrum of this compound analyzes as containing a planar, centrosymmetric (C_{2h}) cation and a slightly distorted (O_h) $[SbCl_6]^-$ anion. Since the Raman spectrum reported for $[I_2Cl]^+[SbCl_6]^-$ is very similar to that of $[I_3Cl_2]^+[SbCl_6]^-$, a single-crystal X-ray analysis of the former compound was warranted. It was found to have the same unit cell parameters as $[I_3Cl_2]^+[SbCl_6]^-$. In view of the Raman and X-ray crystallographic evidence, it seems unlikely that $[I_2Cl]^+[SbCl_6]^-$ is formed by the reaction of I_2 and $SbCl_5$ in excess liquid Cl_2, but rather $[I_3Cl_2]^+[SbCl_6]^-$ is formed. Indeed, the existence of this, and of other asymmetric polyhalogen cations of iodine, $[I_2X]^+$ (X = Br, Cl) and $[XIY]^+$ (X = Br; Y = Cl), may be in doubt until they are fully characterized by crystal structure determinations. This study illustrates the importance of a crystal structure in characterizing new polyhalogen cations, particularly when vibrational spectroscopy cannot offer an unambiguous structural determination.

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Registry No. $[I_3Cl_2]^+[SbCl_6]^-$, 77585-00-3; $SbCl_3$, 10025-91-9; I_2Cl_6, 28190-87-6; I_2, 7553-56-2; $SbCl_5$, 7647-18-9; Cl_2, 7782-50-5.

Supplementary Material Available: Listings of anisotropic thermal parameters and observed and calculated structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

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