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Preparation and Crystal Structure of $[ICl_2]^+[SbF_6]^-$ and Iodine-127 Mössbauer Spectra of Some Compounds Containing the $[ICl_2]^+$ Cation

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The crystal structure of $ISbCl_2F_6$ has been determined from diffractometer data by the heavy-atom method. Crystals of $ISbCl_2F_6$ are orthorhombic, of space group *Cmca*, with $a = 10.751$ (3) Å, $b = 12.087$ (4) Å, $c = 12.982$ (2) Å, $V = 1687.0$ (8) Å^3, and $d_{calcd} = 3.414$ g cm^{-3} for $Z = 8$. The structure was solved by Patterson and Fourier methods and refined by block-diagonal least squares to $R_1 = 0.031$ and $R_2 = 0.039$ for 788 observed ($I > 3\sigma(I)$) reflections. The structure consists of infinite chains of $[SbF_6]^-$ anions cis bridged through fluorine to $[ICl_2]^+$ cations. The iodine atom is found in a rectangular coordination with terminal I–Cl distances of 2.268 (2) Å and bridging I–F distances of 2.650 (6) Å. The latter I–F interaction is extremely short and represents one of the strongest fluorine to iodine secondary interactions known. The ^{127}I Mössbauer spectra of the title compound and the related compound $ISbCl_8$ have been measured and the hyperfine parameters are compared to those of I_2Cl_6, and $K^+[ICl_4]^-$ both of which contain iodine in an almost square-planar environment. The ^{127}I Mössbauer parameters of $[ICl_2]^+[SbF_6]^-$ and $[ICl_2]^+[SbCl_6]^-$ are identical within experimental error, thereby indicating a similar electronic environment about the iodine nucleus despite a dissimilar chemical environment. ^{19}F NMR studies of the title compound show the presence of the $[Sb_2F_{11}]^-$ anion in solution rather than the $[SbF_6]^-$ anion which is found in the solid state.

Introduction

The polyhalogen cations have recently been reviewed.[1] Various physical measurements such as single-crystal X-ray structures, vibrational spectra, multinuclear NMR, and Mössbauer spectroscopy on compounds containing $[XY_2]^+$ symmetric cations support a mainly ionic structural model such that the $[XY_2]^+$ cation possesses C_{2v} symmetry. However, some cation–anion interaction does exist, via halogen bridges of varying strength from two separate anions to the cation. VSEPR theory[2] then would predict an octahedral geometry, $AX_2Y_2E_2$, with the two nonbonding electron pairs occupying the axial positions. The crystal structures of $ISbCl_8$ and $IAlCl_6$ have been reported,[3] and both contain iodine in a square-planar environment. In these structures the cation–anion interactions are quite strong with the bridging I---Cl bond lengths varying from 2.85–3.00 Å. These distances are only slightly longer than the bridging I---Cl distances in I_2Cl_6 which average 2.70 Å.[4] Other square-planar iodine(III) environments are found in $K^+[ICl_4]^-\cdot H_2O$[5] and $[SCl_3]^+[ICl_4]^-$.[6] In both of these compounds the iodine environment is slightly distorted from a square-planar geometry.

Recently Aubke and co-workers[7] reacted I_2Cl_6 with a large excess of SbF_5 and obtained a compound which they formulated as $[ICl_2]^+[Sb_2F_{11}]^-$ with some cation–anion interaction. Such an interaction should result in a square geometry about the iodine from two terminal chlorines and two bridging fluorines. This would be related to $ISbCl_8$ and $IAlCl_6$ which can be written as $[ICl_2]^+[SbCl_6]^-$ and $[ICl_2]^+[AlCl_4]^-$, respectively. These compounds then comprise a series with iodine(III) in a square- or rectangular-planar environment having a range of interactions to chlorine or fluorine. Such a series would be ideal for testing our recent correlation of ^{127}I Mössbauer parameters with the electronegativities of the ligands in the linear $[X–I–Y]^-$ anions.[8]

With such a plan in mind we attempted the preparation of $[ICl_2]^+[Sb_2F_{11}]^-$, but, while evidence for the $[Sb_2F_{11}]^-$ anion in solution was found, that solution yielded crystals of $[ICl_2]^+[SbF_6]^-$. Here we report the X-ray crystal structure of $[ICl_2]^+[SbF_6]^-$, the first example of a structure containing iodine(III) in which the halogen ligands are not all of the same type and in which a strong iodine–fluorine interaction exists. Mössbauer data (^{127}I) for this compound and some related molecules are also discussed. Unlike the case of $[X–I–Y]^-$ series, where a good correlation between the iodine quadrupole coupling constant and the ligand electronegativity was found, we find no such variation in the molecules examined in this study.

Experimental Section

$[ICl_2]^+[SbCl_6]^-$ was prepared by the method of Vonk and Wiebenga[9] by heating I_2Cl_6 in a large excess of $SbCl_5$.

$[ICl_2]^+[SbF_6]^-$ was prepared as follows. A 3.6694-g sample (16.93 mmol) of SbF_5, doubly distilled under dry N_2, was added by means of glass syringe to one side of a glass Dean-type reaction vessel[10] equipped with a 5-mm thin-walled NMR tube. This manipulation was carried out under dry nitrogen atmosphere in a glovebox. Then 1.9753 g (4.233 mmol) of I_2Cl_6 (prepared by the direct oxidation of resublimed I_2 with dry Cl_2) was added to the other side by vacuum sublimation from a preweighed glass vessel, on a vacuum line. SO_2ClF was then distilled onto the SbF_5, and the SbF_5/SO_2ClF solution was quickly poured onto the I_2Cl_6 through the sintered glass frit. After 6 h of stirring, a clear cherry red solution remained. The ^{19}F NMR sample was prepared by pouring some of the solution into the attached NMR tube and sealing it off under vacuum. The solvent SO_2ClF was removed from the remaining solution by slow distillation which left behind a viscous red paste. After some time it was noticed that red crystals had begun to grow and the vessel was then pumped under dynamic vacuum to remove any remaining SbF_5. The crystals were extremely moisture sensitive and needed to be mounted in Lindemann capillaries baked for several hours in vacuo to minimize crystal decomposition. The melting point of a single crystal of $[ICl_2]^+[SbF_6]^-$ is 83 °C, giving a red liquid with no decomposition.

Nuclear Magnetic Resonance Spectroscopy. ^{19}F NMR spectra were obtained with the use of a Bruker WH-90 Fourier transform multinuclear spectrometer equipped with a Nicolet 1080 computer, a Nicolet 294 disk memory, and quadrature phased detection. All spectra were ^2H-locked and accumulated in 16K of memory. The spectrometer frequency was 84.66 MHz, and spectra were obtained in 100 scans with a spectral width of 12 kHz (1.47 Hz/data point, pulse repetition time 0.679 s) and a pulse width of 2 μs. The spectra were obtained by using 5-mm o.d. NMR tubes locked to an external acetone-d_6 capillary in the probe head housing. The spectra were recorded at −120 °C with use of a Bruker temperature controller, and the temperature was monitored by using a copper–constantan ther-

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mocouple inserted directly into the sample region of the probe and was accurate to ±1 °C.

Mössbauer Spectroscopy. Mössbauer spectra (^{127}I) were recorded with use of an Elscint AME-40 drive system operating in the constant acceleration triangular wave form mode. The transmitted radiation was detected by a Harshaw NaI(Tl) scintillation counter and the resulting pulses fed to a Tracor-Northern multichannel analyzer operating in the multiscaling mode. Samples of $[ICl_2]^+[SbCl_6]^-$ and $[ICl_2]^+[SbF_6]^-$ containing $\simeq$30 mg of iodine/cm^2 were mixed thoroughly with dried prefluorinated Teflon powder and placed in a 20-mm i.d. threaded Kel-F sample holder. The Zn^{127}Te source (10 mCi) was purchased from New England Nuclear Corp. Both sample and source were immersed in liquid helium (4.2 K) in a research cryostat manufactured by Janis Research Co. The temperature was monitored by means of a calibrated Allen-Bradley 47 Ω, $^1/_4$-W carbon resistor and a Cryogenic Research Co. temperature controller. The velocity scale was calibrated by using an iron foil absorber and a ^{57}Co/Rh source. The folded spectra were computer fitted by using a program previously described which incorporates full transmission integral procedures.[11]

Crystal Data. $ISbCl_2F_6$: fw = 433.65, orthorhombic; a = 10.751 (3), b = 12.087 (4), c = 12.982 (2) Å; V = 1687.0 (8) Å^3, d_{calcd} = 3.414 g cm^{-3} for Z = 8; Mo Kα radiation; λ = 0.71069 Å; μ(Mo Kα) = 76.77 cm^{-1}; $F(000)$ = 1536.0. Systematic absences hkl, $h + k = 2n$, $0kl$, $k = 2n$, $h0l$, $l = 2n$, and $hk0$, $h = 2n$, indicate the space groups *Cmca* (No. 64) or *Cc2a* (standard setting *Aba*2 (No. 41)). Intensity measurements were made on a Syntex P2$_1$ diffractometer using graphite monochromated Mo Kα radiation. A nearly rectangular-shaped crystal with truncated corners, of size 0.20 × 0.20 × 0.13 mm was selected for intensity measurements. The unit cell parameters were obtained from the least-squares refinement of the diffracting positions of 15 high-angle ($30° \leq 2\theta \leq 35°$) reflections. Reflections were measured by using θ–2θ scans over a scan range (Kα_1 −0.9°) to (Kα_2 +0.9°) with a variable scan rate of 2.55–29.30°/min depending on the intensity of a preliminary count. The intensities of three standard reflections were measured every 70 reflections, and these showed no significant variation during data collection. All reflections in the quadrant (hkl) with $5° \leq 2\theta \leq 55°$ were eventually collected.

Lorentz, polarization, and spherical absorption corrections were applied to the data. A total of 1037 unique reflections were collected of which 788 were considered observed ($I \geq 3\sigma(I)$), and 941 with $I \geq \sigma(I)$ were retained for refinement.

Structure Determination and Refinement. The structure was solved by using conventional heavy-atom techniques in the centric space group *Cmca*. The iodine and antimony atoms were located on a Patterson map and, since Z = 8, were placed on special positions: $^1/_4, y, ^1/_4$ with symmetry 2 and $0, y, z$ with symmetry m, respectively. Subsequent Fourier maps revealed the positions of the remaining atoms and confirmed the positional assignments for the heavy atoms. Full-matrix least-squares refinement in the space group *Cmca* converged to R_1 $(=\sum||F_o| - |F_c||/\sum|F_o|)$ of 0.041 with use of anisotropic temperature factors for all atoms. Subsequent refinement in the space group *Cc2a* resulted in no improvement.

In the final cycles of least-squares refinement weights were calculated by using the expression $w = xy$ where (i) $x = (\sin\theta)/0.37$ if $\sin\theta < 0.37$ or $x = 0.40/\sin\theta$ if $\sin\theta > 0.40$, otherwise $x = 1.0$, and (ii) $y = 70.0/F$ if $F > 70.0$ or $y = F/50.0$ if $F < 50.0$, otherwise $y = 1.0$. Several cycles of block-diagonal least squares using this weighting scheme converged to $R_1 = 0.031$ and $R_2 = 0.039$ ($R_2 = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$). In the final cycle of refinement no parameter shift was greater than 5.3% of its standard error, and a final difference Fourier was featureless with a maximum peak and a minimum trough of +3.4 and −1.2 e/Å^3, respectively, around antimony.

All calculations were performed on a CDC 6400 computer using the program SHELX-76[12] in the initial stages, while the final refinement was completed by using the series of programs in the XRAY 71 system.[13] Atomic scattering factors corrected for anomalous dispersion were taken from ref 13b. The final atomic positional coordinates and the thermal parameters are found in Tables I and II, respectively. The bond lengths and bond angles of the molecule are given in Table III. Table IV contains information on the molecular planes of $[ICl_2]^+$-$[SbF_6]^-$. A tabulation of observed and calculated structure factors is found in the supplementary material.

Table I. Atomic Coordinates (×10^4)

	x/a	y/b	z/c
I(1)	2500	901 (1)	2500
Sb(1)	0	2038 (1)	−568 (1)
Cl(1)	1650 (2)	−340 (2)	3606 (2)
F(1)	0	698 (6)	−1281 (7)
F(2)	0	3429 (6)	51 (7)
F(3)	1251 (6)	1567 (6)	308 (5)
F(4)	1224 (6)	2566 (5)	−1494 (4)

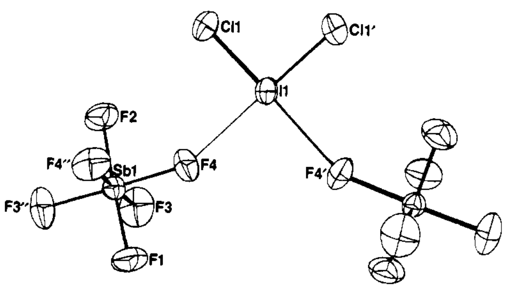

Figure 1. Coordination sphere and atomic number around iodine, including $[SbF_6]^-$ anions. Symmetry transformations: single prime, $^1/_2 - x, y, ^1/_2 - z$; double prime, $-x, y, z$.

Results and Discussion

Structure of $[ICl_2]^+[SbF_6]^-$. The crystal structure consists of infinite chains of $[SbF_6]^-$ anions cis bridged through fluorine to $[ICl_2]^+$ cations. The atomic arrangement 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. The structure then could be considered as consisting of almost rectangular $[ICl_2]^+$ cations and slightly distorted octahedral $[SbF_6]^-$ anions. The $[SbF_6]^-$ anion is not unusual with the terminal Sb–F distances averaging 1.858 Å, while the bridging Sb–F distance is somewhat longer at 1.894 (6) Å. As expected the Sb–F bond trans to the bridging fluorine is the shortest Sb–F distance in the molecule.

The environment about the iodine is similar to that found in both $ISbCl_8$ and $IAlCl_6$,[3] namely, a nearly square-planar configuration, although in our structure the arrangement about iodine is comprised of two chlorines and two fluorines rather than four chlorines. In $[ICl_2]^+[SbF_6]^-$ the terminal I–Cl distance of 2.268 (2) Å may be compared to the corresponding bond lengths in the $[AlCl_4]^-$ and $[SbCl_6]^-$ analogues, which range from 2.26 (4) to 2.33 (4) Å[3]. These distances are significantly shorter than the terminal I–Cl bonds in the neutral I_2Cl_6 molecule[4] (2.38, 2.39 Å) or in the anions K^+-$[ICl_4]^-\cdot H_2O$[5] (2.42, 2.47 Å) and $[SCl_3]^+[ICl_4]^-$[6] (2.437 (2), 2.469 (3) Å). It is apparent that, as the charge on the ion becomes more negative, the terminal I–Cl bond length increases as one might have expected. As the terminal I–Cl bonds become weaker, there is a corresponding strengthening of the I- - -Cl bridge or secondary bonds until they become of similar length to the terminal bonds. This situation is reached in $K^+[ICl_4]^-\cdot H_2O$ and $[SCl_3]^+[ICl_4]^-$ where the bridging contacts from the $[ICl_4]^-$ are rather weak. In the title compound the secondary contacts completing the rectangular arrangement about the iodine are through fluorine so that a direct comparison with the other molecules is not possible.

However this kind of problem has been treated by Weibenga and Kracht,[14] who correlate bond lengths with calculated bond

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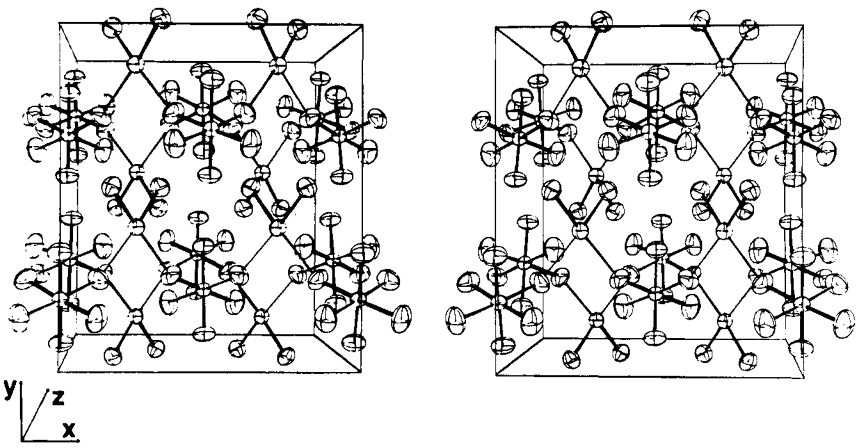

Figure 2. Stereoscopic drawing of the unit cell of $[ICl_2]^+[SbF_6]^-$ viewed down the *c* axis.

Table II. Thermal Parameters[a] for $[ICl_2]^+[SbF_6]^-$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	447 (4)	425 (4)	309 (3)	0	82 (3)	0
Sb(1)	363 (3)	347 (3)	284 (3)	0	0	26 (3)
Cl(1)	591 (12)	585 (11)	501 (10)	−63 (9)	149 (10)	112 (9)
F(1)	824 (54)	382 (32)	735 (51)	0	0	−159 (36)
F(2)	781 (52)	511 (43)	673 (48)	0	0	−243 (36)
F(3)	599 (34)	1051 (49)	671 (34)	105 (33)	−235 (29)	173 (33)
F(4)	656 (31)	637 (29)	627 (29)	−149 (26)	247 (27)	90 (25)

[a] Temperature factors (×10^4) in the form $\exp(-2\pi^2\Sigma_i\Sigma_jU_{ij}H_iH_ja_i^*a_j^*)$.

Table III. Bond Lengths (Å) and Bond Angles (Deg) for $[ICl_2]^+[SbF_6]^-$ [a]

(a) Bond Lengths

I(1)–Cl(1)	2.268 (2)	Sb(1)–F(2)	1.863 (8)
I(1)–F(4)	2.650 (6)	Sb(1)–F(3)	1.851 (7)
Sb(1)–F(1)	1.867 (8)	Sb(1)–F(4)	1.894 (6)

(b) Bond Angles

Cl(1)–I(1)–Cl(1′)	97.2 (1)	F(2)–Sb(1)–F(3)	90.7 (3)
Cl(1)–I(1)–F(4)	86.7 (1)	F(2)–Sb(1)–F(4)	88.3 (3)
F(4)–I(1)–F(4′)	91.2 (2)	F(3)–Sb(1)–F(3″)	93.2 (3)
Cl(1)–I(1)–F(4′)	169.4 (1)	F(3)–Sb(1)–F(4)	89.4 (3)
F(1)–Sb(1)–F(2)	175.8 (4)	F(3)–Sb(1)–F(4′)	177.3 (3)
F(1)–Sb(1)–F(3)	92.2 (3)	F(4)–Sb(1)–F(4″)	88.1 (3)
F(1)–Sb(1)–F(4)	88.7 (3)	I(1)–F(4)–Sb(1)	155.3 (3)

[a] Symmetry transformations: single prime, $^1/_2 - x, y, ^1/_2 - z$ and; double prime, $-x, y, z$. Estimated standard deviations are given in parentheses.

Table IV. Data for Least-Squares Mean Planes in Orthogonal Angstrom Space for $[ICl_2]^+[SbF_6]^-$ [b]

(a) Equations of Planes: $PI + QJ + RK = S^a$

plane	defining atoms	P	Q	R	S
1	Cl(1), I(1), Cl(1′)	0.8433	0	0.5374	4.0108
2	F(4), I(1), F(4′)	0.6895	0	0.7243	4.2039

(b) Angles (Deg) between Planes

1–2 13.90

(c) Atomic Displacement (Å) from These Planes

plane 1: F(4) −0.46, F(4′) +0.46
plane 2: Cl(1) +0.41, Cl(1′) −0.41

[a] The orthogonal unit vector *I* is parallel to *a*, *J* is perpendicular to *a* in the *ac* plane. [b] Symmetry transformations are as in Table III.

orders. Using their relationships, we find that the secondary contacts (mean 2.90 Å) in $[ICl_2]^+[SbCl_6]^-$ and $[ICl_2]^+[AlCl_4]^-$ have a bond order of 0.47 while in I_2Cl_6 the bridge bond is much shorter (2.70 Å) and hence stronger, having a bond order of 0.58. The I- - -F bridging contacts in $[ICl_2]^+[SbF_6]^-$ are 2.650 (6) Å which corresponds to a bond order of 0.42. This is only slightly weaker than that found for the secondary contacts in the hexachloroantimonate and tetrachloroaluminate complexes. This I- - -F distance (2.650 Å) is quite short and may be compared to the covalent single-bond distance of 1.92 Å and the van der Waals contact distance of 3.45 Å.[15] Direct comparisons with other I–F distances are difficult to make because of the paucity of structural data for iodine–fluorine molecules. Iodine pentafluoride has I–F bond lengths ranging from 1.6[16] to 1.88 Å with secondary I- - -F contacts greater than 2.91 (1) Å, but no experimental value for an iodine(III)–fluorine covalent contact is known. Other iodine–fluorine contacts that have been reported are of the secondary or bridging type. In $[S_7I]^+[SbF_6]^-$ [17] the I- - -F distance is 2.92 (2) Å, while in $[I_2]^+[Sb_2F_{11}]^-$ [18] the shortest secondary contact is 2.89 (2) Å. Both of these distances are much longer than that reported here for $[ICl_2]^+[SbF_6]^-$ and correspond to bond orders of <0.3 as determined from the correlation of Wiebenga and Kracht.[14]

Alcock and Countryman[19] recently studied the crystal structures of a series of diphenyliodonium halides in order to examine secondary bonding effects. These compounds provide a useful comparison to $[ICl_2]^+[SbF_6]^-$ because their structures are similar to that of I_2Cl_6. They found that in dimeric $(C_6H_5)_2IX$ (X = Cl, Br, I) the mean bond lengths are I–C = 2.09, I–Cl = 3.09, I–Br = 3.25 and I–I = 3.44 Å. The I–X bonds in each case are about 0.77 Å longer than in the corresponding IX gas, indicating bond orders of approximately 0.35. The iodine–fluorine interaction in $[ICl_2]^+[SbF_6]^-$ (bond order 0.42) is much stronger than the secondary interactions which occur in the above series of compounds.

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Table V. ^{127}I Mössbauer Data

compd	isomer shift, mm s^{-1}	$e^{127}Q_gV_{zz}/h$, MHz	Γ,[a] mm s^{-1}	T_a	χ^2/deg of freedom
$[ICl_2]^+[SbF_6]^-$	−2.51 ± 0.05	3029 ± 37	1.51 ± 0.17	0.70 ± 0.06	1.14
$[ICl_2]^+[SbCl_6]^-$	−2.45 ± 0.05	3066 ± 37	1.72 ± 0.18	1.19 ± 0.07	0.83
I_2Cl_6	−2.28 ± 0.01[b]	3060 ± 10			
$K^+[ICl_4]^-\cdot H_2O$	−2.42 ± 0.05[c]	3094 ± 20			
H_5IO_6	0 (+1.03 ± 0.09)[d]	0			

[a] A constant source line width of 1.6 mm s^{-1} was used. [b] References 20 and 24 (converted from ^{129}I data). [c] Reference 21. [d] Isomer shift of H_5IO_6 relative to ZnTe source.

Deviation of the Cl–I–Cl bond angles from 90° are found for all these $[ICl_2]^+$ compounds, the angles being 92.5 (1.4), 96.7 (1.4) and 97.2 (1)° for the $[SbCl_6]^-$, $[AlCl_4]^-$, and $[SbF_6]^-$ compounds, respectively. The Cl–I–Cl angle opens up as the size of the anion decreases. However much more significant differences are found in the angle at the bridging halogen. In $[ICl_2]^+[SbF_6]^-$ the I–F–Sb angle is 155.3 (3)° which is much larger than the I–Cl–Sb and I–Cl–Al angles, 115.8 and 112° in $[ICl_2]^+[SbCl_6]^-$ and $[ICl_2]^+[AlCl_4]^-$, respectively. One other notable difference between the three $[ICl_2]^+$ molecules lies in the degree of deviation from planarity of the $[ICl_2X_2]$ rectangular unit. In the cases of the hexachloroantimonate and tetrachloroaluminate molecules the maximum deviation of any atom from the plane of $[ICl_4]$ is never more than 0.18 Å, and these are therefore similar to the $[ICl_4]^-$ ion in $K^+[ICl_4]^-\cdot H_2O^5$. A least-squares mean-planes analysis of the $[ICl_2F_2]$ fragment in the title compound shows that the two fluorine atoms lie 0.46 and −0.46 Å out of the plane defined by the iodine and two chlorines. These distortions must arise as a result of constraints imposed on the structure by the cis-bridged arrangements at both the cation and anion. Such constraints are apparently not so critical in the $[SbCl_6]^-$ and $[AlCl_4]^-$ cases, which are also cis-bridged structures, because of the larger size of the bridging halogen in these latter molecules.

It has been suggested[3] that these compounds containing the $[ICl_2]^+$ fragment could be represented as resonance hybrids of the type

$$[ICl_2]^+[SbCl_6]^- \leftrightarrow [ICl_4]^-[SbCl_4]^+$$

but since the $[SbCl_6]^-$ or $[SbF_6]^-$ anions are barely distorted from regular Oh geometry this does not appear reasonable. We prefer to describe our structure as a nearly covalent cis-bridged polymer.

^{127}I Mössbauer Spectroscopy. Iodine-127 Mössbauer data have been obtained for $[ICl_2]^+[SbF_6]^-$ and $[ICl_6]^+[SbCl_6]^-$, and these data are presented in Table V together with literature data for I_2Cl_6[20,24] and $K^+[ICl_4]^-\cdot H_2O$.[21] The isomer shift for I_2Cl_6 has been converted from ^{129}I data by multiplying the ^{129}I chemical isomer shift by −0.345.[22] Spectra were fitted as described earlier, and the absorber line widths, which were allowed to vary in the transmission integral fitting, are slightly greater than the natural line width of 1.25 mm s^{-1}. Figure 3 shows the spectrum of $[ICl_2]^+[SbF_6]^-$ which resembles that of the $[ICl_4]^-$ anion in that transition no. 2 is well resolved at high negative velocity.[23,24] This means that the quadrupole coupling constant $e^{127}Q_gV_{zz}/h$ is large and positive for all of these compounds. Since $e^{127}Q_g$ is negative, V_{zz} is therefore negative, and hence the values are those expected for a central iodine being bonded to four halogens in the *xy* plane, with the nonbonded electron pairs along the *z* axis. Examination of Table V reveals that, within the experimental error, the quadrupole coupling constants for all four compounds are the same, although that for the $K^+[ICl_4]^-\cdot H_2O$ in which $[ICl_4]^-$ carries a negative charge does have the largest value at +3094 MHz. This lack of variation was at first surprising since we had already established a correlation between the quadrupole coupling constants with the electronegativity of the X and Y ligands in the $[X–I–Y]^-$ linear molecules:[8] the more electronegative the ligand, the more negative the quadrupole coupling constant. On replacing two bridging chlorines by two bridging fluorines in the approximately square-planar environment

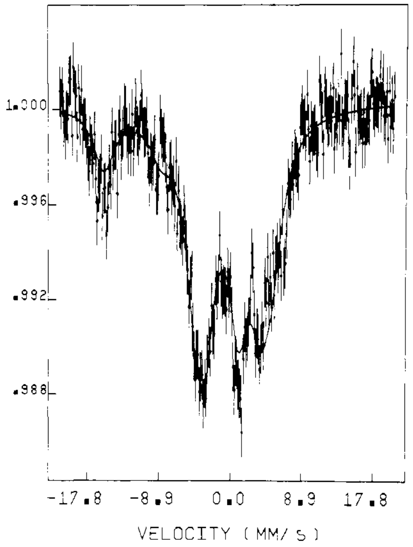

Figure 3. Iodine-127 Mössbauer spectrum at 4.2 K of $[ICl_2]^+[SbF_6]^-$. The solid lines are the best fit to the data.

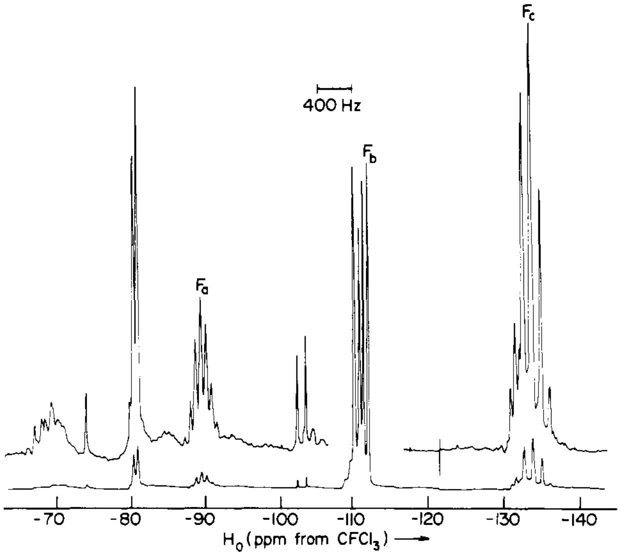

Figure 4. ^{19}F NMR spectrum of SO_2ClF solution of I_2Cl_6/SbF_5 recorded at −120 °C.

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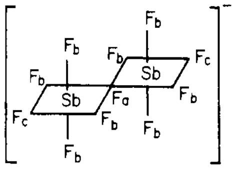
about an I(III), i.e., on going from $[ICl_2]^+[SbCl_6]^-$ to $[ICl_2]^+[SbF_6]^-$, one would have predicted that the quadrupole coupling constant would become more positive. This does not happen, and the trend, if real, is rather in the opposite sense. As the terminal I-Cl bond becomes stronger, then the I---Cl(F) bond becomes weaker so that the total electron density in the *xy* plane does not change significantly, and hence the quadrupole coupling constant remains the same.

Isomer shift changes in ^{127}I Mössbauer spectroscopy are generally quite small, and little change was expected in this series. The measured values for $[ICl_2]^+[SbF_6]^-$ and $[ICl_2]^+[SbCl_6]^-$ are the same within experimental error, and the differences for I_2Cl_6 and $K^+[ICl_4]^-\cdot H_2O$ are more likely due to errors introduced by converting data from other laboratories than to real changes in s-electron density. Perhaps this aspect should be examined more carefully.

^{19}F NMR. The ^{19}F NMR spectrum of a solution of I_2Cl_6/SbF_5 in SO_2ClF which ultimately produced crystals of $[ICl_2]^+[SbF_6]^-$ is shown in Figure 4. It is clear that in this solution, at low temperature, the $[Sb_2F_{11}]^-$ anion (I) predominates. The low-field multiplet observed at −89.9 ppm (all shifts relative to external $CFCl_3$) is assigned to the bridging fluorine F_a which couples to F_b with J_{Fa-Fb} = 63 Hz. The doublet of doublets at −111.9 ppm is due to the eight equivalent fluorines F_b. Finally a high-field quintet at −135.6 ppm is due to the two equivalent fluorines F_c such that J_{Fc-Fb} = 105 Hz. A partially resolved coupling of ca. 10 Hz to the bridging fluorine Fa is also observed. Two additional weak lines in the spectrum at −103.2 and −104.4 ppm are attributed to the presence of a small amount of SbF_5: the same lines are present in the ^{19}F NMR spectrum of SbF_5 in SO_2ClF. Multiplets found at ∼−70 and ∼−81 ppm are thought to be due to the presence of antimony chloride fluorides. Since no single sharp line is observed in the spectrum, this indicates that there is no appreciable quantity of $[SbF_6]^-$ present in solution. Thus it appears that, while the $[Sb_2F_{11}]^-$ anion is more stable in solution in the presence of excess SbF_5, the $[SbF_6]^-$ anion is able to stabilize the $[ICl_2]^+$ cation in the solid state. That Aubke and co-workers[7] were able to obtain a red solid analyzing as $[ICl_2]^+[Sb_2F_{11}]^-$ by pumping under vacuum on a mixture of I_2Cl_6 and excess SbF_5 remains something of a mystery. Presumably the SbF_5 initially removes a chlorine from the I_2Cl_6 to produce an antimony chloride fluoride which undergoes exchange with SbF_5 to give an $[Sb_2F_{11}]^-$ salt according to eq 1. The molecule SbF_4Cl has never been isolated



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$$I_2Cl_6 + 6SbF_5 \rightarrow 2[ICl_2]^+[Sb_2F_{11}]^- + 2SbF_4Cl \quad (1)$$

but presumably rearranges to produce other antimony(V) chloride fluorides all of which are quite volatile.[25-27] The lines at ∼−70 to −80 ppm in the ^{19}F NMR spectrum are thought to be due to these species. In the SO_2ClF solution an equilibrium between $[Sb_2F_{11}]^-$, $[SbF_6]^-$, and SbF_5 (eq 2) probably exists with the equilibrium lying largely to the left-hand side.

$$[ICl_2]^+[Sb_2F_{11}]^- \rightleftharpoons [ICl_2]^+[SbF_6]^- + SbF_5 \quad (2)$$

Conclusions

Single-crystal X-ray crystallographic studies on the product of the reaction between I_2Cl_6 and excess SbF_5 in SO_2ClF solution have shown that it is the $[SbF_6]^-$ rather than the $[Sb_2F_{11}]^-$ compound that is produced. ^{19}F NMR indicates the presence of the $[Sb_2F_{11}]^-$ species in solution. The arrangement about the iodine(III) in the cation is that of a distorted square with two short terminal I-Cl bonds and two unusually short I---F bridge bonds of length 2.650 (6) Å, indicating a rather strong cation-anion interaction. ^{127}I Mössbauer spectroscopic studies of $[ICl_2]^+[SbF_6]^-$ and $[ICl_2]^+[SbCl_6]^-$ show that the bridging I---F interaction in the former compound is of comparable strength to that of the I---Cl interaction in the latter molecule.

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Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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The Molybdenum-Molybdenum Triple Bond. 9.[1] Bis(1,3-di-*p*-tolyltriazenido)bis(dimethylamido)dimethyldimolybdenum

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1,2-$Mo_2Me_2(NMe_2)_4$ reacts in hydrocarbon solvents with 1,3-di-*p*-tolyltriazine, $C_7H_7NNNHC_7H_7$, to give the title compound as a red crystalline solid. An X-ray study shows that, in the solid state, the molecule has a crystallographically imposed C_2 axis of symmetry. The Mo≡Mo bond (2.174 (1) Å) is bridged by a cis pair of triazenido ligands which afford sufficient flexibility to allow a noneclipsed geometry. Each molybdenum atom is coordinated to three nitrogen atoms and one carbon atom which roughly lie in a plane. Pertinent bond distances are Mo-C(methyl) = 2.193 (4) Å, Mo-N(dimethylamido) = 1.948 (3) Å, and Mo-N(triazenido) = 2.157 (3) and 2.283 (3) Å, with the longer distance associated with the Mo-N bond which is trans to the Mo-CH_3 bond. These observations are compared with other findings in dimolybdenum and ditungsten chemistry (M≡M). Crystal data for $Mo_2Me_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$ are a = 21.608 (5) Å, b = 9.440 (2) Å, c = 24.076 (6) Å, β = 135.49 (1)°, V = 3442.5 (1) Å^3, Z = 4, d_{calcd} = 1.464 g cm^{-3}, and space group $C2/c$.

An extensive coordination chemistry surrounds the $(M{\equiv}M)^{6+}$ unit for molybdenum and tungsten. The metal atoms may be coordinated to 3, 4, 5, or 6 ligand atoms, and, for a given coordination number, there appears to be a preference