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Preparation and Solid-State and Solution Studies of Three Compounds of the Tetraiodine Dication I_4^{2+}: $I_4^{2+}(AsF_6^-)_2$, $I_4^{2+}(SbF_6^-)_2$, and $I_4^{2+}(Sb_3F_{14}^-)(SbF_6^-)$

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Iodine is oxidized by AsF_5 and SbF_5 in solution in sulfur dioxide to give $I_4(AsF_6)_2$ (**1**) and $I_4(Sb_3F_{14})(SbF_6)$ (**2**), respectively. $I_4(SbF_6)_2$ (**3**) was prepared by the reaction of $I_2Sb_2F_{11}$ with fluoride ion. Crystals of **1** are monoclinic, space group $A2/m$, with a = 5.876 (2) Å, b = 9.810 (4) Å, c = 12.411 (5) Å, β = 104.06 (4)°, V = 694.0 (4) Å^3, and D_{calc} = 4.17 g·cm^{-3} for Z = 2. Crystals of **2** are also monoclinic, space group $P2_1/c$, with a = 8.431 (2) Å, b = 15.968 (4) Å, c = 16.818 (3) Å, β = 100.48 (1)°, V = 2226.4 (8) Å^3, and D_{calc} = 4.10 g·cm^{-3} for Z = 4. Crystals of **3** are triclinic, space group $P\bar{1}$, with a = 5.995 (1) Å, b = 10.054 (2) Å, c = 9.177 (2) Å, α = 122.85 (1)°, β = 119.08 (1)°, γ = 90.66 (1)°, V = 376.47 (14) Å^3, and D_{calc} = 4.32 g·cm^{-3} for Z = 1. The structures of **1** and **2** were solved by means of Patterson functions, and that of **3** was solved by direct methods. The three structures were refined by least squares to final agreement indices of R_1 (R_2) = 0.050 (0.059), 0.058 (0.062), and 0.066 (0.083) for 812, 3550, and 1316 independent reflections, respectively. **1** and **3** consist of discrete I_4^{2+} and AsF_6^- and SbF_6^- ions, respectively, and **2** consists of I_4^{2+}, $Sb_3F_{14}^-$, and SbF_6^- ions. The I_4^{2+} cation in all three compounds has a rectangular structure and may be considered to consist of two I_2^+ cations joined by two long weak bonds. Resonance Raman spectra were obtained from the solid compounds. The spectra had a single line at 232 cm^{-1} together with several overtones. In solution in SO_2 and HSO_3F at room temperature, the I_4^{2+} ion is dissociated to I_2^+, but at −78 °C in HSO_3F and SO_2, I_4^{2+} is the predominant species.

The iodine cations I_2^+, I_3^+, I_5^+, and I_{15}^{3+} have been prepared and characterized in solution in highly acidic media such as HSO_3F and H_2SO_4, and several crystalline salts of these ions have been isolated.[1,2] The structures of $I_2^+(Sb_2F_{11}^-)$, $I_3^+(AsF_6^-)$, $I_5^+(AsF_6^-)$, and $I_{15}^{3+}(SbF_6^-)$ have been determined by X-ray crystallography.[2-5] In one of the early studies[3] on the cation I_2^+ it was observed that, on cooling of a solution of the cation in HSO_3F, the color of the solution changed from an intense blue to a deep red-brown at about −80 °C and at the same time the paramagnetism of the solution decreased considerably.[6] These results were explained by assuming that at low temperatures paramagnetic I_2^+ dimerizes to the diamagnetic I_4^{2+} ion. Cryoscopic and conductometric measurements on solutions of $I_2^+(SO_3F^-)$ in fluorosulfuric acid were also consistent with the formation of I_4^{2+} at −78 °C.[6] No information on the structure of this species was obtained at that time, however.

We have now found that $I_4^{2+}(AsF_6^-)_2$ and $I_4^{2+}(SbF_6^-)(Sb_3F_{14}^-)$ can be obtained as products of the room-temperature reactions of I_2 with AsF_5 and SbF_5 in solution in SO_2, respectively, and that the compound $I_4^+(SbF_6^-)_2$ can be obtained by the room-temperature reaction of $I_2(Sb_2F_{11}^-)$ with fluoride ion. This paper reports the preparation of these solid crystalline compounds and their characterization by means of Raman spectroscopy and X-ray crystallography. The formation of the I_4^{2+} ion in solution and the equilibrium with I_2^+ have also been further studied. A preliminary report of the X-ray crystal structures of **1** and **2** has been published previously.[7]

Experimental Section

Materials and General Procedures. Antimony pentafluoride (Ozark-Mahoning Co.) was purified by double distillation in an all-glass apparatus under a dry N_2 atmosphere and stored in FEP bottles with Kel-F stoppers in a drybox. Arsenic pentafluoride was prepared by the direct fluorination of freshly sublimed arsenic in a nickel can at liquid-N_2 temperature. Iodine (BDH Analytical reagent) was further purified by sublimination. Sulfur dioxide (Canadian Liquid Air Ltd.) was distilled from and kept over phosphoric oxide before use.

Reactions were carried out in a two-bulb glass vessel incorporating a medium sintered-glass frit, a Rotoflow valve, and a Teflon-covered stirring bar. A drybox equipped with a microscope was used to select suitable crystals for X-ray structural determination. These crystals were sealed in Lindemann capillaries (0.2–0.3-mm diameter) under a dry nitrogen atmosphere. Raman spectra were recorded with a Spex Industries Model 1400 spectrometer equipped with a double monochromator, an RCA C31034 phototube detector, an electrometer amplifier, and a recorder. The exciting radiation was either the red 6328-Å line of a Spectra-Physics 125 He–Ne laser or the green 5145-Å line of a Spectra-Physics Model 140 Ar$^+$ laser. Both solid and liquid samples were sealed in 0.25-in.-o.d. Pyrex tubes. These were spun, when it was appropriate, to minimize decomposition. Low-temperature spectra were recorded by mounting the sample in a double-walled Pyrex glass Dewar flask. Liquid nitrogen was boiled off from a Dewar flask at a controlled rate by an electric heater and the cold gas passed through the sample Dewar flask. The temperature was monitored with a copper–constantan thermocouple positioned just upstream of the sample. The infrared spectrum of $I_4(AsF_6)_2$ was recorded on a Perkin-Elmer Type 283 grating infrared spectrometer (4000–200 cm^{-1}) in a KBr pellet.

Magnetic Susceptibility. Magnetic susceptibility measurements were carried out on a fully automated Faraday magnetic balance[8] calibrated with $Hg[Co(NCS)_4]$. Temperatures were measured with a National Research Council thermocouple. A diamagnetic correction was determined for the sample container. Other diamagnetic corrections (cm^3·mol^{-1}) used were as follows: F^-, 0.3 × 10^6; Sb(V), −14.0 × 10^6; I^-, −44.6 × 10^6.[9]

UV–Visible Absorption Spectroscopy. Solution spectra were recorded (220–750 nm) on a Cary 14 spectrometer. Solutions in SO_2 were prepared in an apparatus composed of a 1.0-cm rectangular silica cell (Helma) with a graded seal to a Rotoflow valve and a Pyrex vessel equipped with a magnetic stirrer. Lower temperature spectra were taken in a quartz Dewar flask with quartz windows. The Dewar flask was cooled by passing cold N_2 from a liquid-nitrogen boiler, and the temperature was measured with a thermocouple.

Preparations. (a) $I_4^{2+}(AsF_6^-)_2$. Iodine (10 mmol, 2.54 g) was allowed to react with AsF_5 (15 mmol, 2.55 g) in solution in SO_2 at room temperature.

$$2I_2 + 3AsF_5 \rightarrow I_4^{2+}(AsF_6^-)_2 + AsF_3$$

The dark green solution was stirred for 48 h, after which the volatile components of the reaction were slowly removed, producing dark crystals. These crystals gave a red powder on grinding. The same reaction was carried out in solution in SO_2ClF and gave an immediate precipitate of a red amorphous powder. This powder was dissolved in SO_2, and crystalline material was obtained from this solution by slow removal of the solvent. Crystals from both preparations were shown, by an X-ray crystallographic study, to be the compound $I_4(AsF_6)_2$.

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(1) Gillespie, R. J.; Passmore, J. In *Advances in Inorganic Chemistry and Radiochemistry*; Emeleus, H. J., Sharpe, A. J., Eds.; Academic: New York, 1975; Vol. 17, pp 49–87 and references therein.

(2) Passmore, J.; Taylor, P.; Whidden, T.; White, P. S. *Can. J. Chem.* **1979**, *57*, 968–973.

(3) Davies, C. G.; Gillespie, R. J.; Ireland, P. R.; Sowa, J. M. *Can. J. Chem.* **1974**, *52*, 2048–2052.

(4) Passmore, J.; Sutherland, G.; White, P. S. *Inorg. Chem.* **1981**, *20*, 2169–2171.

(5) Apblett, A.; Grein, F.; Johnson, J. P.; Passmore, J.; White, P. S. *Inorg. Chem.* **1986**, *25*, 422–426.

(6) Gillespie, R. J.; Milne, J. B.; Morton, M. J. *Inorg. Chem.* **1968**, *7*, 2221–2225.

(7) Gillespie, R. J.; Kapoor, R.; Faggiani, R.; Lock, C. J. L.; Murchie, M.; Passmore, J. *J. Chem. Soc., Chem. Commun.* **1983**, 8–9.

(8) Donini, J. C.; Hollebone, B. R.; Kochlet, R. A.; Lever, A. B. P. *J. Phys. E* **1972**, *5*, 385.

(9) Figgis, B. N.; Lewis, J. In *Modern Coordination Chemistry*; Lewis, J., Wilkins, R. G., Eds.; Interscience: New York, 1960.

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Table I. Summary of the Structure Determinations

	$I_4(AsF_6)_2$	$I_4(SbF_6)_2$	$I_4(Sb_3F_{14})(SbF_6)$
fw	885.438	979.094	1374.578
cryst size, mm	0.2 × 0.17 × 0.33	0.2 × 0.27 × 0.33	0.06 × 0.10 × 0.33
syst absences	hkl, $k + l = 2n + 1$		$h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$
space group	$A2/m$[a]	$P\bar{1}$	$P2_1/c$
unit cell consts: Å, deg	$a = 5.876$ (2), $b = 9.810$ (4), $c = 12.411$ (5); $\beta = 104.06$ (4)	$a = 5.995$ (1), $b = 10.054$ (2), $c = 9.177$ (2); $\alpha = 122.85$ (1), $\beta = 119.08$ (1), $\gamma = 90.66$ (1)	$a = 8.431$ (2), $b = 15.968$ (4), $c = 16.818$ (3); $\beta = 100.48$ (1)
V, Å^3	694.0 (4)	376.4 (1)	2226.4 (8)
Z	2	1	4
ρ_{calc}, g·cm^{-3}	4.2	4.3	4.1
temp, °C	−35	22	22
abs coeff μ, cm^{-1} (μ_{calc} from SHELX, cm^{-1})	140.8 (131.2)	119.9 (113.9)	106.3 (101.6)
max 2θ, deg	55	50	50
octants	$0 \leqslant h \leqslant 7$, $0 \leqslant k \leqslant 12$, $-15 \leqslant l \leqslant 15$	$0 \leqslant h \leqslant 7$, $-11 \leqslant k \leqslant 11$, $-10 \leqslant l \leqslant 8$	$-5 \leqslant h \leqslant 10$, $-5 \leqslant k \leqslant 19$, $-20 \leqslant l \leqslant 19$
std reflcns (esd)	$\bar{3}02$ (0.013); $1\bar{3}3$ (0.013)	122 (0.014); $2\bar{3}\bar{2}$ (0.017)	215 (0.012); $\bar{1}5\bar{5}$ (0.012)
no. of reflcns collcd	941	1516	5333
R_{merg}	0.038	0.013	0.019
no. of indep reflcns	812	1316	3550
no. of reflcns with $I > 0$ used	811	1316	2439[b]
final residuals: R_1;[c] R_2[c]	0.052; 0.059	0.066; 0.083	0.058; 0.062
final shift/error: max; av.	0.001; <0.001	0.025; 0.008	0.056; 0.004
final diff map peaks, e·Å^{-3}: max; min	2.02; −1.61	1.91; −1.68	2.83; −1.58
secondary extinctn χ	0.000 97	0.008 74	0.000 18
weighting function	$w = (\sigma_F^2 + 0.002854F_o^2)^{-1}$	$w = (\sigma_F^2 + 0.00318F_o^2)^{-1}$	$w = (\sigma_F^2 + 0.00086F_o^2)^{-1}$
error in observn of unit wt	1.1806	1.87	1.7545

[a] This cell may be converted to the standard cell $C2/m$, with $a = 12.411$ (5) Å, $b = 9.810$ (4) Å, $c = 5.876$ (2) Å, and $\beta = 104.06$ (4)°, by the matrix (0,0,−1/0,1,0/−1,0,0). [b] Number with $I > 3\sigma I$ used. [c] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

(b) $I_4^{2+}(Sb_3F_{14}^-)(SbF_6^-)$. Iodine (20 mmol, 5.08 g) was allowed to react with SbF_5 (44 mmol, 9.54 g) in solution in a 1/2 mole ratio in SO_2 at room temperature. A dark brown solution was obtained on stirring. After filtration a white insoluble material (probably SbF_3 or a compound of SbF_3 and SbF_5) was isolated from the solution. Dark crystals of $I_4Sb_4F_{20}$ were obtained from this solution by slow evaporation of the solvent. The main reaction can probably be represented by the equation

$$2I_2 + 4SbF_5 \rightarrow I_4(Sb_3F_{14})(SbF_6)$$

The product was characterized by an X-ray crystallographic determination of its structure.

(c) $I_4^{2+}(SbF_6^-)_2$. In a typical experiment 1.166 g (1.65 mmol) of $I_2Sb_2F_{11}$ and 0.07 g (1.66 mmol) of NaF were added separately to the arms of a double-ampule apparatus. Sulfur dioxide (15 mL) was then distilled onto the $I_2Sb_2F_{11}$ and the blue solution transferred into the other ampule containing NaF. The color of the solution immediately turned brown. The contents were stirred for 24 h, and the solution was filtered through the frit to remove insoluble $NaSbF_6$. The solvent was slowly distilled into the other ampule by cooling it in liquid N_2. The SO_2 was completely removed in about 2 h, and the arm containing $I_4(SbF_6)_2$ was then flame sealed. The crystals looked black but gave a red powder on crushing. The yield of $NaSbF_6$ was quantitative, and its composition was confirmed by its Raman spectrum, which showed peaks at 670 vs (ν_1), 580 w (ν_2), and 280 (ν_3) cm^{-1}.

In other experiments a 2/3 mole ratio of I_2 to SbF_5 was used in an attempt to prepare $I_4(SbF_6)_2$ according to the equation

$$2I_2 + 3SbF_5 \rightarrow I_4(SbF_6)_2 + SbF_3$$

In a typical experiment a solution of SbF_5 (0.6806 g, 3.140 mmol) in sulfur dioxide (ca. 12 cm^3) was added to a solution of iodine (0.5316 g, 2.095 mmol) in SO_2 (ca. 10 cm^3) at room temperature. A red-brown solution was formed immediately together with a white insoluble material. Slow removal of the volatiles at about −3 °C resulted in an oily material, which was slowly cooled to about −78 °C over a period of 3 days. Black well-formed crystals were obtained. Single crystals randomly selected from this preparation had cell parameters identical with those of $I_4^{2+}(Sb_3F_{14}^-)(SbF_6^-)$. A needle-shaped crystal of suitable dimensions was chosen to collect an improved data set, from which a further refinement of the structure was obtained. The white insoluble material, a byproduct of this reaction, was washed thoroughly with SO_2 and pumped to dryness, and its Raman spectrum was obtained. This was neither the spectrum of SbF_3 nor that of $SbF_3{\cdot}SbF_5$ but was probably that of an $xSbF_3{\cdot}ySbF_5$ compound.

(d) Reactions Using an Excess of AsF_5 or SbF_5. Several experiments were carried out using amounts of SbF_5 and AsF_5 in excess of the ratios $AsF_5/I_2 = 2/3$ and $SbF_5/I_2 = 1/2$ needed to obtain the compounds $I_4^{2+}(AsF_6^-)$ and $I_4^{2+}(Sb_3F_{14}^-)(SbF_6^-)$, in order to determine if any compounds containing iodine in the +1 oxidation state, analogous to the compound $I(SO_3F)_2I$, could be obtained.[10] For ratios of AsF_5/I_2 up to 3/1 only the compound $I_4^{2+}(AsF_6^-)_2$ was obtained from the dark green solutions. In the case of the SbF_5 reaction, mole ratios up to 2.2/1 gave similar red-brown solutions from which $I_4^{2+}(Sb_3F_{14}^-)(SbF_6^-)$ could be crystallized. Ratios of SbF_5/I_2 of 3/1 up to 8/1 gave blue solutions from which the deep blue compound $I_2^+(Sb_2F_{11}^-)$ could be crystallized.[3]

Table II. Atomic Positional Parameters (×10^3) and Temperature Factors (Å^2 × 10^3) for $I_4(AsF_6)_2$

atom	x	y	z	U_{eq}[a]
I	120.4 (1)	333.3 (1)	426.1 (1)	35
As	436.5 (3)	0	694.1 (1)	26
F1	566 (3)	0	829 (1)	136
F2	613 (4)	−117 (2)	664 (2)	169
F3	257 (3)	−120 (1)	727 (1)	111
F4	287 (5)	0	562 (1)	139

[a] $U_{eq} = {}^1/_3(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta)$.

Collection of the X-ray Data and Solution of the Structures. All crystals were sealed in quartz tubes. Precession photographs revealed the symmetry, and unit cell parameters were obtained from a least-squares fit of χ, ϕ, and 2θ for 15 reflections for each compound in the ranges 19° < 2θ < 40° (**1**), 18° < 2θ < 35° (**2**) and 20° < 2θ < 30° (**3**), recorded on a Syntex P2$_1$ diffractometer with use of Mo Kα radiation (λ = 0.710 69 Å). Crystal data and other parameters related to data collection are summarized in Table I. Densities were not determined because of the instability of the compounds in air. Intensities were measured on the Syntex P2$_1$ diffractometer with a θ(crystal)–2θ(counter) scan. The methods of selection of scan rate and initial data treatment have been described.[11] Corrections were made for Lorentz–polarization effects and absorption. Empirical ψ-scan and analytical absorption corrections were applied.[12] For compounds **1** and **2**, the iodine and antimony atoms were

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(10) Collins, M. J.; Denes, G.; Gillespie, R. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1296–1297.

(11) Hughes, R. P.; Krishnamachari, N.; Lock, C. J. L.; Powell, J.; Turner, J. *Inorg. Chem.* **1977**, *16*, 314–319. Lippert, B.; Lock, C. J. L.; Rosenberg, B.; Zvagulis, M. *Inorg. Chem.* **1977**, *16*, 1525–1529.

(12) Calabrese, J. C.; Burnett, R. M. "TAPER"; 1980. This was locally modified for the SYBER by Z. Tun, with permission of the Nicolet XRD Corp. Bond, W. L. In *International Tables for X-Ray Crystallography*; Kasper, J. S., Lonsdale, K., Eds.; Kynoch: Birmingham, England, 1959; Vol. II, pp 219–306.

Table III. Atomic Positional Parameters (×10^3) and Temperature Factors (Å × 10^3) for $I_4(SbF_6)(Sb_3F_{14})$

atom	x	y	z	$U_{eq}{}^a$ or U_{iso}
I1	265.9 (2)	500.1 (1)	513.6 (1)	57*
I2	501.5 (2)	412.4 (1)	405.3 (1)	40*
I3	339.5 (2)	489.3 (1)	83.2 (1)	46*
I4	463.0 (3)	621.2 (1)	30.4 (1)	61*
Sb1	420.5 (2)	709.6 (1)	306.7 (1)	32*
Sb2	868.6 (2)	776.4 (1)	279.8 (1)	26*
Sb3	1093.1	1000.7	268.8 (1)	37*
Sb4	−19.3 (2)	757.8 (1)	38.0 (1)	32*
F11	203 (2)	711 (1)	312 (1)	68 (5)
F12	648 (2)	707.3 (9)	302.8 (9)	48 (4)
F13	460 (4)	620 (2)	374 (2)	193 (14)
F14	403 (4)	790 (2)	235 (2)	200 (15)
F15	392 (4)	636 (2)	227 (2)	177 (13)
F16	478 (4)	775 (2)	394 (2)	179 (13)
F21	725 (2)	819.0 (9)	187.7 (8)	46 (4)
F22	791 (2)	859.2 (9)	344.3 (8)	43 (4)
F31	1167 (2)	1111 (1)	281 (1)	71 (5)
F32	1027 (2)	885 (1)	258 (1)	67 (5)
F33	1208 (3)	974 (2)	368 (2)	138 (10)
F34	985 (3)	1018 (2)	165 (2)	135 (10)
F35	1255 (3)	969 (2)	219 (1)	116 (8)
F36	917 (3)	1025 (1)	313 (1)	100 (7)
F41	198 (2)	781 (1)	49 (1)	67 (5)
F42	−238 (2)	738 (1)	27 (1)	81 (6)
F43	−53 (2)	872 (1)	51 (1)	73 (5)
F44	23 (2)	651 (1)	21 (1)	87 (6)
F45	−48 (2)	781 (1)	−74 (1)	67 (5)
F46	7 (2)	744 (1)	150 (1)	55 (4)

[a] Asterisk indicates U_{eq} value, where $U_{eq} = {}^1/_3(U_{11} + U_{22} + U_{33} + 2U_{13} \cos \beta)$.

Table IV. Atomic Positional Parameters (×10^3) and Temperature Factors (Å^2 × 10^3) for $I_4(SbF_6)_2$

atom	x	y	z	$U_{eq}{}^a$
I1	266.3 (1)	239.7	155.1 (2)	24
I2	−258.3 (2)	95.8 (1)	−137.2 (2)	27
Sb1	51.7 (2)	303.6 (1)	614.7 (1)	18
F1	−244 (3)	161 (2)	553 (3)	50
F2	333 (3)	434 (3)	665 (3)	66
F3	−196 (3)	384 (2)	506 (3)	55
F4	−99 (4)	142 (3)	328 (2)	85
F5	283 (4)	219 (3)	728 (4)	80
F6	162 (6)	463 (4)	891 (3)	102

[a] $U_{eq} = {}^1/_3[U_{11} + U_{22} + U_{33} + 2(U_{12} \cos \gamma + U_{13} \cos \beta + U_{23} \cos \alpha)]$.

found from three-dimensional Patterson maps whereas, for compound 3, these atoms were located with the use of direct-methods routines of the program SHELX.[13] Subsequent full-matrix least-squares refinement and electron density difference syntheses revealed all the atoms. Further refinement with use of anisotropic temperature factors for all atoms minimized $\sum_w(|F_o| - |F_c|)^2$ and was terminated when the maximum shift/error fell below 0.1. Corrections were made for secondary extinction by the SHELX method.[13] Scattering curves were from ref 14 as were the anomalous dispersion corrections applied to the scattering curves for I and Sb.[15] The atom parameters are listed in Tables II–IV.[16]

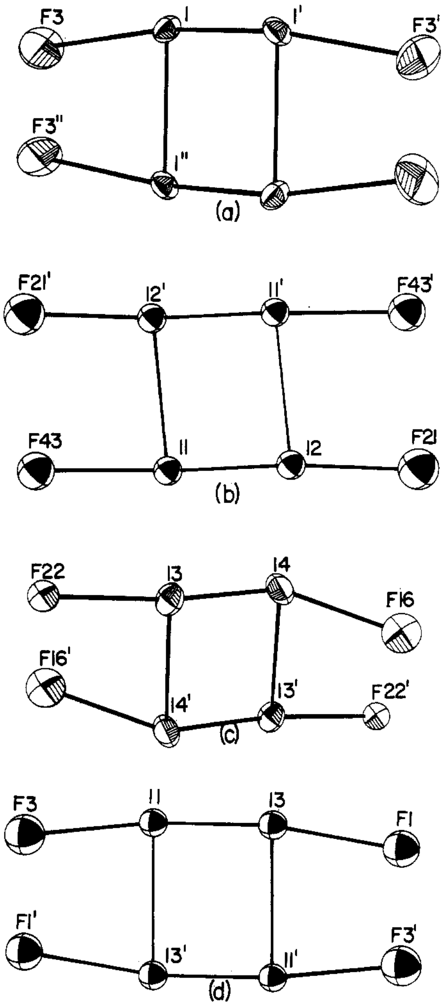

Figure 1. $I_4{}^{2+}$ cations with weakly covalently bonded fluorine atoms (I···F < 2.9 Å): (a) $I_4(AsF_6)_2$; (b, c) $I_4(Sb_3F_{14})(SbF_6)$; (d) $I_4(SbF_6)_2$.

Table V. Selected Interatomic Distances (Å) and Angles (deg) in $I_4(AsF_6)_2$

I–I′	2.575 (1)	I–I″	3.270 (1)
I···F2	3.01 (2)	I···F3	2.82 (2)
As–F1	1.66 (1)	As–F2	1.65 (2)
As–F3	1.69 (2)	As–F4	1.67 (2)

I′–I–I″	90.00 (3)	I′–I···F2	133.6 (4)
I′–I···F3	161.6 (3)	I″–I···F2	134.9 (4)
I″–I···F3	80.6 (2)	F2···I···F3	60.2 (5)
F1–As–F2	94.1 (8)	F1–As–F3	85.1 (7)
F1–As–F4	176 (1)	F2–As–F2	88 (1)
F2–As–F3	92.0 (9)	F2–As–F3	179.2 (7)
F2–As–F4	89.1 (9)	F3–As–F3	87.9 (8)
F3–As–F4	91.7 (9)	I···F2–As	171.1 (9)
I···F3–As	132.2 (7)		

Discussion

The $I_4{}^{2+}$ cations have very similar structures in all three compounds (Figure 1). Bond lengths and angles are given in Tables V–VII. Each cation has a planar rectangular arrangement of iodine atoms and can be considered as two $I_2{}^+$ units joined by two weak I–I bonds. Fluorine atoms from the anions are weakly bound to both ends of each $I_2{}^+$ unit so that the I–I···F angles are approximately 180°, except that the I3–I4···F16 angle is 146.2 (6)°. This is probably because another fluorine atom is relatively close [I4···F42 = 3.14 (2) Å], and the I3–I4···F42 angle is 149.9 (3)°. The $I_4 \cdots F_{42}$ interaction should probably not be considered as a weak covalent bonding interaction. Examination of the shortest I–F distances shows that they fall into two groups: those in which we have invoked a weak covalent bonding interaction (2.82 (2), 2.81 (2), 2.69 (1), 2.74 (2), 2.86 (3), 2.76 (1) Å), which lie below 2.9 Å with a spread of 0.17 Å, and the other short distances (3.01

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(13) Sheldrick, G. M. "SHELX: A Program for Crystal Structure Solution"; Cambridge University: Cambridge, England, 1976.

(14) Cromer, D. T.; Waber, J. T. In *International Tables for X-Ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(15) Cromer, D. T. In *International Tables for X-Ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(16) All computations were carried out on a CYBER 170/730, CYBER 170/815, or VAX 8600 computer. Programs used for initial data treatment: Stewart, J. M. "XRAY 76"; Technical Report TR-446; University of Maryland: College Park, MD, 1976. Stewart, J. M.; Hall, S. R. "XTAL System of Crystallographic Programs"; University of Maryland: College Park, MD, 1983. The structures were solved with use of SHELX.[13] Planes were calculated with the following program: Ahmed, F. R.; Pippy, M. E. "NRC-22"; National Research Council of Canada: Ottawa, 1978. Diagrams were prepared from the program: Johnson, C. K. "ORTEP II"; Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Table VI. Selected Interatomic Distances (Å) and Angles (deg) in $I_4(SbF_6)(Sb_3F_{14})$

I1–I2	2.586 (3)	I1–I2′	3.247 (3)	I3–I4	2.577 (3)
I3–I4′	3.270 (3)	I1···F43	2.81 (2)	I2···F21	2.69 (1)
I3···F22	2.74 (2)	I3···F36	3.07 (2)	I4···F16	2.86 (3)
Sb1–F11	1.86 (2)	Sb1–F12	1.93 (2)	Sb1–F13	1.82 (4)
Sb1–F14	1.75 (4)	Sb1–F15	1.77 (3)	Sb1–F16	1.79 (3)
Sb2–F12	2.26 (2)	Sb2–F21	1.91 (1)	Sb2–F22	1.90 (2)
Sb2–F32	2.26 (2)	Sb2···F45	2.60 (2)	Sb2···F46	2.71 (2)
Sb3–F31	1.87 (2)	Sb3–F32	1.93 (2)	Sb3–F33	1.82 (3)
Sb3–F34	1.84 (3)	Sb3–F35	1.80 (3)	Sb3–F36	1.82 (2)
I2–I1–I2′	92.64 (8)	I′–I2–I1′	87.36 (8)	I2–I1···F43	165.5 (4)
I2′–I1···F43	83.1 (4)	I1–I2···F21	175.4 (3)	I1′–I2···F43	97.1 (3)
I4–I3–I4′	87.65 (8)	I3–I4–I3′	92.35 (8)	I4–I3···F22	173.4 (3)
I4′–I3···F22	98.0 (3)	I4–I3···F36	114.4 (4)	I4′–I3···F36	156.8 (4)
F22···I3···F36	60.5 (5)	I3–I4···F16	146.2 (6)	I3′–I4···F16	108.4 (7)
F11–Sb1–F12	179.1 (7)	F11–Sb1–F13	93 (1)	F11–Sb1–F14	94 (1)
F11–Sb1–F15	92 (1)	F11–Sb1–F16	95 (1)	F12–Sb1–F13	86 (1)
F12–Sb1–F14	87 (1)	F12–Sb1–F15	88 (1)	F12–Sb1–F16	85 (1)
F13–Sb1–F14	172 (2)	F13–Sb1–F15	86 (2)	F13–Sb1–F16	88 (1)
F14–Sb1–F15	89 (2)	F14–Sb1–F16	96 (2)	F15–Sb1–F16	171 (1)
F12–Sb2–F21	83.8 (6)	F12–Sb2–F22	82.1 (6)	F12–Sb2–F32	159.0 (6)
F12–Sb2···F45	75.8 (5)	F12–Sb2···F46	122.3 (5)	F21–Sb2–F22	88.9 (6)
F21–Sb2–F32	84.4 (6)	F21–Sb2···F45	156.2 (6)	F21–Sb2···F46	73.7 (6)
F22–Sb2–F32	80.4 (7)	F22–Sb2···F45	76.4 (6)	F22–Sb2···F46	147.0 (6)
F32–Sb2···F45	110.9 (6)	F32–Sb2···F46	70.3 (6)	F45···Sb2···F46	127.9 (5)
F31–Sb3–F32	177.4 (7)	F31–Sb3–F33	91 (1)	F31–Sb3–F34	93 (1)
F31–Sb3–F35	93 (1)	F31–Sb3–F36	91.9 (9)	F32–Sb3–F33	87 (1)
F32–Sb3–F34	88 (1)	F32–Sb3–F35	85.2 (9)	F32–Sb3–F36	90.1 (1)
F33–Sb3–F34	174 (1)	F33–Sb3–F35	92 (1)	F33–Sb3–F36	91 (1)
F34–Sb3–F35	83 (1)	F34–Sb3–F36	93 (1)	F35–Sb3–F36	174 (1)
F41–Sb4–F42	178.2 (8)	F41–Sb4–F43	87.7 (8)	F41–Sb4–F44	89.2 (8)
F41–Sb4–F45	90.1 (7)	F41–Sb4–F46	89.5 (7)	F42–Sb4–F43	90.6 (8)
F42–Sb4–F44	92.5 (9)	F42–Sb4–F45	89.5 (8)	F42–Sb4–F46	90.8 (8)
F43–Sb4–F44	175.9 (9)	F43–Sb4–F45	86.4 (8)	F43–Sb4–F46	89.3 (7)
F44–Sb4–F34	90.9 (8)	F44–Sb4–F46	93.4 (8)	F45–Sb4–F46	175.7 (7)
Sb1–F12–Sb2	148.3 (8)	Sb2–F32–Sb3	153 (1)	Sb2···F45–Sb4	147.2 (9)
Sb2···F46–Sb4	143.9 (8)				

Table VII. Selected Interatomic Distances (Å) and Angles (deg) in $I_4(SbF_6)_2$

I1–I2	2.581 (1)	I1–I2′	3.285 (2)	I1···F3	2.76 (1)
I1···F2	3.06 (3)	I2···F1′	2.86 (1)	I2···F5	3.01 (3)
Sb1–F1	1.89 (2)	Sb1–F2	1.82 (3)	Sb1–F3	1.83 (2)
Sb1–F4	1.86 (2)	Sb1–F5	1.82 (3)	Sb1–F6	1.83 (3)

I2–I1–I2′	90.01 (5)	I2–I1–F3	170.0 (6)
I2–I1–F2′	127.9 (5)	I2′–I1–F3	84.4 (4)
I2′–I1–F2′	141.1 (4)	F3–I1–F2′	59.3 (7)
F1′–I2–F5	65.2 (5)	F1′–I2–I1	155.8 (4)
F1′–I2–I1′	78.7 (5)	F1′–I2–F1	75.8 (6)
F5–I2–I1	135.3 (4)	F5–I2–I1′	130.0 (6)
F5–I2–F1	74 (1)	I1–I2–I1′	90.0 (1)
I1–I2–F1	96.2 (3)	I1′–I2–F1	130.1 (3)
F1–Sb1–F2	178 (1)	F1–Sb1–F3	86 (1)
F1–Sb1–F5	90 (1)	F1–Sb1–F6	91 (1)
F2–Sb1–F3	94 (1)	F2–Sb1–F5	90 (1)
F2–Sb1–F6	91 (1)	F3–Sb1–F5	176 (2)
F3–Sb1–F6	95 (1)	F4–Sb1–F1	86 (1)
F4–Sb1–F2	92 (1)	F4–Sb1–F3	81 (1)
F4–Sb1–F5	101 (1)	F4–Sb1–F6	175 (1)
F5–Sb1–F6	83 (2)		

(2), 3.07 (2), 3.06 (3), 3.01 (3) Å), all of which lie above 3.0 Å. The latter distances are shorter than the accepted $I^-\cdots F^-$ van der Waals distance (3.45 Å),[17] but, since a cation is involved, a nonbonding contact might well be as short as the $Cs^+\cdots F^-$ distance of 3.05 Å. Clearly, the shorter distances lie well below this limit and represent a weak covalent bonding interaction. The second set, which are separated from the first by a gap of over 0.15 Å, fall close to the $Cs^+\cdots F^-$ distance and, hence, probably do not indicate any weak covalent interaction.

The bonds within the I_2^+ units [2.574 (1) Å (**1**); 2.586 (3), 2.577 (3) Å, (**2**); 2.581 (1) Å (**3**)] are shorter than those in iodine [2.666 (3) Å[18]] and I_3^+ [2.669 (3), 2.660 (2) Å[4]] and are only slightly longer than that in I_2^+ [2.557 (4) Å[3]]. The bonds between the I_2^+ units [3.270 (1) Å (**1**); 3.247 (3), 3.270 (3) Å (**2**); 3.285 (2) Å (**3**)] are slightly longer than the longer bonds in asymmetric I_3^- in CsI_3 [3.042 (4) Å[19]] and NH_4I_3 [3.113 (4) Å[20]] and in I_5^- [3.14 (4) Å[21]] but are shorter than the weak bonding distances in I_{15}^{3+} [3.416 (3) Å[2]] and I_7^- [3.435 (3) Å[22]] and the shortest "nonbonding" distances between ions in $(CH_3)_4I_5$ [3.55 (4) Å[21]], I_5SbF_6 [3.496 (6) Å[2]], CsI_3 [4.01 (1) Å[19]], and NH_4I_3 [3.88 (1) Å[20]]. That $I_4(SbF_6)_2$ is not isomorphous with $I_4(AsF_6)_2$ is perhaps surprising. It appears that the larger SbF_6^- ion [Sb–F(av) = 1.84 Å vs As–F(av) = 1.67 Å] packs more effectively in the lower symmetry and more ordered space group. The observed space group for $I_4(SbF_6)_2$, $P\bar{1}$, is related to that for $I_4(AsF_6)_2$, $A2/m$, by the matrix $(-1,0,0/0,-1,0/1,{}^1/_2,{}^1/_2)$.

Several examples of the system $(Sb_3F_{14}^-)(SbF_6^-)$ have been found previously.[23-26] The $Sb_3F_{14}^-$ anion may be considered as an SbF_2^+ unit bound to two SbF_6^- units through bridging fluorine atoms. The important features of the structure agree well with published values. Sawyer and Gillespie[27] have discussed the other weak interactions of the fluorine atoms with the central $-F-Sb^{III}F_2^+-F-$ unit and have shown that there may be as many as four to six extra contacts shorter than the van der Waals distances. In **2** there are four such contacts [Sb2···F45 = 2.60 (2) Å;

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(17) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(18) Huber, K. B.; Herzberg, G. *Constants of Diatomic Molecules*, 1st ed.; Van Nostrand: Toronto, Canada, 1979; p 332.

(19) Rusiuk, J.; Swen-Walstra, S.; Migchelsen, T. *Acta Crystallogr.* **1972**, *B28*, 1331–1335.

(20) Cheesman, G. H.; Finney, A. J. T. *Acta Crystallogr.* **1970**, *B26*, 904–906.

(21) Hach, R. J.; Rundle, R. E. *J. Am. Chem. Soc.* **1951**, *73*, 4321–4324.

(22) Havinga, E. E.; Wiebenga, E. H. *Acta Crystallogr.* **1958**, *11*, 733–737.

(23) Gillespie, R. J.; Kent, J. P.; Sawyer, J. F.; Slim, D. R.; Tyrer, D. J.; *Inorg. Chem.* **1981**, *20*, 3799–3812.

(24) Boldrini, P.; Brown, I. D.; Collins, M. J.; Gillespie, R. J.; Maharajh, E.; Slim, D. R.; Sawyer, F. J. *Inorg. Chem.* **1985**, *24*, 4302–4307.

(25) Burns, R. C.; collins, M. J.; Eicher, S. M.; Gillespie, R. J.; Sawyer, J. F. *Inorg. Chem.* **1988**, *27*, 1807–1813.

(26) Collins, M. J.; Faggiani, R.; Gillespie, R. J.; Sawyer, F. J.; Vekris, J. E., in manuscript preparation.

(27) Gillespie, R. J.; Sawyer, J. F. *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley: New York, 1986; Vol. 34, pp 65–113.

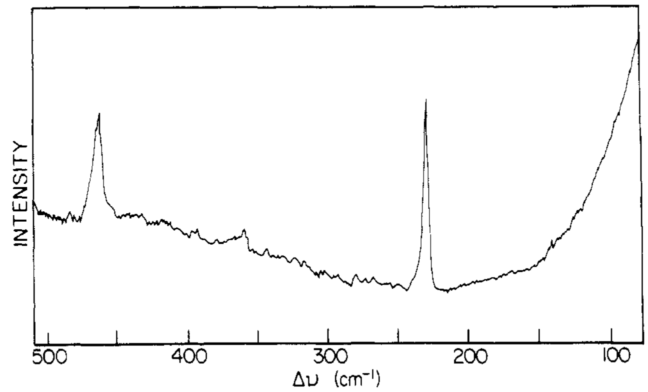

Figure 2. Resonance Raman spectrum of $I_4(AsF_6)_2$.

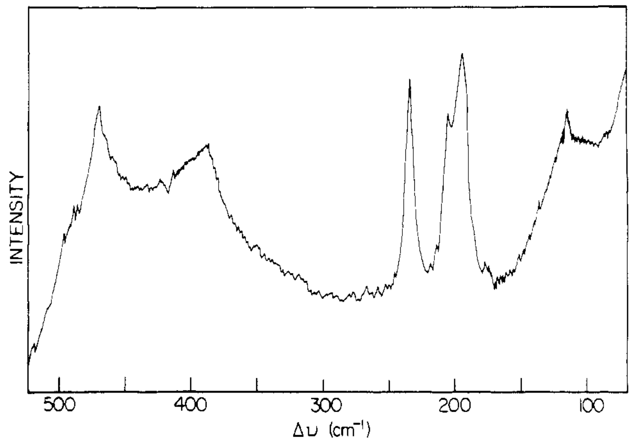

Figure 3. Raman spectrum (25 °C) of a solution of $I_2Sb_2F_{11}$ in SO_2.

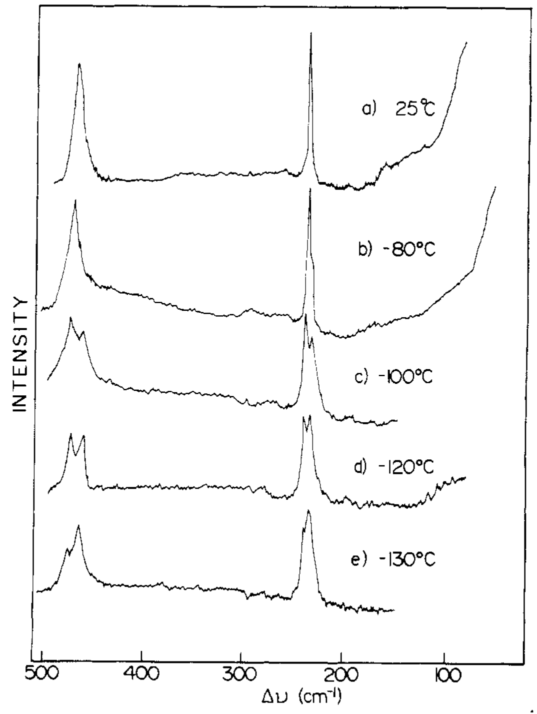

Figure 4. Raman spectra of $I_2Sb_2F_{11}$ in HSO_3F as a function of temperature.

Sb2···F46 = 2.71 (2) Å; Sb2···F31 = 2.82 (2) Å; Sb2···F11 = 2.96 (2) Å] that lie well within the range for other systems with four contacts.

All three compounds gave resonance Raman spectra with 514.5-nm radiation, consisting of a fundamental at 232 cm^{-1} and an overtone at 464 cm^{-1}. Further, weak overtones were sometimes observed at 696 and 928 cm^{-1} (Figure 2). No anion peaks were observed, but the infrared spectrum of $I_4(AsF_6)_2$ had the characteristic bands of AsF_6^- at 390 and 690 cm^{-1}.[28] The I–I stretch in I_4^{2+} is at a slightly lower frequency than that in I_2^+ (238 cm^{-1}).[29] This is consistent with the observation that the I–I bond in I_4^{2+} is slightly longer (2.58 Å) and therefore presumably slightly weaker than that in I_2^+ (2.56 Å).

The weak bonding between the two I_2^+ ions can best be represented in terms of a four-center orbital formed from the singly occupied π^* orbitals of each I_2^+. A very similar bonding has been observed between the S–S bonds of two $S_3N_2^+$ ions in the dimer $S_6N_4^{2+}$.[30] The slight decrease in the stretching frequency from 238 cm^{-1} in I_2^+ to 232 cm^{-1} in I_4^{2+} is consistent with this description of the bonding.

Solution Studies. Earlier work had shown that I_4^{2+} is formed from a solution of I_2^+ in HSO_3F on cooling to approximately −78 °C,[6] but in the present work we found that all three compounds could be crystallized from SO_2 solutions at room temperature. These solutions were prepared from I_2 and AsF_5 or SbF_5 in appropriate ratios to form compounds containing iodine in the $+^1/_2$ oxidation state or were directly prepared from $I_2^+Sb_2F_{11}^-$. However, the room-temperature Raman spectra of the solutions showed that they do not contain the I_4^{2+} cation (232 cm^{-1}) in a concentration that could be detected by the Raman spectrum. The 238-cm^{-1} band clearly showed the presence of I_2^+,[29] but this was not the only iodine-containing species present in the solution. There were also bands at 116, 207, and 232 cm^{-1}, which are due to I_3^+, and a band at 197 cm^{-1}, which has not been assigned with complete certainty, but which appears to be caused by a species containing iodine in the +1 oxidation state that is probably related to $I(SO_3F)_2I$[10] (see Figure 3). Thus, I_4^{2+} is extensively dissociated to I_2^+ in solution in SO_2 at room temperature, but this ion is not completely stable under these conditions and disproportionates to species containing iodine in the $+^1/_3$ and +1 oxidation states.

$$I_4^{2+} \rightleftarrows 2I_2^+ \rightleftarrows I_3^+ + \text{“}I^+\text{”}$$

Nevertheless, on evaporation of these solutions a compound of I_4^{2+} crystallizes out. The only anion that is so far known to stabilize the I_2^+ cation in the solid state is $Sb_2F_{11}^-$.[3] If iodine is oxidized with SbF_5 with a slight excess over the amount needed to produce the $Sb_2F_{11}^-$ ion

$$2I_2 + 5SbF_5 \rightarrow 2I_2^+ + Sb_2F_{11}^-$$

i.e., the SbF_5/I_2 ratio is 2.5, the dark blue solution contains the I_2^+ ion only and the compound $I_2^+Sb_2F_{11}^-$ can be crystallized from the solution. But if the SbF_5/I_2 ratio is 2.2 or less, the compound $I_4^{2+}(Sb_3F_{14}^-)(SbF_6^-)$ is obtained. When a sufficient amount of F^- ion as NaF was added to a blue solution of $I_2^+Sb_2F_{11}^-$ to convert all the $Sb_2F_{11}^-$ to SbF_6^-, the solution became dark brown and the 238-cm^{-1} band of the I_2^+ ion was replaced in the Raman spectrum by bands at 116, 207, and 233 cm^{-1} caused by I_3^+ and a band at 197 cm^{-1}, which we have tentatively attributed to a +1 iodine species.[10] The compound $I_4^{2+}(SbF_6^-)_2$ was crystallized from this solution. The $As_2F_{11}^-$ ion is not stable at room temperature so it is perhaps not surprising that even when a large excess of AsF_5 was used to oxidize iodine, the deep blue solution characteristic of I_2^+ was not obtained. These solutions had Raman spectra that, like those for the solutions obtained with insufficient SbF_5 which produced $Sb_2F_{11}^-$, had bands at 238 cm^{-1} caused by I_2^+, at 116, 207, and 233 cm^{-1} caused by I_3^+, and at 197 cm^{-1}. Crystallization of these solutions gave the brown solid $I_4^{2+}(AsF_6^-)_2$. The absorption spectra of these solutions are also consistent with these conclusions from the Raman spectra. The band at 357 nm, which has been assigned to I_4^{2+} in the red solutions of I_2^+ in HSO_3F at low temperatures,[6] is not observed in the solution spectra of any of the three I_4^{2+} salts in HSO_3F. However, these solutions exhibit bands at 295 and 470 nm (I_3^+ and I^+) and 640 nm (I_2^+).[31] Their

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(28) Begun, G. M.; Rutenberg, A. C. *Inorg. Chem.* **1967**, *6*, 2212–2216.
(29) Gillespie, R. J.; Morton, M. J. *J. Mol. Spectrosc.* **1969**, *30*, 178–183.
(30) Gillespie, R. J.; Kent, J. P.; Sawyer, J. F. *Inorg. Chem.* **1981**, *20*, 3784–3799.
(31) Gillespie, R. J.; Milne, J. B. *Inorg. Chem.* **1966**, *5*, 1577–1582.

Inorg. Chem. **1988**, *27*, 4355–4361 **4355**

absorption spectra in SO_2 showed bands at 475 nm (I_3^+) and 648 nm (I_2^+). Because of strong absorption by SO_2, bands below 350 nm could not be observed.

Gillespie et al. have reported that solutions of I_2^+ in HSO_3F change from the characteristic deep blue color of I_2^+ at room temperature to a red-brown color at −80 °C.[6] They showed by a combination of magnetic, cryoscopic, and conductometric measurements that I^{2+} dimerizes to I_4^{2+} at low temperature. In the present investigation, we have studied Raman spectra of a solution of $I_2^+(Sb_2F_{11}^-)$ in HSO_3F as a function of temperature (Figure 4). Between room temperature and −60 °C, the spectra showed only the characteristic peak of I_2^+ at 238 cm^{-1}.[29] At lower temperatures, however, as the color of the solution changed from blue to red, a new peak appeared at 232 cm^{-1} and the 238-cm^{-1} peak decreased in intensity. The first overtone of each peak was observed at 464 and 476 cm^{-1}, respectively. At −120 °C, the 232-cm^{-1} peak was much stronger than the 238-cm^{-1} peak, indicating that the dimerization was essentially complete.

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Registry No. **1**, 84493-41-4; **2**, 117041-29-9; **3**, 117041-30-2; I_2, 7553-56-2; AsF_5, 7784-36-3; SbF_5, 7783-70-2; $I_2Sb_2F_{11}$, 53108-64-8; NaF, 7681-49-4.

Supplementary Material Available: For **1**–**3**, Tables A–C (anisotropic temperature factors) (2 pages); tables of observed and calculated structure factors (45 pages). Ordering information is given on any current masthead page.

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Equilibria within the $Ru_3(CO)_{12}$/Halide System

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The results reported herein, when combined with those from earlier studies, present a comprehensive picture of the various equilibria that exist in $Ru_3(CO)_{12}$ solutions containing halide ions. A remarkable number of complexes have been found to form and interconvert, with the position of the equilibria dependent upon temperature, the CO partial pressure, and the specific halide employed. All experiments described herein have used the $[(Ph_3P)_2N]^+$ halide salts, except as noted. As previously noted by Kaesz and co-workers, $Ru_3(CO)_{12}$ rapidly reacts with Cl^- and Br^- ions to initially form the clusters $[Ru_3(X)(CO)_{11}]^-$ (**2a**,**b**), which reversibly lose CO to produce the species $[Ru_3(\mu_2\text{-}X)(CO)_{10}]^-$ (**3a**,**b**). The reaction of $Ru_3(CO)_{12}$ with iodide proceeds immediately to form $[Ru_3(\mu_2\text{-}I)(CO)_{10}]^-$ (**3c**) but with no evidence for the intermediacy of a cluster analogous to **2a** and **2b**. Clusters **3a** and **3b** rapidly add CO at 1 atm to form **2a** and **2b**, but cluster **3c** does not take up CO under these mild conditions. When heated, the trinuclear clusters **3a**–**c** all lose CO to transform reversibly into other species, but with the final product dependent upon the halide. The chloro and bromo derivatives **3a** and **3b** form the tetranuclear butterfly clusters $[Ru_4(\mu_2\text{-}X)(CO)_{13}]^-$ (**6a** and **6b**), along with $^1/_4$ equiv of halide ion, and these reactions are cleanly reversed by placing **6a** and **6b** with the necessary halide under 1 atm of CO. The iodo cluster **3c** loses CO upon heating to form the trinuclear species $[Ru_3(\mu_3\text{-}I)(CO)_9]^-$ (**7c**), which has been crystallographically defined as the $[Na(18\text{-crown-}6)]^+$ salt: space group *Pnma*, $a = 20.214$ (5) Å, $b = 21.592$ (6) Å, $c = 15.199$ (3) Å, $V = 6634$ (2) Å^3, $Z = 8$, $R(F) = 7.92\%$, $R_w(F) = 8.92\%$ for 2879 reflections with $F_o \geq 4\sigma F_o$. The triangular metal core of **7c** is symmetrically capped by a μ_3-iodide ligand. Each Ru atom has two terminal CO's, and CO ligands bridge each of the Ru–Ru bonds. Cluster **7c** can be reversibly protonated to form the known species $HRu_3(\mu_3\text{-}I)(CO)_9$. Cluster **7c** also rapidly forms upon reaction of **3c** with H_2O, a reaction that also produces CO_2 and H_2, and **3c** is a catalyst for the water gas shift reaction. When the reaction of $Ru_3(CO)_{12}$ with iodide was conducted under an H_2/CO atmosphere, disproportionation occurred to form $[HRu_3(CO)_{11}]^-$ and $[RuI_3(CO)_3]^-$. A similar reaction occurred when cluster **7c** was placed under H_2. Cluster **7c** has also been found to thermally decompose to form $[Ru_6(CO)_{18}]^{2-}$ when heated to 100 °C. However, at 140 °C, **7c** forms the carbide cluster $[Ru_6C(CO)_{16}]^{2-}$. The reaction of $Fe_3(CO)_{12}$ with iodide has been reinvestigated and found to produce $[Fe(CO)_4I]^-$ along with small amounts of $[HFe_3(CO)_{11}]^-$ that form from traces of water.

Introduction

Halides are highly effective promoters of a number of reactions catalyzed by $Ru_3(CO)_{12}$,[1-5] but the role of the halide is in general poorly understood. The one catalytic reaction that has been most thoroughly studied from a phenomenological perspective is the halide-promoted formation of methanol, ethylene glycol, and acetic acid from synthesis gas.[1-3] It is known that significant rate enhancements and altered selectivities are provided in these systems by halides, but a full understanding of the roles of these promoters has yet to be developed. It is known, however, that the catalytic solutions in these reactions often contain ruthenium halide complexes and anionic clusters. One role of the halides may be to stabilize complexes in the catalytically important oxidation states.[6]

To understand the promoting role of halide on $Ru_3(CO)_{12}$ catalysis, it is essential to understand first the basic reactions that occur when halides react with $Ru_3(CO)_{12}$. Kaesz and his coworkers have provided an important insight in this area through their demonstration that halides stoichiometrically react with $Ru_3(CO)_{12}$ to form the anionic clusters **3a**–**c**, (Scheme I).[7] These complexes were further shown to yield the neutral hydride clusters **4a**–**c** upon protonation, and it was also reported that complex **4c** reversibly loses CO to form the cluster **5c** with a triply bridging iodide ligand.[8] Spectroscopic data have been reported for complexes **3a**, **4a**–**c**, and **5c**. Furthermore, complexes **4b** and **5c** have been fully defined by X-ray diffraction studies.[8] The use of LiX salts coupled with Me_3NO as a carbonyl labilizer was originally used to induce the formation of **3a**–**c**, but such reaction gave only

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(1) (a) Dombek, B. D. *J. Organomet. Chem.* **1983**, *250*, 467. (b) Dombek, B. D. *J. Am. Chem. Soc.* **1981**, *103*, 6508. (c) Dombek, B. D. *Eur. Pat. Appl.* **1979**, 0013008. (d) Dombek, B. D. *Organometallics* **1985**, *4*, 1707.

(2) (a) Knifton, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 3959. (b) Knifton, J. F. *J. Mol. Catal.* **1981**, *11*, 91.

(3) Yoshida, S. I.; Mori, S.; Kinoshita, H.; Watanabe, Y. *J. Mol. Catal.* **1987**, *42*, 215.

(4) Hidai, M.; Koyasu, Y.; Chikanari, K.; Uchida, Y. *J. Mol. Catal.* **1987**, *40*, 243.

(5) Cenini, S.; Pizoti, M.; Crotti, C.; Porta, F.; Monica, G. L. *J. Chem. Soc., Chem. Commun.* **1985**, 241.

(6) Dombek, B. D. *Comments Inorg. Chem.* **1985**, *4*, 241.

(7) Lavigne, G.; Kaesz, H. D. *J. Am. Chem. Soc.* **1984**, *106*, 4647.

(8) Kampe, C. E.; Boag, N. M.; Knobler, C. B.; Kaesz, H. D. *Inorg. Chem.* **1984**, *23*, 1390.