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Preparation and X-ray Crystal Structure of $[I_5^+][AsF_6^-]$ and Electronic Structure of the I_5^+ Cation

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Iodine was oxidized quantitatively by AsF_5 in sulfur dioxide solution to give highly crystalline $[I_5^+][AsF_6^-]$ (pentaiodinium hexafluoroarsenate(V)), the structure of which has been determined by X-ray crystallography. The crystals were monoclinic, space group *C*2/*c*, with a = 10.529 (6) Å, b = 18.568 (2) Å, c = 8.320 (5) Å, β = 128.51 (4)°, Z = 4, and final R = 0.066 for 925 observed reflections. The structure consists of planar centrosymmetric I_5^+ cations and AsF_6^- anions with cation–anion interactions. The terminal and central I–I bond distances are 2.645 (1) and 2.895 (1) Å with no significant iodine- - -iodine interactions between the I_5^+ cations. The I–$\hat{I}$–I bond angles are 97.0 (1) and 180°. The electronic structure and energies of various rotamers of Cl_5^+, as models of I_5^+, were calculated by the ab initio (STO-3G) method. The energies of the various rotamers of Cl_5^+ were found to be very similar, with the planar centrosymmetric structure the most stable. The magnitude of the energy difference between rotamers corresponded to the small electrostatic repulsion energy between the partially charged terminal chlorine atoms. An account is given of minor but definite differences in geometries of I_5^+ in $[I_5^+][AsF_6^-]$ and $[I_{15}^{3+}][SbF_6^-]_3$.

Introduction

A wide variety of polyatomic iodine anions have been well characterized[1,2] for some time. More recently the X-ray structures of various polyatomic iodine cations have been determined. These cations are of interest in their own right and as reagents, or intermediates, in the synthesis of novel sulfur–iodine and selenium–iodine cations such as $[S_2I_4^{2+}][AsF_6^-]_2$[3] and $[Se_2I_4^{2+}][Sb_2F_{11}^-]_2$.[4]

The cations I_2^+, I_3^+, I_5^+, I_4^{2+}, and possibly I_7^+, formed by the oxidation of elemental iodine, have previously been shown to exist in a strong acid medium.[5] The X-ray crystal structures of $[I_2^+][Sb_2F_{11}^-]$,[6] $[I_3^+][AsF_6^-]$,[7] $[I_{15}^{3+}][SbF_6^-]_3$,[8] $[I_4^{2+}][AsF_6^-]_2$, and $[I_4^{2+}][Sb_3F_{14}^-][SbF_6^-]$[9] have been reported. Very recently the crystal structure of a material of empirical formula ISO_3F, showed that it was in fact, iodine(III) bis(fluorosulfate) iodide $I(SO_3F)_2I$.[10] Crystallographic data established that $[I_2^+][Sb_2F_{11}^-]$ contains monomeric I_2^+ radical cations[6] while the analogous AsF_6^- and $[Sb_3F_{14}^-][SbF_6^-]$ salts contain the diamagnetic I_4^{i+} dimers.[9] The two I_2^+ units in the rectangular I_4^{2+} cations are joined together by two relatively weak bonds (~3.26 Å),[9] which are substantially shorter than the sum of the van der Waals radii (3.92 Å).[11] Similarly the I_{15}^{3+} cations may be regarded as three I_5^+ units joined by two weak bonds (~3.42 Å) to form an I_{15}^{3+} chain.[8] We report below the preparation and crystal structure of $[I_5^+][AsF_6^-]$, which contains a discrete I_5^+ cation. We also report the results of ab initio quantum-mechanical calculations of the energies and electronic structure of various rotomers of Cl_5^+ as models for I_5^+. We account for the small, but definite differences in bond distances and angles of the I_5^+ cations in $[I_5^+][AsF_6^-]$ and $[I_{15}^{3+}][SbF_6^-]_3$.

Experimental Section

General Procedures. Apparatus, techniques, and chemicals have been described in ref 12. Crystalline $[SN^+][AsF_6^-]$[13] was prepared by a modification of the reported preparation of a solution of $[SN^+][PF_6^-]$ in nitromethane.[14] Reactions were carried out in a two-bulbed glass vessel incorporating a medium sintered-glass frit, a Rotoflow valve, and a stirring bar. Solids were manipulated in a Vacuum Atmospheres Dri-Lab equipped with a Dri-Train (Model HE-493) and an internal circulating drying unit containing 1260 g of 3A molecular sieves. Hand-drawn Pyrex capillary tubes flame-sealed to the appropriate length were predried at 170 °C prior to transfer to the drybox. Crystals for X-ray analysis were manipulated in the drybox with the aid of an externally mounted Wild M3 microscope of long focal length. IR spectra were recorded in the 4000–300 cm^{-1} range with use of KBr windows.

Preparation of $[I_5^+][AsF_6^-]$. In a typical reaction, AsF_5 (0.353 g, 2.08 mmol) was condensed onto I_2 (0.874 g, 3.44 mmol) and SO_2 (8.51 g, 133 mmol), which were cooled to −80 °C. The mixture was allowed to warm to room temperature, and the brown solution was stirred. After 1 day, the solvent was slowly condensed to the empty side of the vessel by immersing that side in cold running water overnight. In this way a crystalline block (1 cm × 1 cm × 0.25 cm), which was black in color, was obtained. The volatiles were removed by pumping for 3 h. Solid $[I_5^+][AsF_6^-]$ (1.15 g, 1.39 mmol) was obtained, melting point 72–73 °C, and had the following analysis. Anal. Calcd for $[I_5^+][AsF_6^-]$: I, 77.06; As, 9.10; F, 13.85; Found: I, 77.05; As, 9.17; F, 13.90. The infrared spectrum of the solid consisted of two sharp bands at 700 (s, $\nu_3[AsF_6^-]$) and 390 (m, $\nu_4[AsF_6^-]$) cm^{-1}.[15]

Crystals. Single crystals from the reaction described above had identical cell dimensions to that from which intensity data were obtained. The crystal used in the full X-ray crystallographic study was a product of the reaction of $[SN^+][AsF_6^-]$ (0.105 g, 0.446 mmol) and I_2 (0.120 g, 0.471 mmol) in sulfur dioxide solution.[16] $[SN^+][AsF_6^-]$, dissolved in SO_2, was poured into the SO_2–I_2 mixture, which turned from light red to a very intense brown color. Slow removal of the solvent gave black crystals and a less soluble grey crystalline solid. The vessel was evacuated to dryness and the solid mixture was redissolved in SO_2–SO_2ClF (2:1) (8.21 g total). The slow removal of the solvent produced a mixture of well-formed green-black crystals and gray powder. Single crystals of $[I_5^+][AsF_6^-]$ were separated from the mixture in the drybox with the aid of a microscope and sealed in dry glass capillaries.

Crystal Data and Initial Processing of Data. A summary of the crystal structure data collection and initial analysis is given in Table I. Three standard reflections were measured every 100 reflections and these showed a small (<8σ) but significant variation during data collection, possibly because of surface decomposition. The data set was scaled, and a spherical absorption correction was applied to the data set (μR = 3.38). Corrections for Lorentz and polarization factors were applied to the data. Statistical treatment of the normalized structure factors indicated a centric crystal system, and the structure determination was attempted in the space group *C*2/*c*.

Structure Determination and Refinement. Initial positional parameters of the three iodine atoms and one arsenic atom in the asymmetric unit

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Table I. Summary of Crystallographic Data

mol formula	I_5AsF_6
fw	823.43
cryst syst	monoclinic
space group	$C2/c$
a, Å	10.529 (6)
b, Å	18.568 (2)
c, Å	8.320 (5)
β, deg	128.51 (4)
V, Å^3	1272.8 (9)
Z	4
d_{calcd}, Mg m^{-3}	4.30
color	green-black
shape	irregular
mean radius, mm	0.23
radiation (λ Mo Kα), Å	0.71073
μ(Mo Kα), mm^{-1}	14.7
F(000)	1408
monochromator	graphite
initial cell	precession method
diffractometer	Picker FACS-1
accurate cell params and orientation matrix	refined, centered coordinates of 20 reflcns and Friedel opposites, $34° \leqslant 2\theta \leqslant 47°$
scan	ω–2θ
scan speed, deg(2θ)/min	2
scan range (2θ), deg	2° (corrected for dispersion)
bkgd time, s	0.1 of scan time on either side of peak, plus profile analysis
2θ limits, deg	$5 \leqslant 2\theta \leqslant 50$
temp, K	298
no. of standards/interval (long-term variation, σ)	3/100 (8)
data collcd	2230
octants	hkl; $\bar{h}kl$; $h\bar{k}l$; $\bar{h}\bar{k}l$
no. of systematically absent data	39
no. of reflcns avgd after spherical abs cor	2191
no. of unique reflcns ($R_{merge} = \sum\Delta I/\sum I$, from merging equiv reflcns)	1120 (0.096)
no. of data used ($I \geqslant 3\sigma(I)$)	925
statistical treatment of normalized structure factors	centric cryst syst

Table II. Fractional Atomic Coordinates with Estimated Standard Deviations in Parentheses

atom	x/a	y/b	z/c
I(1)	0.73630 (16)	0.02873 (6)	0.56838 (20)
I(2)	0.58140 (14)	0.14310 (6)	0.55769 (18)
I(3)	0.75000	0.25000	0.50000
As(1)	0.00000	0.15594 (11)	0.25000
F(1)	0.1943 (17)	0.1566 (10)	0.3353 (27)
F(2)	0.0483 (20)	0.2161 (9)	0.4317 (31)
F(3)	0.0494 (23)	0.0883 (8)	0.4104 (24)

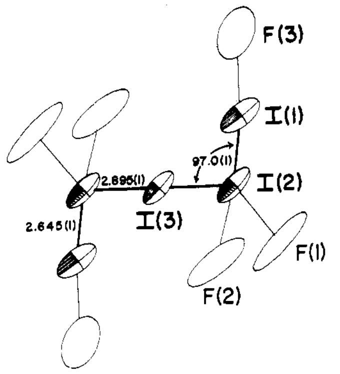

Figure 1. I_5^+ cation with fluorine contacts less than 3.47 Å in $[I_5^+][AsF_6^-]$.

Table III. Interatomic Distances (Å) and Angles (deg) for $[I_5^+][AsF_6^-]$ with Estimated Standard Deviations in Parentheses

	(a) Bond Lengths^a		
I(1)–I(2)	2.645 (1)	As(1)–F(1)	1.698 (13)
I(2)–I(3)	2.895 (1)	As(1)–F(2)	1.683 (15)
		As(1)–F(3)	1.662 (13)
	(b) Bond Angles		
I(1)–I(2)–I(3)	97.0 (1)	F(1)–As(1)–F(2)	90.5 (8)
		F(1)–As(1)–F(3)	88.7 (9)
		F(2)–As(1)–F(3)	90.7 (10)
	(c) Cation–Anion Interactions^b		
F(3)- - -I(1)	3.06 (1)	F(1)- - -I(2)	3.27 (1)
F(2)- - -I(2)	2.98 (1)		
	(d) Cation–Anion Interaction Angles		
F(1)- - -I(2)–I(1)	127.3 (4)	F(2)- - -I(2)–I(3)	92.8 (4)
F(1)- - -I(2)–I(3)	122.0 (3)	F(3)- - -I(1)–I(2)	171.9 (4)
F(2)- - -I(2)–I(1)	169.6 (4)	F(1)- - -I(2)- - -F(2)	46.9 (6)

^{a}All I–I distances ≤ 4.16 Å. ^{b}All I–F distances ≤ 3.47.

were obtained by using the MULTAN-80 suite[17] of direct-methods programs. The positional parameters of the fluorine atoms were located by a subsequent difference synthesis. A DIFABS empirical absorption correction[18] was applied to the data set ($R_{merge} = 0.054$). The structure was refined by full-matrix least-squares with the use of anisotropic thermal parameters for all the atoms. The function minimized was $\sum w(\Delta F)^2$ with $w = [\sigma(F)^2 + 0.009F_o^2]^{-1}$ where $\sigma(F)$ is directly derived from $\sigma(I)$. The final refinement converged at $R_1 = \sum|\Delta F|/\sum|F_o|$ and $R_2 = (\sum w|\Delta F|^2/\sum w|F_o|^2)^{1/2}$ of 0.066 and 0.071 (0.077 and 0.084, including unobserved reflections, respectively). The final refinement included a SHELX empirical extinction correction ($x = 0.0009$ (1)) for a total of 58 refined parameters. The structure refinement was performed by using SHELX-76.[19] A final difference map did not reveal any additional atoms. The largest features were peaks of <2.1 e Å^{-3} near the iodine atoms, with minimums of −1.4 e Å^{-3} within 1.7 Å of these atoms. All the remaining electron density varied within ±1 e Å^{-3} throughout the cell. Atomic scattering factors corrected for anomalous dispersion were taken from ref 20. The final positional coordinates of the atoms in the asymmetric unit are given in Table II. A stereoscopic view of crystal packing in $[I_5^+][AsF_6^-]$ and tables of anisotropic thermal parameters and calculated and observed structure factors may be found in the supplementary material.

Results and Discussion

Preparation of $[I_5^+][AsF_6^-]$. Highly crystalline $[I_5^+][AsF_6^-]$ was prepared quantitatively by the oxidation of iodine with arsenic pentafluoride in liquid sulfur dioxide according to eq 1.

$$5I_2 + 3AsF_5 \rightarrow 2[I_5^+][AsF_6^-] + AsF_3 \qquad (1)$$

$[I_3^+][AsF_6^-]$[7] and $[I_4^{2+}][AsF_6^-]_2$[9] can also be prepared similarly by using the appropriate ratios of iodine and arsenic pentafluoride. Our various attempts to prepare solid $[I^+][AsF_6^-]$ and $[I_7^+][AsF_6^-]$ have been unsuccessful.

Crystals of $[I_5^+][AsF_6^-]$ were also obtained as one of the products of the oxidation of iodine by $[SN^+][AsF_6^-]$.[16] As far as we are aware, the AsF_6^- salt of I_5^+ has not been previously reported. However, the preparation of compounds of empirical formulas $[I_5^+][SbF_6^-]$[8] and $[I_5^+][AlCl_4^-]$[21] have been described.

Crystal Structure of $[I_5^+][AsF_6^-]$. The structure of the iodine cation, including fluorine anion- - -cation contacts are illustrated in Figure 1. Appropriate bond distances and angles are presented in Table III. There are no cation–anion contacts less than 2.9 Å (Table III), suggesting that $[I_5^+][AsF_6^-]$ is essentially an ionic species.

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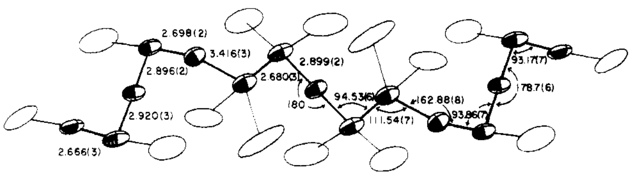


Figure 2. Alternation of bond lengths and angles in the I_{15}^{3+} cation of $[I_{15}^{3+}][SbF_6^-]_3$[8] with fluorine contacts less than 3.40 Å.

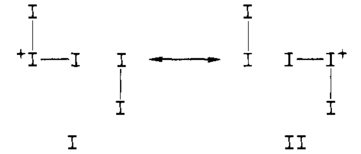
The distances between the I_5^+ cations in $[I_5^+][AsF_6^-]$ are greater than the sum of the van der Waals radii for iodine (3.92 Å),[11] showing that the I_5^+ cations are isolated. Such is not the case for the I_5^+ units in $[I_{15}^{3+}][SbF_6^-]_3$ where the central I_5^+ unit is weakly bonded to two terminal I_5^+ units by iodine- - -iodine contacts of 3.416 (3) Å, and the moiety can be regarded as an I_{15}^{3+} chain.[8] Thus, this is in fact the first structural determination of an isolated I_5^+ cation, which for some time has been proposed to exist in strongly acidic medium.[5]

The central iodine atom of the I_5^+ cation in $[I_5^+][AsF_6^-]$ lies on a crystallographic center of symmetry such that the cation is planar and of C_{2h} symmetry. The bond distances and angles in the I_5^+ cation are very similar, but not identical with those of the I_5^+ units in I_{15}^{3+} (Figure 2).

There are weak interactions between some of the iodine atoms of the cation in $[I_5^+][AsF_6^-]$ and the fluorines of the anion (Figure 1), which are shorter than the sum of the van der Waals radii (3.45 Å).[11] In VSEPR terms,[22] the three independent iodine atoms in the cation (I(1), I(2), I(3)) may be considered to have $AXYE_3$, AX_2YE_2, and AX_2E_3 coordination when I- - -F contacts less than 3.20 Å are included (F(2) and F(3) included, but not F(1)). The pattern of contacts for $[I_3^+]$[7] and $[I_{15}^{3+}]$[8] (I- - -F < 3.2 Å) although quite different, are also explicable in VSEPR[22] terms, including the weak iodine–iodine bonds (3.416 (3) Å), which link the I_5^+ subunits into the I_{15}^3 chain (see Figure 2). The fluorine contacts less than 3.20 Å are all opposite to the iodine–iodine bonds in the cation; i.e., $F - \hat{I} - I$ angles are all about 180°. The weak contacts can be considered as arising from partial donation of an electron pair from the fluorine of the weakly basic anion, to appropriate LUMO's of electrophilic I_3^+, I_5^+, and I_{15}^{3+} cations (see below). The orientation of the I- - -F contacts greater than 3.20 Å are not readily accounted for.

The AsF_6^- anion is a regular octahedron with an average bond distance of 1.68 (1) Å and $F - \hat{As} - F$ angle of 90 (1)°. Each fluorine atom has one I- - -F contact.

Simple Explanations of the Geometry and Bonding in I_5^+. The structures of all the I_5^+ units may be described in terms of valence bond structures I and II suggesting bond orders of 0.5 and 1.0



I II

for the central collinear and terminal bonds, respectively. Alternately the central iodine atoms may be regarded as bonded by a three-centered four-electron bond. The terminal iodine–iodine bond distance, 2.645 (1) Å, is very similar to the average iodine–iodine bond distance in $[I_3^+][AsF_6^-]$ of 2.665 (2) Å[7] and corresponds to a formal bond order of 1. The average central colinear bond distance, 2.895 (1) Å, is comparable to the observed iodine–iodine bond distance in the symmetric I_3^- anion ($[(C_6H_5)_4As^+][I_3^-]$, 2.920 (2) Å)[23] and corresponds to a formal bond order of 0.5. The $I_3Cl_2^+$ cation in $[I_3Cl_2^+][SbCl_6^-]$,[24-26] and the $I_3Br_2^+$ cation in $[I_3Br_2^+][SbCl_6^-]$[26] have the same structures as I_5^+. However the structure of the $I_3Cl_2^+$ cation in $[I_3Cl_2^+][AlCl_4^-]$[26] is bent with a ClI_3/I_3Cl torsion angle of 128°.

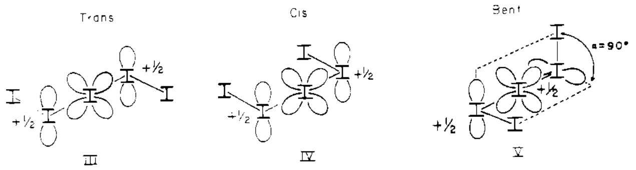


Figure 3. Possible structures for the I_5^+ cation.

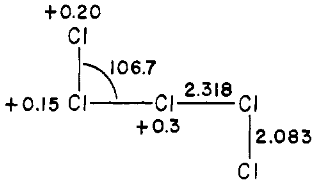


Figure 4. Optimized geometry (Å, deg) and atomic charges in Cl_5^+.

The electronic structure of I_5^+ is depicted schematically in Figure 3, assuming that only 5p electrons are involved in bonding and that the $5s^2$ electrons are inert. All the rotomers III, IV, and V (Figure 3) should have identical electronic energies, as the electron density of the nonbonding 5p electrons, on the central iodine atom perpendicular to the central I–I–I bond, is independent of angle. However, all three crystallographically different I_5^+ cations in $[I_5^+][AsF_6^-]$ and $[I_{15}^{3+}][SbF_6^-]$ have the trans planar structure (III). In order to determine why I_5^+ is trans planar and to more qualitatively describe the bonding in the I_5^+ cation, quantum-mechanical ab initio calculations were performed on Cl_5^+.

Electronic Structure of Cl_5^+. A Model for I_5^+. It is assumed that Cl_5^+, on which calculations were possible, provides an adequate model of I_5^+. As far as we are aware, salts of Cl_5^+ have not been prepared, although $[Cl_3^+][AsF_6^-]$ has been identified at low temperatures.[27] The STO-3G basis set (without d orbitals)[28] and the GAUSSIAN80[29,30] computer programs were used for calculations, unless otherwise specified. The geometries corresponding to the minimum energies of Cl_5^+ with trans (III), cis (IV), and bent (V) structures (α = 90, 120°), were calculated. The central Cl–Cl–Cl angle was held at 180°, and the bond distances and other angles were allowed to vary. The calculated bond distances, angles, and energies are virtually the same in all cases. The results for the most stable geometry, trans planar Cl_5^+, are given in Figure 4. The bond distances are also similar to those estimated for Cl_5^+ by empirical extrapolation from I_5^+ (R(1–2) = 1.98 Å, R(2–3) = 2.29 Å). The trans structure has the lowest energy, but it only differs by 0.05, 0.13, and 0.39 kcal mol^{-1} from structures V(α = 120°), V(α = 90°), and IV (cis), respectively; i.e., the energy decreases with increasing separation of the two terminal chlorine atoms. The calculated energy differences correspond to the differences in nuclear repulsion between the terminal chlorine atoms (using a calculated charge of 0.2). The energy differences between the rotomers are very small, and it is likely that solid-state effects also favor the observed I_5^+ geometry.

The 3s and $3p_z$ atomic orbitals of Cl_5^+ are completely filled and there is no net π bonding perpendicular to the Cl_5^+ plane (z = direction). The five $3p_x$ and five $3p_y$ orbitals combine to give the MO's illustrated in Figure 5. Four of the five MO's arising from the $3p_y$ atomic orbitals are filled. Of these, one is bonding,

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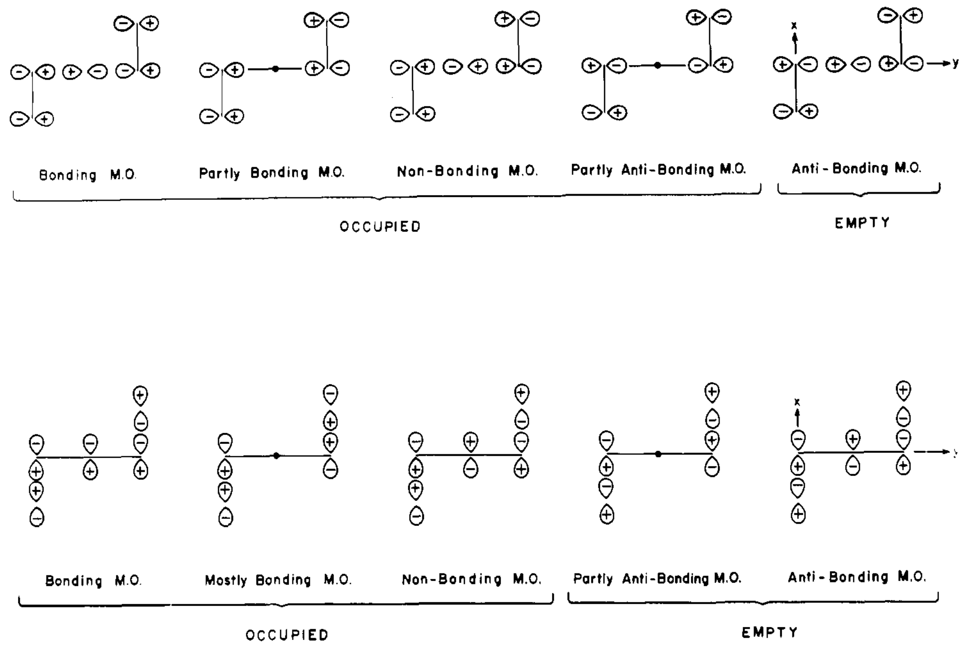

Figure 5. Schematic representation of the bonding in Cl_5^+.

one is partly bonding, one is nonbonding, and one is partly antibonding (the HOMO). The resultant bonding from the three higher energy occupied MO's is zero. The contribution from the remaining bonding orbital is largely in the central Cl–Cl–Cl region of Cl_5^+, giving an overall formal bond order of 0.5 per central Cl–Cl bond. Three of the five MO's arising from the $3p_x$ orbitals are filled; of these, one is bonding, one is partly bonding, and one is nonbonding. The bonding in the two bonding MO's is largely between the two terminal sets of chlorine atoms, giving a resultant formal bond order of 1 per terminal chlorine–chlorine bond. The empty, partly antibonding MO of this set is the LUMO. This treatment of Cl_5^+ is therefore essentially equivalent to that of a simple valence bond model. Presumably the driving force (−13.2 kcal mol^{-1} calcd) for the formation of Cl_5^+, containing three bonds, from Cl_3^+ and Cl_2, with the number of bonds remaining the same, is the energy associated with the delocalization of positive charge.

Distribution of Charge in I_5^+ (Cl_5^+). The atomic charges in Cl_5^+ are shown in Figure 4, and are very different from those anticipated by a simple valence bond model (see I and II). A positive charge on the middle chlorine atom in Cl_5^+ is expected from the calculation, whereas, in all three I_5^+ cations, the central iodine atom has no iodine–fluorine contacts less than 3.58 Å, indicating that it carried little positive charge. It has been pointed out that the ab initio method used can lead to unrealistic charges.[32]

Comparison of Geometries of I_5^+ in $[I_5^+][AsF_6^-]$ and $[I_{15}^{3+}][SbF_6^-]$. The bond distances in the I_5^+ cation in $[I_5^+][AsF_6^-]$ are shorter, or equal to, the corresponding bond distances within the I_5^+ units in $[I_{15}^{3+}][SbF_6^-]_3$ (see Figures 1 and 2). It is reasonable to suppose that as the strength of the cation- - -anion fluorine contacts increases, the weaker the bonds become within the cation. The more basic AsF_6^- anion has stronger and more numerous contacts per I_5^+ unit than does the less basic SbF_6^- anion. Thus, it would be expected that the weakening (and lengthening) of the bonds within the cations would be greater in $[I_5^+][AsF_6^-]$ than in $[I_{15}^{3+}][SbF_6^-]_3$. However, the iodine–iodine bonds are shorter in $[I_5^+][AsF_6^-]$. Thus the weak iodine–iodine bonds (3.416 (3) Å) between the I_5^+ units in I_{15}^{3+} are formed at the expense of some bonding within the three I_5^+ units of the I_{15}^{3+} cation. Support for this possibility is obtained from calculations on two Cl_5^+ cations separated by 2.57 Å. A very small drop in energy (0.07 kcal mol^{-1}) was accompanied by slight lengthening of both the terminal [2.083 → 2.089 Å] and the central Cl–Cl [2.318 → 2.323 Å] distances.

The weak bond between I_5^+ units in I_{15}^{3+} is presumably formed by donation of charge from the HOMO of the central I_5^+ into the LUMO of the two terminal I_5^+ cations (of the I_{15}^{3+} chain). Consistently the fluorine–cation contacts to the central I_5^+ units are stronger than those to the terminal I_5^+ cation.[8] In addition, the iodine–iodine bond lengths are overall slightly shorter in the central I_5^+ cation (antibonding electrons are removed), than the outermost I_5^+ cations (electrons added into antibonding orbital) (see Figures 2 and 5 and Table IV).

Table IV. Comparison of the Sum of I–I Distance and I–I–I Bond Angles in Iodine Cations

cation	compd	I–I bond dist, Å	sum of I–I bond dist, Å	bond angles, deg
I_3^+	$[I_3^+][AsF_6^-]$	2.660 (2), 2.669 (2)	5.329 (3)	101.75 (6)
I_5^+	$[I_5^+][AsF_6^-]$	2.645 (1), 2.895 (1)	5.540 (2)	97.0 (1)
I_{15}^{3+}	$[I_{15}^{3+}][SbF_6^-]_3$			
	central I_5^+	2.680 (3), 2.899 (2)	5.579 (4)	94.53 (6)
	terminal I_5^+	2.666 (3), 2.920 (2)	5.586 (4)	93.86 (7)
		2.698 (2), 2.896 (2)	5.594 (3)	93.17 (7)

The I–Î–I bond angle of 97.0 (1)° in $[I_5^+][AsF_6^-]$ is 3° greater than the average of the corresponding angles in I_{15}^{3+}, reflecting the stronger bonds and therefore the greater bond/bond repulsions in the isolated I_5^+ cations. The corresponding I–Î–I angles increase as the sum of the adjacent bond distances increases in the known iodine cations (see Table IV), consistent with a VSEPR model.[22] We note that the I–Î–I bond angle in the central I_5^+ of I_{15}^{3+} is slightly larger than those in the terminal I_5^+, reflecting the slightly stronger bonds in the central I_5^+.

It was calculated that the energy of the two Cl_5^+ units, with optimized isolated Cl_5^+ geometries, decreased as their separation increased. The energy difference between Cl_{10}^{2+} and two Cl_5^+, was found to be about equal to the electrostatic repulsion energy between the Cl_5^+ cations in Cl_{10}^{2+}, with the charge at the center of the cations. Thus the energy of formation of I_{15}^{3+} from $3[I_5^+]$ is a small positive quantity. Presumably this small loss of energy in forming I_{15}^{3+} from $3[I_5^+]$ is offset by other gains in energy in solid $[I_{15}^{3+}][SbF_6^-]_3$. We note that the iodine–iodine contacts between I_5^+ in $[I_{15}^{3+}][SbF_6^-]_3$ are replaced by fluorine–iodine contacts in $[I_5^+][AsF_6^-]$. Fluorine contacts from AsF_6^- are stronger than those from SbF_6^-, favoring the formation of an isolated I_5^+ cation in $[I_5^+][AsF_6^-]$. On the other hand the dimer I_4^{2+} is found in $[I_4^{2+}][AsF_6^-]_2$[9] and the monomer I_2^+ is found in $[I_2^+][Sb_2F_{11}^-]$,[6] containing the very weakly basic $Sb_2F_{11}^-$ anion.

The formation of I_2^+ and I_4^{2+} as well as I_5^+ and I_{15}^{3+} in the solid state suggests other oligomers of I_5^+ may also exist. $[I_3^+]_x$ may also exist in the solid state, but is less likely as electrostatic

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[32] Fliszár, S.; Goursot, A.; Dugas, H. *J. Am. Chem. Soc.* **1974**, *96*, 4358.

repulsion would be greater between I_3^+ cations than I_5^+ cations.

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Registry No. $[I_5^+][AsF_6^-]$, 99618-36-7; AsF_5, 7784-36-3; I_2, 7553-56-2; Cl_5^+, 99618-37-8.

Supplementary Material Available: A stereoview of the unit cell of $[I_5^+][AsF_6^-]$ (Figure I) and tables of anisotropic thermal parameters and calculated and observed structure factors (9 pages). Ordering information is given on any current masthead page.

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Chromium Oxide Trifluoride ($CrOF_3$). Preparation and Crystal Structure

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A new high-yield preparative route to chromium oxide trifluoride, $CrOF_3$, has been accomplished via the reaction of xenon difluoride with chromyl fluoride. The deep purple product was obtained for the first time in crystalline form via this route. Its crystal structure was determined by a single-crystal X-ray study. The crystals are tetragonal, space group $P4_1$ or $P4_3$, and have the following cell parameters: $a = 5.174\ (2)$ Å, $c = 8.921\ (6)$ Å, $V = 238.8$ Å^3, $Z = 4$, $\rho = 3.50$ g/cm^3. The crystal structure consists of an infinite three-dimensional array of corner-shared $CrOF_5$ octahedra. The structure is unrelated to other MOX_3 structures and appears to be a new structure type.

Introduction

The first successful preparation of pure $CrOF_3$ has been previously reported.[2] The synthesis route involved the brick red interhalogen compound, with a variable composition of $CrOF_3 \cdot 0.10ClF$ to $CrOF_3 \cdot 0.21ClF$, formed from the reaction of ClF with CrO_3 or CrO_2F_2. When subjected to multiple treatments with fluorine at 120 °C, this product was converted to the bright purple solid $CrOF_3$. Also, $CrOF_3$ can be prepared from CrO_3 and BrF_3, followed by cautious fluorination.[3] More recently, it was found that hydrolysis of CrF_5 in liquid HF produces $CrOF_3$.[4] We have found a new method for not only preparing $CrOF_3$ of the highest purity but also preparing it in a crystalline form. Heating chromyl fluoride (CrO_2F_2) with XeF_2 at temperatures up to 278 °C produces crystalline $CrOF_3$ in high yields:

$$XeF_2 + 2CrO_2F_2 \rightarrow 2CrOF_3 + Xe + O_2 \qquad (1)$$

It is possible that chromium oxide tetrafluoride, $CrOF_4$, was formed as an intermediate in eq 1; this behavior was noted for MoO_2F_2 or WO_2F_2 when treated with xenon difluoride in anhydrous fluoride.[5] Decomposition of $CrOF_4$ would give $CrOF_3$ and fluorine. The fluorine would react with xenon to re-form XeF_2 (this cycle would operate until all the fluorine from XeF_2 was consumed).

The $CrOF_3$ produced by this route was essentially the same material as originally reported; close agreement was found for both the infrared spectrum and X-ray powder spectrum. However, it was noted that the $CrOF_3$ produced from XeF_2 was less hygroscopic and could be exposed to moist air for several minutes without change. The $CrOF_3$ produced from XeF_2 resulted in crystals suitable for an X-ray structure determination.

The XeF_2 route is superior to other known routes, particularly in light of possible interhalogen contamination[2,3] with ClF/BrF_3 and with the difficulties associated in the preparation of CrF_5 and the handling of liquid hydrogen fluoride.[4]

Table I. Experimental Data for the X-ray Diffraction Study of $CrOF_3$

temp	25 °C
crystal habit; dimens	prismatic needle; 0.28 × 0.38 × 0.38 mm
crystal system	tetragonal
space group	$P4_1$ or $P4_3$
cell params	$a = 5.174\ (2)$ Å $c = 8.921\ (6)$ Å $V = 238.8$ Å $Z = 4$ $\rho = 3.50$ g/cm^3
Data Collection Parameters	
diffractometer	Picker four-circle
radiation	Mo Kα (0.71069 Å)
reflcns collcd	$hkl \geq 0$
2θ range	2°–78.0°
scan type	θ–2θ
scan speeds	2 s/0.05° step
std reflcns	3 every 41 reflcns
no. of reflcns collcd	846
no. of reflections obsd	724 unique, 644 with $F > 2\delta$
abs. coeff	$\mu/\rho = 13.736$
transmission factors	0.63–0.67
$R_w = \sum w\lvert F_o^2 - F_c^2\rvert / \sum wF_o^2$	0.056
$R = \sum \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \sum \lvert F_o\rvert$	0.053 ($F > 2\sigma$)

Table II. Positional Parameters for Chromium(V) Oxide Trifluoride

atom	x	y	z
Cr	−0.1096 (1)	−0.4171 (1)	0.00000
F(1)	0.1563 (7)	−0.4272 (7)	0.1201 (4)
F(2)	0.0617 (7)	−0.1960 (6)	−0.1274 (4)
F(3)	−0.4333 (7)	−0.3136 (6)	−0.0934 (4)
O	−0.0745 (9)	−0.6686 (9)	−0.0905 (5)

Experimental Section

Chemicals. Chromyl fluoride (CrO_2F_2) was prepared[6] via the reaction of WF_6 with dry CrO_3 at 125 °C. The CrO_2F_2 was stored over dry KF in a stainless-steel vessel.[2] The other compounds used in this work were obtained from commercial sources: CrO_3 (Mallinckrodt, reagent grade),

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