angle is near the value found for plastocyanin,[39] it suggests that the $A_{\parallel}$ value of type I copper(II) centers is a very good measure of twist angle regardless of the ligand atom type. The thioketone sulfur is apparently adequate to mimic ESR parameters of the protein. The d–d optical features of type I centers however appear to depend more heavily on ligand atom identity.[36]

While it is speculative, it is also a useful exercise to attempt to predict the twist angles in other type I copper(II) centers. Table VII lists representative examples of other type I centers and the predicted twist angles. It is interesting to note that even the *very low* value of stellacyanin can be accommodated within this approach.

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Registry No. $Cu(S_4N_2C_{18}H_{26})$ ($n = 4$), 77110-99-7; $Cu(S_4N_2C_{16}H_{22})$ ($n = 2$), 63665-42-9; $Cu(S_4N_2C_{17}H_{24})$ ($n = 3$), 70814-01-6.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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X-ray Crystal Structure of Triiodine(1+) Hexafluoroarsenate(V), I_3AsF_6

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The crystal structure of the compound I_3AsF_6 has been determined from three-dimensional X-ray counter data. Crystals are triclinic with $a = 8.054$ (3) Å, $b = 5.942$ (1) Å, $c = 10.503$ (2) Å, $\alpha = 103.08$ (2)°, $\beta = 88.95$ (2)°, $\gamma = 100.35$ (2)°, and $V = 481$ Å^3. The structure was refined in the space group $P\bar{1}$ to a conventional R factor of 0.091 for 1268 independent reflections with $I \geq 3\sigma(I)$. The structure consists of discrete I_3^+ cations and AsF_6^- anions with some cation–anion interaction. The iodine–iodine distances are 2.660 (2) and 2.669 (2) Å with a bond angle of 101.75 (6)°.

Introduction

The I_3^+ cation was the first of the homoatomic cations of the halogens to be identified.[1,2] In 1938 its existence was postulated by Masson from his studies of aromatic iodinations,[3] and subsequently its presence in 100% sulfuric[4] and fluorosulfuric acid[5] was confirmed from detailed conductometric and cryoscopic measurements. The solids I_3SO_3F,[6] I_3AlCl_4,[7] I_3AsF_6,[8] and I_3SbF_6[9] have also been prepared. A bent structure for I_3^+ has been deduced from Raman[9] and NQR spectra.[7] The crystal structures of various triatomic interhalogen cations have been reported, as well as those of the iodine polyatomic cations I_2^+ and I_5^+ in $I_2Sb_2F_{11}$[10] and $I_{15}(SbF_6)_3$.[11] However, no crystal structure has been reported for any trihalogen homoatomic cation. In the course of our work, we readily obtained good crystals of I_3AsF_6 and report its crystal structure below.

Experimental Section

I_3AsF_6 was prepared quantitatively in SO_2 solution by the reaction of stoichiometric quantities of I_2 and AsF_5, as previously described.[8] Highly crystalline material was obtained upon removal of all volatiles.

X-ray Data Collection. A well-formed crystal was mounted, under dry nitrogen, in a capillary tube as previously described.[12] Preliminary unit cell parameters were obtained from precession photographs which showed the crystal system to be triclinic. The crystal was mounted on a Picker FACS-I diffractometer equipped with a molybdenum tube ($\lambda(K\alpha) = 0.71069$ Å) and a graphite monochromator. Final cell dimensions were obtained by a least-squares fit to the coordinates of 20 well-centered reflections.

Intensity data were collected with use of an ω–2θ scan of 2° (2θ) corrected for dispersion of the $K\alpha$ doublet. Backgrounds were estimated from a stationary count for 1/10 of the scan time at each end of the scan. If the net intensity was greater than $2\sigma(I)$, then an analysis was made of the scan profile, and those portions not part of the peak were included in the background estimate. Data were collected for $2\theta \leq 50°$ which resulted in 1694 unique reflections of

Table I. Crystal Data for I_3AsF_6

fw	569.6	temp of data collection	20 °C
d_{calcd}	3.93 Mg m^{-3}	λ(Mo Kα)	0.710 69 Å
Z, formula units/unit cell	2	scan range	2.0°
crystal size	0.20 × 0.22 × 0.07 mm	scan rate	2° (2θ) min^{-1}
a	8.054 (3) Å	maximum 2θ	50°
b	5.942 (1) Å	no. of unique reflections	1694
c	10.503 (2)	no. of unique reflections with $I \geqslant 3\sigma(I)$	1268
α	103.08 (2)°		
β	88.95 (2)°		
γ	100.35 (2)°		
V	481 Å^3		

Table II. Atomic Coordinates[a] for I_3AsF_6 (×10^4)

atom	x	y	z
I(1)	8297 (1)	8175 (1)	2157 (1)
I(2)	6199 (1)	10962 (2)	1785 (1)
I(3)	7627 (1)	7785 (2)	4604 (1)
As(1)	7753 (1)	5525 (2)	8065 (1)
F(1)	7430 (19)	7497 (26)	7166 (14)
F(2)	8753 (18)	7814 (24)	9269 (13)
F(3)	5903 (16)	5765 (29)	8787 (15)
F(4)	8112 (21)	3602 (28)	8952 (16)
F(5)	9624 (15)	5402 (24)	7337 (16)
F(6)	6800 (24)	3331 (28)	6848 (20)

[a] Standard deviations in parentheses.

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Table III. Anisotropic Thermal Parameters[a] for I_3AsF_6 ($\times 10^2$)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	5.68 (6)	5.66 (5)	5.97 (6)	2.66 (5)	1.36 (5)	2.36 (5)
I(2)	5.79 (7)	5.30 (6)	9.15 (9)	2.24 (5)	−0.29 (6)	2.04 (6)
I(3)	6.33 (7)	7.57 (7)	5.75 (6)	1.47 (6)	0.81 (5)	2.18 (6)
As(1)	4.00 (7)	5.09 (8)	6.08 (9)	1.85 (6)	0.78 (7)	1.92 (7)
F(1)	12.7 (13)	11.1 (11)	9.1 (9)	6.2 (10)	3.3 (9)	5.5 (8)
F(2)	11.1 (11)	8.4 (9)	8.4 (9)	−0.6 (7)	−0.8 (8)	1.4 (7)
F(3)	5.3 (6)	14.6 (13)	12.6 (11)	3.8 (7)	2.7 (7)	5.7 (10)
F(4)	12.6 (14)	11.1 (11)	11.5 (11)	3.3 (9)	2.1 (9)	7.5 (9)
F(5)	5.5 (7)	11.2 (10)	15.2 (13)	5.2 (7)	3.3 (8)	4.6 (10)
F(6)	14.2 (15)	8.1 (10)	15.8 (16)	0.9 (10)	−3.6 (12)	−1.3 (10)

[a] The form of the temperature factor is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. Standard deviations are in parentheses.

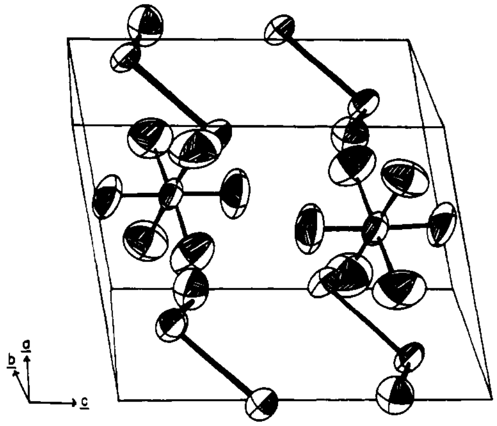

Figure 1. Crystal packing in I_3AsF_6.

which 1268 were considered observed ($I \geq 3\sigma(I)$) and included in the subsequent refinement. Three standard reflections monitored throughout data collection showed no significant change in their intensities. The crystal data are summarized in Table I.

Structure Determination and Refinement. After correction for absorption, the structure was solved by multiple solution direct methods with use of a version of MULTAN[13] modified for use on a Digital Equipment Corporation PDP8/A mini computer,[14] assuming the space group to be $P\bar{1}$. The positions of the iodines and the arsenic were determined from an E map and the fluorine positions from a subsequent difference synthesis. The structure was refined by block-matrix least-squares with the use of anisotropic thermal parameters for all atoms. The function minimized was $\sum w(\Delta F)^2$ with $w = 1/(\sigma(F)^2 + pF^2)$, the factor p was determined from the measurements of the standards to be 0.005. The scattering factors were taken from ref 15 and corrected for anomalous dispersion. The final values of $R = \sum|\Delta F|/\sum|F_o|$ and $R_w = (\sum w|\Delta F|^2/\sum w|F_o|^2)^{1/2}$ were 0.091 and 0.115 (0.107 and 0.121 including unobserved reflections), respectively. An attempt to refine the structure in the space group $P1$ did not result in a significant improvement of the R factors, indicating that $P\bar{1}$ was the correct choice. Final positional parameters are given in Table II and final thermal parameters in Table III.

Results and Discussion

Figure 1 shows the packing in I_3AsF_6, and Tables IV and V list relevant bond distances and angles. The I_3^+ cation with shortest anion–cation contacts is illustrated in Figure 2. The shortest I–F contact is 2.73 (1) Å, indicating that the structure is essentially ionic.

Table IV. Bond Distances[a]

atom 1	atom 2	dist, Å
	Intraionic	
I(1)	I(2)	2.660 (2)
I(1)	I(3)	2.669 (2)
As(1)	F(1)	1.72 (1)
As(1)	F(2)	1.72 (1)
As(1)	F(3)	1.67 (1)
As(1)	F(4)	1.69 (1)
As(1)	F(5)	1.68 (1)
As(1)	F(6)	1.69 (2)
	Interionic[b]	
I(1)	F(2)	3.01 (1)
I(1)	F(4)	3.35 (2)
I(1)	F(5)	3.07 (1)
I(2)	F(1)	3.31 (1)
I(2)	F(3)	2.96 (2)
I(3)	F(1)	2.73 (1)

[a] Standard deviations in parentheses. [b] Length of I···F ⩽ 3.36 Å.

Table V. Bond Angles[a]

atom 1	vertex, atom 2	atom 3	angle, deg
I(2)	I(1)	I(3)	101.75 (6)
F(1)	As(1)	F(2)	89.6 (8)
F(1)	As(1)	F(3)	89.8 (7)
F(1)	As(1)	F(4)	178.9 (8)
F(1)	As(1)	F(5)	88.2 (7)
F(1)	As(1)	F(6)	88.8 (9)
F(2)	As(1)	F(3)	90.1 (8)
F(2)	As(1)	F(4)	89.8 (8)
F(2)	As(1)	F(5)	88.6 (8)
F(2)	As(1)	F(6)	178.1 (9)
F(3)	As(1)	F(4)	91.2 (8)
F(3)	As(1)	F(5)	177.6 (8)
F(3)	As(1)	F(6)	91.0 (9)
F(4)	As(1)	F(5)	90.8 (7)
F(4)	As(1)	F(6)	91.8 (10)
F(5)	As(1)	F(6)	90.2 (9)

[a] Standard deviations in parentheses.

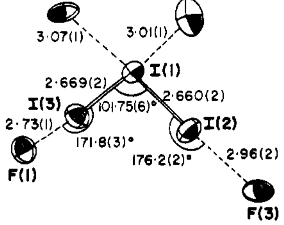

Figure 2. I_3^+ cation with closest anion–cation contacts.

The I_3^+ cation is bent, as previously concluded from Raman data.[1] The bond angle at 101.75 (6)° is similar to that (97°) estimated from NQR data[7] for I_3^+ in the tetrachloroaluminate salt. There are two crystallographically independent iodine

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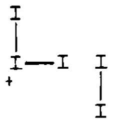
Table VI[a]

ion	compd	bond dist, Å	bond angle, deg
I_3^+	I_3AsF_6	2.660 (2), 2.669 (2)	101.75 (6)
Te_3^{2-}	$(cryptK)_2Te_3\cdot en$	2.692 (5), 2.720 (4)	113.1 (2)
Te_3^{2-}	K_2Te_3	2.802, 2.805	104.4

[a] Standard deviations in parentheses.

bonds in I_3^+ which are possibly different ($\Delta = 2.3(\sigma_1 + \sigma_2)$). The strongest iodine–fluorine contact is adjacent to the longer bond, suggesting the difference is real. The average iodine–iodine bond distance of 2.665 (1) Å is similar to that of gaseous iodine (2.666 (3) Å)[16] and the two terminal iodine–iodine bonds of the $(I_{15})^{3+}$ chain (2.666(3) Å)[11] and corresponds to a bond order of 1.

The I_3^+ bond distances are slightly shorter than the average of the terminal bonds (2.681 Å) of the three I_5^+ units in $(I_{15})^{3+}$,[11] and the I_3^+ bond angle is greater than the corresponding average angle (94.02°) in I_5^+. This is consistent with the view that the bonding in I_5^+ can be represented by valence structures I and II with a bond order of 1 for the terminal iodine bonds and 0.5 for the central bonds. Bond–bond repulsions in I_5^+ are therefore less than in I_3^+, leading to the observed smaller I_5^+ bond angle.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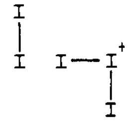
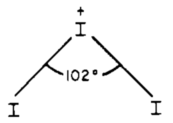
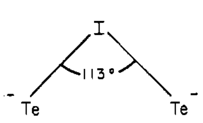

II

The structure of I_3^+ is compared with the isoelectronic anion Te_3^{2-} contained in $(cryptK)_2Te_3\cdot en$[16] and K_2Te_3[17] in Table VI The geometry of Te_3^{2-} in the $(cryptK)^+$ salt will be less affected by the large $(cryptK^+)$ cation than by the more polarizing K^+ ion salt, and therefore it is more reasonable to use $(cryptK)_2Te_3\cdot en$ results for purposes of comparison with I_3^+ data. The bond distances are shorter in I_3^+ than in Te_3^{2-}, consistent with the nuclear change on iodine being 1 unit greater than that of tellurium. The neutral dihalogens similarly have, generally, shorter bond distances[18-22] than their isoelectronic dichalcogen anion partners. The formal charge distribution in I_3^+ and Te_3^{2-} may be represented to a first order of approximation by III and IV. The repulsion between terminal tellurium atoms carrying a formal negative charge may account for its larger bond angle.



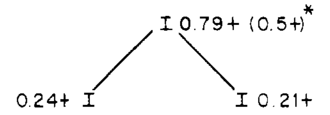
III



IV

The I_3^+ cation and two fluorine contacts to the central iodine are essentially planar. A similar arrangement of cation–anion contacts are found for ICl_2SbCl_6,[23] ICl_2AlCl_4,[23] BrF_2AsF_6,[24] ClF_2AsF_6,[25] and ClF_2SbF_6.[26] In addition, the terminal iodines have approximately linear fluorine contacts giving rise to an approximately planar network (see Figure 2). Other nearly linear iodine–fluorine cation–anion contacts are well established.[10,11,28,29] In VSEPR terms,[30] the central and terminal iodine atoms may be viewed as having $AX_2Y_2E_2$ and $AXYE_3$ coordination, respectively, if all contacts are included in the respective coordination spheres. The structure may be regarded as mostly $[I_3^+][AsF_6^-]$, with some anion–cation interaction. In valence-bond terms these contacts may be regarded as arising from a small contribution of structures formed by donation of fluoride ion from $[AsF_6^-]$ to the interacting iodine. Presumably an isolated I_3^+ would have shorter bonds than those observed in I_3AsF_6 and gaseous I_2.

An estimate of the charge distribution for I_3^+ in I_3AlCl_4 has been made from NQR measurements[7] and is given in



V

where the asterisked value was obtained by subtraction from unity of experimentally determined total charge on terminal iodines.

The central iodine carrying the greatest positive charge has two contacts, at 3.01 and 3.07 Å, longer than either of the single contacts to the terminal iodines at 2.73 and 2.96 Å. Therefore, the extent of cation–anion interaction may be, in part, a function not only of contact distance but also the number of contacts; two contacts at 3.01 and 3.07 Å may represent greater interaction than either one at 2.73 or 2.96 Å. Similarly, the shortest contacts in $Br_2Sb_3F_{16}$[31] and $I_2Sb_2F_{11}$[10] are at 13% and 17% less than the sum of Br···F and I···F van der Waals radii, respectively, although the I_2^+ cation is less electrophilic than Br_2^+. However, there are more bromine–fluorine contacts in $Br_2Sb_3F_{16}$ [2 × (2.86, 2.97, 3.07, 3.15 and 3.28 Å)] than iodine–fluorine contacts in $I_2Sb_2F_{11}$ [2 × (2.89, 3.29 Å)]. The I_2^+ cation has the same charge as I_3^+, but it is smaller and therefore more electrophilic. However, the cation–anion contacts in I_2SbF_{11}[10] [2 × (2.89, 3.29 Å)] are somewhat longer than those in I_3AsF_6 [2.73, 2.96, 3.01 and 3.07 Å]. This may be a consequence of the lower basicity of $Sb_2F_{11}^-$ relative to AsF_6^-; i.e., fluoride ions are more readily removed from AsF_6^- than $Sb_2F_{11}^-$.

The AsF_6^- unit is essentially octahedral with an average bond distance of 1.695 Å and angle of 90.0°.

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Registry No. I_3AsF_6, 59555-19-0.

Supplementary Material Available: Tables of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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