HOMOPOLYATOMIC CATIONS OF THE ELEMENTS

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I. Introduction

During the last 10 years a number of homopolyatomic cations (M_y^{x+}, where $x \leqslant y$) have been prepared and characterized. For a long time the only known example of this type of species was the mercurous ion Hg_2^{2+} but this can no longer be regarded as a chemical oddity, as it has now been joined not only by the analogous species Zn_2^{2+} and Cd_2^{2+} but also by Hg_3^{2+} and many cations of the nonmetals such as I_2^+, O_2^+, S_8^{2+}, and Te_4^{2+}. It is not surprising that some of the earliest examples of this type of cation, e.g., O_2^+ and Bi_9^{5+}, were discovered quite accidentally, but it is perhaps surprising that some of the species have been known for at least 150 years but were not recognized as such. For example, during the early nineteenth century it was reported that sulfur, selenium, and tellurium dissolve in concentrated sulfuric acid or in oleum (H_2SO_4–SO_3) to give various highly colored solutions. The origin of these colors was never clearly established, but it has now been shown that they are due to various polyatomic cations of these elements such as S_8^{2+}, Se_4^{2+}, and Te_4^{2+}. Chemists have long been fascinated by the possibility that elements such as iodine might be obtained in the cationic form I^+ as well as in the well-known anionic form I^-. However, although there is no evidence for the existence of I^+ or of Br^+ or Cl^+ as stable species in solution or in the solid state, the search for such species has led to the discovery of polyatomic cations of the halogens such as I_2^+, Br_3^+, and Cl_3^+ which under appropriate conditions are quite stable.

The structures of the homopolyatomic cations are of obvious interest particularly because of their simplicity in that they contain only one kind of atom. Thus, although homonuclear clusters of atoms are well-known among the transition metals in "cluster" compounds, such as $Mo_6Cl_8^{4+}$, and in the boron hydrides, e.g., $B_{12}H_{12}^{2-}$, the description of the bonding in these compounds is somewhat complicated by the presence of the ligands that are at least partially responsible for holding the metal atoms together.

These new cations, particularly those of the nonmetals, are "electron-deficient" with respect to the element itself and, thus, they are highly electrophilic. They are, accordingly, only stable in the absence of bases with which they readily react, generally disproportionating to more stable valency states. Water is, for example, a sufficiently strong base to react with these ions, which, in general, disproportionate to the element and one of the familiar oxidation states of the element that is stable in aqueous solution. It is not surprising, therefore, that the discovery of these cations owes much to recent developments in the chemistry of nonaqueous solvent systems, particularly highly acidic systems, including acidic fused salt media. Some of the cations, e.g., Br_2^+, are stable only in the most highly acidic and most weakly basic solvent media known, e.g., HSO_3F–SbF_5. In the solid state, stable crystalline salts can only be obtained with the anions of very strong acids, e.g., SO_3F^-, $Sb_2F_{11}^-$, and $AlCl_4^-$, typically large singly charged anions containing the electronegative elements F, O, and Cl. In addition to highly acidic media, the very weakly basic and rather unreactive solvent SO_2 has proved to be very useful in the preparation and study of these cations.

II. Polyatomic Cations of Group VII

A. Iodine Cations

The existence of I_3^+ and I_5^+ was deduced over 30 years ago by Masson (*1*) from his studies of aromatic iodination reactions, but it is only recently that his conclusions have been confirmed by physical measurements. The controversy over the nature of the blue solutions of iodine in various highly acidic media has now been resolved, and it has been shown conclusively that these solutions contain I_2^+ (*2–4*) and not I^+ as suggested earlier (*5*). There is, moreover, no convincing evidence for the existence of Cl^+ or Br^+ as stable species in solution or in the solid state. There is, however, evidence for polyatomic cations of chlorine and bromine analogous to the iodine cations, i.e., Cl_3^+, Br_3^+, and Br_2^+.

1. I_3^+ *and* I_5^+

The first evidence for the existence of a stable iodine cation was obtained by Masson (*1*) in 1938. He postulated the presence of I_3^+ and I_5^+ in solutions of iodine and iodic acid in sulfuric acid in order to explain the stoichiometry of the reaction of such solutions with chlorobenzene to form both iodo and iodoso derivatives. Later, Symons and co-workers (*6*) gave conductometric evidence for I_3^+ formed from iodic acid and iodine in 100% sulfuric acid and suggested that I_5^+ may be formed on the basis of changes in the UV and visible spectra when iodine is added to I_3^+ solutions. Gillespie and co-workers (*7*) on the basis of detailed conductometric and cryoscopic measurements confirmed that I_3^+ is formed from HIO_3 and I_2 in 100% sulfuric acid according to Eq. (1). The I_3^+ cation may also be prepared in fluoro-

$$HIO_3 + 7I_2 + 8H_2SO_4 \longrightarrow 5I_3^+ + 3H_2O + 8HSO_4^- \quad (1)$$

$$3I_2 + S_2O_6F_2 \longrightarrow 2I_3^+ + 2SO_3F^- \quad (2)$$

sulfuric acid (*2*) by the reaction in Eq. (2). Solutions of red–brown I_3^+ in H_2SO_4 or HSO_3F have characteristic absorption maxima at 305 and 470 nm, with a molar extinction coefficient of 5200 at 305 nm.

Solutions of I_3^+ in 100% H_2SO_4 (*7*), or in fluorosulfuric acid (*2*), dissolve at least 1 mole of iodine per mole of I_3^+, and a new absorption spectrum is obtained which has bands at 270, 340, and 470 nm. At the same time, there is no change in either the conductivity or the freezing point of the solutions; therefore, it has to be concluded that I_5^+ is formed according to Eq. (3). Some further iodine will dissolve in solutions of I_5^+, indicating possible formation of I_7^+.

$$I_3^+ + I_2 \longrightarrow I_5^+ \tag{3}$$

Recently, Corbett *et al.* (*8*) have prepared the compounds $I_3^+AlCl_4^-$ and $I_5^+AlCl_4^-$, which they characterized by phase equilibria studies and nuclear quadrupole resonance spectroscopy. The shiny black phase $I_{3.0\pm0.15}AlCl_4$ melts congruently at 45° $\pm$ 1°C, and the green "metallic" I_5AlCl_4 ($4.8 < I/AlCl_4 < 5.3$) melts slightly incongruently at 50° to 50.5°. Chung and Cady (*8a*) have determined the melting points for the system I_2–$S_2O_6F_2$ and confirmed the previously known solids $I(SO_3F)_3$, ISO_3F, and I_3SO_3F. A new compound, I_7SO_3F, was also established. No evidence for I_5SO_3F or I_2SO_3F was obtained, and the nature of the compound ISO_3F remains uncertain.

In 1906, Ruff (*9*) reported that excess iodine and SbF_5 react to form a brown solid which he formulated as SbF_5I. Kemmitt *et al.* (*4*) have since shown from the absorption spectrum of the solid in liquid AsF_3 that it contains some I_3^+ cation. However, it must be concluded from the method of preparation that this material is not a single compound, and almost certainly contains Sb(III).

2. I_2^+

Gillespie and Milne (*2*) have shown, by conductometric, spectrophotometric, and magnetic susceptibility measurements in fluorosulfuric acid, that the blue iodine species observed in strong acids is I_2^+. When iodine was oxidized by peroxodisulfuryl difluoride in fluorosulfuric acid, the concentration of the blue iodine species reached a maximum at the 2:1 $I_2/S_2O_6F_2$ mole ratio [Eq. (4)] and not at the 1:1 mole ratio as would

$$2I_2 + S_2O_6F_2 \longrightarrow 2I_2^+ + 2SO_3F^- \tag{4}$$

$$I_2 + S_2O_6F_2 \longrightarrow 2I^+ + 2SO_3F^- \tag{5}$$

be anticipated for the formation of I^+ [Eq. (5)]. The conductivities of 2:1 solutions of iodine–$S_2O_6F_2$ at low concentrations were found to be very similar to solutions of KSO_3F at the same concentration, showing that 1 mole of SO_3F^- had been formed per mole of iodine. The magnetic moment of the blue species in fluorosulfuric acid was found to be $2.0 \pm 0.1\ \mu_B$ which agrees with the value expected for the $^3\Pi_{3/2}$ ground state of the I_2^+ cation. The I_2^+ has characteristic peaks in its absorption spectrum at 640, 490, and 410 nm and has a molar extinction coefficient at 640 nm of 2560.

The I_2^+ cation is not completely stable in fluorosulfuric acid and undergoes some disproportionation to the more stable I_3^+ species and $I(SO_3F)_3$ according to Eq. (6). This disproportionation is largely pre-

$$8I_2^+ + 3SO_3F^- \rightleftharpoons I(SO_3F)_3 + 5I_3^+ \quad (6)$$

vented in a 1:1 I_2–$S_2O_6F_2$ solution in which $I(SO_3F)_3$ is also formed [Eq.

$$5I_2 + 5S_2O_6F_2 \longrightarrow 4I_2^+ + 4SO_3F^- + 2I(SO_3F)_3 \quad (7)$$

(7)]. The disproportionation can also be prevented if the fluorosulfate ion concentration in fluorosulfuric acid is lowered by addition of antimony pentafluoride [Eq. (8)] or by using the less basic solvent 65% oleum.

$$SbF_5 + SO_3F^- \longrightarrow (SbF_5 \cdot SO_3F)^- \quad (8)$$

In 100% H_2SO_4 the disproportionation of I_2^+ to I_3^+ and an iodine(III) species, probably $I(SO_4H)_3$, is essentially complete, and only traces of I_2^+ can be detected by means of its resonance Raman spectrum.

Solutions of the blue iodine cation in oleum have been reinvestigated (*3*) by conductometric, spectrophotometric, and cryoscopic methods confirming the formation of I_2^+. In 65% oleum, iodine is oxidized to I_2^+ according to Eq. (9).

$$2I_2 + 5SO_3 + H_2S_4O_{13} \longrightarrow 2I_2^+ + HS_4O_{13}^- + SO_2 \quad (9)$$

Adhami and Herlem (*10*) have carried out a coulometric titration at controlled potential of iodine in fluorosulfuric acid and have shown that iodine is quantitatively oxidized to I_2^+ by removal of one electron per mole of iodine.

The blue solid prepared by Ruff *et al.* (*9*) in 1906 and thought to be $(SbF_5)_2I$ was probably a mixture of an I_2^+ fluoroantimonate salt, and some Sb(III)-containing material. Pure crystalline $I_2^+Sb_2F_{11}^-$ has recently been prepared by the reaction of iodine with antimony pentafluoride in liquid sulfur dioxide as solvent (*11*). After removal of insoluble SbF_3, deep blue crystals of $I_2^+Sb_2F_{11}^-$ were obtained from the solution. An X-ray crystallographic structure determination showed the presence of the discrete ions I_2^+ and $Sb_2F_{11}^-$. Crystalline solids that can be formulated as $I_2^+Sb_2F_{11}^-$ and $I_2^+Ta_2F_{11}$ have also been prepared by Kemmitt *et al.* (*4*) by the reaction of iodine with antimony or tantalum pentafluorides in iodine pentafluoride solutions.

B. Bromine Cations

1. Br_3^+

A compound formulated as SbF_5Br was prepared by Ruff (*9*) in 1906 by the reaction of Br_2 and SbF_5, but the nature of this compound remained a mystery. Later McRae (*12*) reported evidence that Br_3^+ was formed in this system. Gillespie and Morton (*13*, *14*) showed more recently that Br_3^+ is formed quantitatively in the superacid medium $HSO_3F–SbF_5–SO_3$ according to Eq. (10). These solutions are brown

$$3Br_2 + S_2O_6F_2 \longrightarrow 2Br_3^+ + 2SO_3F^- \qquad (10)$$

and have a strong absorption at 300 nm with a shoulder at 375 nm. Solutions of Br_3^+ can also be obtained in a similar way in fluorosulfuric acid; however, they are not completely stable in this more basic solvent and undergo some disproportionation according to Eq. (11).

$$Br_3^+ + SO_3F^- \rightleftharpoons Br_2 + BrOSO_2F \qquad (11)$$

Glemser and Smalc (*15*) have prepared the compound $Br_3^+AsF_6^-$ by the displacement of oxygen in dioxygenyl hexafluoroarsenate by bromine [Eq. (12)] and by the reaction of bromine pentafluoride,

$$2O_2^+AsF_6 + 3Br_2 \longrightarrow 2Br_3^+AsF_6^- + 2O_2 \qquad (12)$$

$$7Br_2 + BrF_5 + 5AsF_5 \longrightarrow 5Br_3^+ + 5AsF_6^- \qquad (13)$$

bromine, and arsenic pentafluoride [Eq. (13)]. The compound is chocolate-brown and in solution has absorption bands at 300 and 375 nm; it has fair thermal stability and can be sublimed at 30° to 50° under an atmosphere of nitrogen.

2. Br_2^+

The Br_2^+ cation can be prepared (*14*) by oxidation of bromine by $S_2O_6F_2$ in the superacid $HSO_3F–SbF_5–3SO_3$; however, even in this very weakly basic medium, the Br_2^+ ion is not completely stable as it undergoes appreciable disproportionation according to Eq. (14).

$$2Br_2^+ + 2HSO_3F \rightleftharpoons Br_3^+ + BrOSO_2F + H_2SO_3F^+ \qquad (14)$$

Moreover, the $BrOSO_2F$ that is formed itself undergoes some disproportionation to Br_2^+, Br_3^+, and $Br(OSO_2F_3)_3$, so that the equilibria in these solutions are quite complex involving not only Eq. (14) but Eqs. (15) and (16) as well.

$$5BrOSO_2F + 2H_2SO_3F^+ \rightleftharpoons 2Br_2^+ + Br(OSO_2F)_3 + 4HSO_3F \qquad (15)$$

$$4BrOSO_2F + H_2SO_3F^+ \rightleftharpoons Br_3^+ + Br(OSO_2F)_3 + 2HSO_3F \qquad (16)$$

Solutions of Br_2^+ in superacid have a characteristic cherry red color with maximum absorption at 510 nm and a single band in the Raman spectrum at 360 cm^{-1}.

The paramagnetic scarlet crystalline compound $Br_2^+Sb_3F_{16}^-$ (*16, 17*) has been prepared by the reaction [Eq. (17)].

$$9Br_2 + 2BrF_5 + 30SbF_5 \longrightarrow 10Br_2^+Sb_3F_{16}^- \quad (17)$$

It is a stable salt and can be sublimed at 200°.

C. Chlorine Cations

1. Cl_3^+

There is no evidence for either Cl_2^+ or Cl_3^+ in superacid media (*18*); however, Cl_2, ClF, and AsF_5 react at −70° to form Cl_3AsF_6 according to Eq. (18) (*19*). The Cl_3^+ cation has also been identified by its Raman

$$Cl_2 + ClF + AsF_5 \longrightarrow Cl_3AsF_6 \quad (18)$$

spectrum in the yellow solid which precipitates from a solution of Cl_2 and ClF in HF–SbF_5 at −76°. At room temperature the Cl_3^+ cation completely disproportionates in this solvent to chlorine and ClF_2^+ salts. There is no evidence that Cl_3BF_4 is formed from mixtures of chlorine, chlorine monofluoride, and boron trifluoride at temperatures ranging from ambient to −130°.

2. Cl_2^+

The Cl_2^+ ion has been observed in the gas phase at very low pressures, and a value of ω_e of 645.3 cm^{-1} was obtained from the electronic absorption spectrum (*20*). More recently, Olah and Comisarow (*21, 22*) have claimed to have identified Cl_2^+ and ClF^+ in solutions on the basis of ESR spectra of chlorine fluorides in SbF_5, HSO_3F–SbF_5, or HF—SbF_5, but this claim has been disputed by various workers. Symons *et al.* (*23*) have argued that the ESR spectrum assigned to ClF^+ arises from $ClOF^+$, and that assigned to Cl_2^+ from $ClOCl^+$. Christe and Muirhead (*24*) have reported that they have not detected radicals in the reaction of highly purified SbF_5 and ClF_3, or ClF_5, and they suggest that the radicals observed by Olah and Comisarow must have been due to impurities. Gillespie and Morton (*18*) reported a very large increase in intensity of the ESR signal previously assigned to ClF^+ on adding a trace of water to a sample of $ClF_2^+SbF_6^-$ in SbF_5, supporting the assignment to an oxyradical, which, they argue, is probably $FClO^+$ which is isoelectronic with ClO_2 or ClO_2F^+ which is isoelectronic with ClO_3.

A simple calculation of the heats of formation of salts of Cl_2^+ and O_2^+, based on the ionization potentials and the lattice energies given by Kapustinskii's (*25*) second equation, gives values for the Cl_2^+ salts with hexafluoride anions only 3 kcal less favorable than the corresponding (*26*) O_2^+ salts. Although this indicates that the salts $Cl_2^+PtF_6^-$ and $Cl_2^+Sb_2F_{11}^-$ are thermodynamically feasible, we expect no kinetic barrier to fluorination via fluorine bridging to give salts of the Cl_2F^+ cation. Thus attempts to prepare salts of Cl_2^+ cations are analogous to attempts to prepare those of Xe^+ in which the product seems always to be the XeF^+ cation (*27*).

D. Relative Stabilities of Halogen Polyatomic Cations

The problem of stabilizing halogen cations appears to be essentially one of providing a sufficiently weakly basic medium to prevent negative ion transfer, the first step in the decomposition of the polyatomic cation. The more polarizing the cation the more difficult it is to effect stabilization. For example, whereas Cl_2^+ has not been prepared in solution or in the solid state, Br_2^+ exists in equilibrium with other species [see Eq. (14)] in the superacid $HSO_3F–SbF_5–3SO_3$ and as the crystalline salt $Br_2^+Sb_3F_{16}^-$. The larger I_2^+, on the other hand, is stable in the superacid and is only slightly disproportionated in the more basic solvent, HSO_3F. A similar trend is observed for the triatomic cations: I_3^+ is stable in 100% H_2SO_4; Br_3^+ is only stable in the more acidic $HSO_3F–SbF_5–SO_3$; whereas Cl_3^+ has only been detected in the solid state at $-78°$ as the AsF_6^- salt. In all cases the triatomic cation is more readily stabilized than the smaller, more polarizing, diatomic cation. In general the most stable environment for halogen polyatomic cations appears to be as a crystalline salt with the AsF_6^-, SbF_6^-, $Sb_2F_{11}^-$, or $Sb_3F_{16}^-$ anions.

E. Structures of Halogen Cations

1. *Diatomic Cations*

The structures of $Br_2^+Sb_3F_{16}^-$ and $I_2^+Sb_2F_{11}^-$ have been determined by X-ray crystallography (*11, 16, 17*). They both contain a discrete diatomic cation and a fluoroantimonate anion. The bond lengths in the Br_2^+ and I_2^+ cations were found to be 2.13 and 2.56 Å, respectively. The cations have a shorter bond length than the corresponding neutral diatomic molecules and this is consistent with an increase in bond order resulting from the loss of an antibonding electron from the neutral molecule.

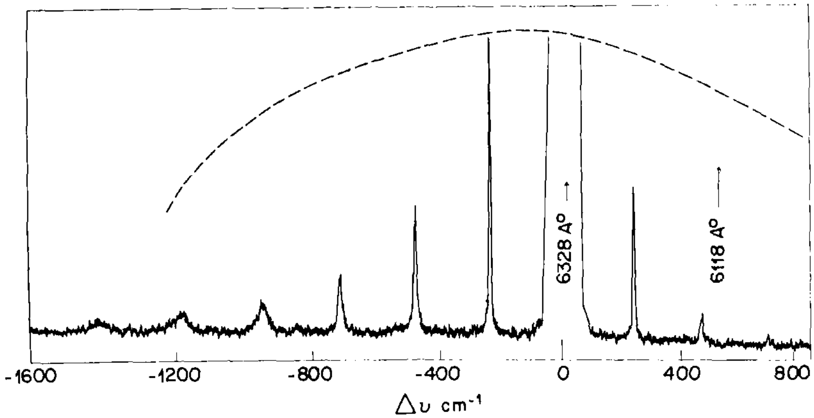


FIG. 1. Resonance Raman spectrum of I_2^+. Dashed line—contour of visible absorption band.

Initial attempts (*4*) to observe the vibrational frequency of the I_2^+ cation by Raman spectroscopy were unsuccessful owing to the absorption of the existing radiation by the highly colored solutions. Later it was shown (*28*, *29*) that the resonance Raman spectrum of the I_2^+ cation can be observed using 6328 Å He–Ne excitation and very dilute solutions. The resonance Raman spectrum of a 10^{-2} *M* solution of the I_2^+ cation in fluorosulfuric acid (Fig. 1) shows in addition to the fundamental at 238 cm^{-1}, a number of intense overtones which gradually become progressively broader and weaker. In this particular case the relatively weak Raman scattering from the fluorosulfuric acid solvent is completely absorbed by the solution and only the very strong resonance

TABLE I

STRETCHING FREQUENCIES, ABSORPTION MAXIMA, AND BOND LENGTHS OF THE HALOGENS AND DIATOMIC HALOGEN CATIONS

Cation	Stretching frequency (cm^{-1})	Principal absorption (nm)	Bond length Å	Ionization energy[b] (eV)
Cl_2	564.9[a]	330	1.98	11.50
Cl_2^+	645.3[a]	—	1.89	—
Br_2	320	410	2.28	10.51
Br_2^+	360	510	2.13[a]	—
I_2	215	510	2.66	9.31
I_2^+	238	646	2.56	—

[a] Herzberg (*20*).
[b] Frost *et al.* (*30*).

Raman spectrum of I_2^+ is observed. A solution of the Br_2^+ cation also gives a resonance Raman spectrum with a fundamental of 360 cm^{-1} and strong overtones (*14*). Edwards and Jones (*17*) reported that solid $Br_2^+Sb_3F_{16}^-$ has a Raman band at 368 cm^{-1} which they attributed to the Br_2^+ cation. Table I shows the stretching frequencies, absorption maxima, and bond lengths of the halogens and the diatomic halogen cations (*20, 30*). The increase in stretching frequency of Cl_2^+, Br_2^+, and I_2^+ relative to Cl_2, Br_2, and I_2 is consistent with a decrease in bond distance and an increase in bond strength on removal of an antibonding electron.

2. *Triatomic Halogen Cations*

The Raman spectrum (*19*) of $Cl_3^+AsF_6^-$ shows bands due to the AsF_6^- ion, together with three relatively intense bands at 490 (split to 485 and 492), 225, and 508 cm^{-1} which have been assigned to ν_1, ν_2, and ν_3, respectively, of the bent Cl_3^+ cation. The assigned frequencies are very close to the vibrational frequencies of the isoelectronic SCl_2 molecule (*31*) (514, 208, and 535 cm^{-1}) which has a bond angle of 93°, and it is concluded that the Cl_3^+ cation has a similar structure. Using a simple valence force field, good agreement was obtained for the observed frequencies of the Cl_3^+ cation with a bond angle of $\sim 100°$ and a stretching force constant $f = 2.5$ mdyn Å^{-1} (Table II). For a solution of Br_3^+ in HSO_3F—SbF_5 the only band that can be definitely assigned to Br_3^+ is a relatively strong band at 290 cm^{-1} which is assigned as the symmetrical and asymmetrical stretching vibrations ν_1 and ν_3. However, ther seems no reason to doubt that Br_3^+ is a bent molecule the same as Cl_3^+ and I_3^+.

Solutions of I_3^+ in H_2SO_4 give Raman spectra (*28*) that have three bands, in addition to the solvent peaks, at 114, 207, and 233 cm^{-1} which may be assigned as the ν_2, ν_1, and ν_3 vibrations of an angular

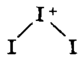
TABLE II

VIBRATIONAL FREQUENCIES AND FORCE CONSTANTS FOR THE TRIATOMIC HALOGEN CATIONS

Cation	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	f (mdyn/Å^{-1})	d (mdyn/Å^{-1})
Cl_3^+	485, 493	225	508	2.5	0.36
Br_3^+	290	(140)[a]	290	—	—
I_3^+	207	114	233	1.7	0.32

[a] Calculated.

molecule. The force constants calculated from the frequencies are given in Table II. It may be noted that the average stretching frequency of 220 cm^{-1} in the I_3^+ molecule is appreciably lower than the stretching frequency of 238 cm^{-1} for the I_2^+ molecule and, in fact, closer to the frequency of 213 cm^{-1} for the neutral molecule. This is consistent with I_3^+ having a formal I–I bond order of 1.0 as in the simple valence bond formulation,



whereas that in I_2^+ is 1.5.

Recently, Corbett *et al.* (*8*) on the basis of ^{127}I nuclear quadrupole resonance (NQR) studies of $I_3^+AlCl_4^-$ have predicted a bond angle of 97° between the two bonding orbitals on the central atom.

III. Polyatomic Cations of Group VI

A. The O_2^+ Cation

The existence of O_2^+ in the gas phase at low pressures has been well established (*32*). However, it was not until 1962 that a compound containing O_2^+ was identified (*33*). It was discovered as a reaction product of the fluorination of platinum in a silica apparatus. The product was first thought to be $PtOF_4$ (*34*), but later it was shown to be $O_2^+PtF_6^-$ (*33*). It was then prepared by direct oxidation of molecular oxygen by platinum hexafluoride at room temperature. Bartlett speculated that, if oxygen [ionization potential (IP) = 12.2 eV] could be oxidized by platinum hexafluoride, then so could xenon (IP = 12.13 eV). Consequently, he reacted xenon and platinum hexafluoride and thus prepared $XePtF_6$ (*35*)—the first compound of the so-called inert gases.

It now appears that the dioxygenyl salt $O_2^+BF_4^-$ may have been prepared prior to 1962 (*36*), although the nature of the material was not elucidated. This and other interesting related work was reviewed in 1966 (*36*) with extensive reference to sources that are not readily available in the literature. Several O_2^+ salts have now been prepared (see Table III) (*37–43*). In addition, there is a preliminary report of the preparation of $O_2^+VF_6^-$ by the reaction of O_2F_2 and VF_5 (*44*) and a patent referring to $O_2^+BiF_6^-$ prepared by the same method (*45*). Also, Bantov and co-workers have reported the reaction of O_2F_2 with various fluorides including SnF_4 which gives $(O_2)_2SnF_6$ (*46*). The antimony salt prepared by Young (*38*) has been reported by Nikitina and Rosolovskii (*39*) to be $O_2^+Sb_2F_{11}^-$ rather than $O_2^+SbF_6^-$.

TABLE III

PREPARATIVE ROUTES TO O_2^+-CONTAINING COMPOUNDS

Product	Reaction	Conditions	References
O_2PtF_6	$F_2 + O_2 + PtF_6$ (sponge)	425°–450°. Flow system	(37)
O_2PtF_6	F_2O + Pt(sponge)	Above 400°. Flow system	(37)
O_2PtF_6	$F_2 + PtCl_2, PtCl_4, PtBr_4, PtI_4$	Above 400° in glass. Flow system	(37)
O_2PtF_6	$O_2 + PtF_6$	Tensimetric titration at room temperature	(37)
O_2PF_6, O_2AsF_6	$O_2F_2 + PF_5, AsF_5$	Excess O_2F_2. Reaction at about −163.5°	(38)
O_2SbF_6	$O_2Sb_2F_{11}$	(Heat $O_2Sb_2F_{11}$ at 130° *in vacuo*)	(39)
$O_2Sb_2F_{11}$	$O_2F_2 + SbF_5$	Low temperatures	(39)
O_2BF_4, O_2PF_6	$O_2F_2 + BF_3, PF_5$	Excess BF_3, PF_5; −126°	(40, 41)
O_2BF_4	$O_4F_2 + BF_3$	Excess BF_3; −138°	(40)
O_2AsF_6, O_2SbF_6	$O_2 + F_2 + AsF_5, SbF_5$	$F_2/O_2/AsF_5$, SbF_5 ratio 0.5:1:1; 150 atm; 200°, 5 days	(42)
O_2AsF_5, O_2SbF_6	$O_2 + F_2 + AsF_5, SbF_5$	Excess F_2 and O_2. Pyrex or Kel-F vessel. Expose to sunlight	(43)
O_2AsF_6	$N_2FAsF_6 + O_2$	2 atm (O_2)	(36)

The most convenient route to O_2^+ salts appears to be the photochemical synthesis of $O_2^+AsF_6^-(SbF_6)^-$ from oxygen, fluorine, and arsenic (antimony) pentafluoride (*43*). Most O_2^+ preparations involve the reaction of fluoride ion acceptors with O_2F_2 or O_4F_2 at low temperatures or with O_2 and F_2 mixtures under conditions favoring synthesis of the long-lived O_2F radical, e.g.,

$$O_2 + F_2 \xrightarrow{h\nu} O_2F + F \tag{19}$$

$$O_2F + AsF_5 \longrightarrow O_2^+AsF_6^- \tag{20}$$

Compounds containing O_2^+ are colorless with the exception of $O_2^+PtF_6^-$ which is red due to the PtF_6^- ion. The compound $O_2^+PF_6^-$ decomposes slowly (*38*) at $-80°$, and rapidly at room temperature, giving oxygen, fluorine, and phosphorous pentafluoride; $O_2^+BF_4^-$ decomposes at a moderate rate at 0° into similar products. Kinetic data and ^{18}F tracer studies have led to the conclusion that the mechanism of the decomposition involves the equilibrium

$$O_2BF_4 \rightleftharpoons O_2F(g) + BF_3(g) \tag{21}$$

followed by a bimolecular decomposition of O_2F (*40*).

Dioxygenyl hexafluoroantimonate has been studied by differential thermal analysis (*39*). Decomposition of $O_2^+SbF_6^-$ proceeds in two stages, according to the mechanism

$$2O_2SbF_6 \xrightarrow{\sim 240°} O_2 + \tfrac{1}{2}F_2 + O_2Sb_2F_{11} \tag{22}$$

$$O_2Sb_2F_{11} \xrightarrow{280°} O_2 + \tfrac{1}{2}F_2 + 2SbF_5 \tag{23}$$

The $O_2^+Sb_2F_{11}^-$ was converted into $O_2^+SbF_6^-$ by heating at 130° *in vacuo*, and conversely, $O_2^+Sb_2F_{11}^-$ was prepared by reaction of $O_2^+SbF_6^-$ and SbF_5 at 180° to 200°. Dioxygenyl hexafluoroarsenate is markedly less stable than the fluoroantimonate salts; it decomposes rapidly at 130° to 180° (*38*). $O_2^+PtF_6^-$ can be sublimed above 90° *in vacuo* and melts with some decomposition at 219° in a sealed tube (*37*).

X-Ray powder data obtained from the cubic form of O_2PtF_6 were consistent with the presence of O_2^+ and PtF_6^- ions (*37*). The structure was refined using neutron diffraction powder data. The PtF_6^- ion was located unambiguously, but the length of the O—O bond could not be determined with certainty, probably because of disorder of the O_2^+ ion in the structure (*47*). Table IV lists the crystal type and cell parameters of some O_2^+-containing salts (*37*, *38*, *43*, *48*). Confusing results on the powder diffraction of $O_2^+SbF_6^-$ have recently been cleared up by McKee and Bartlett (*43*). In every case there is a structural relationship to the analogous nitrosyl salts.

TABLE IV

CRYSTAL TYPE AND CELL PARAMETERS OF SOME O_2^+-CONTAINING SALTS

Compound	Symmetry of unit cell	z	Cell parameters	Reference
O_2PtF_6	Cubic	8	$a = 10.032$	(*37*)
O_2PtF_6	Rhombohedral	1	$a \sim 4.96$; 97.5°	(*37*)
O_2BF_4	Orthorhombic	4	$a = 8.777$, $b = 5.581$, $c = 7.036$	(*48*)
O_2AsF_6	Cubic	4	$a = 8.10$	(*43*)
O_2AsF_6	Cubic	4	$a = 8.00$	(*38*)
O_2SbF_6	Cubic	4	$a = 10.132$	(*43*)

The Raman spectra of various O_2^+ salts have been obtained and all show a strong absorption attributable to O_2^+ as well as those due to the corresponding anions; namely, $O_2^+PtF_6^-$ (*49*) 1837 cm^{-1}, $O_2^+AsF_6^-$ 1858 cm^{-1}, $O_2^+SbF_6^-$ 1862 cm^{-1}, and $O_2^+SbF_6^-$ in SbF_5 1860 cm^{-1} (*50*). The infrared spectrum of $O_2^+BF_4^-$ (*51*) at $-196°$ has a weak doublet at 1868 and 1866 cm^{-1}. The assignment of these bands to the O_2^+ vibration was confirmed by ^{18}O substitution, which led to a shift of the doublet to 1764 and 1762 cm^{-1}. These frequencies may be compared with the value of 1876 cm^{-1} determined (*32*) from the electronic band spectrum of gaseous O_2^+.

The magnetic behavior of O_2^+ in $O_2^+PtF_6^-$ over the temperature range 77°–298°K is similar to that of nitric oxide showing the presence of one unpaired electron ($^2\Pi$ ground state). The magnetic moment of O_2^+ was found to be $\mu_{eff} = 1.57\,\mu_B$ at room temperature (*52*). A magnetic moment of 1.66 μ_B has been reported for $O_2^+SbF_6^-$ (*53*), and a value of 1.7 μ_B for $O_2^+BF_4^-$ (*53a*). An ESR spectrum has been observed for $O_2^+AsF_6^-$ with a single line with a g value at $-80°C$ of 1.9980 corresponding to one free electron.

The chemistry of the O_2^+ cation does not appear to have been extensively studied although various displacement reactions of the type

$$XF + O_2^+PtF_6^- \longrightarrow X^+PtF_6^- + O_2 + \tfrac{1}{2}F_2 \qquad (24)$$

$$XF = KF, ClF_3, IF_5$$

have been described (*37*). Another interesting oxygen displacement is the reaction of $O_2^+AsF_6^-$ and bromine leading to the preparation of $Br_3^+AsF_6^-$ (*15*):

$$\tfrac{3}{2}Br_2 + O_2AsF_6 = Br_3^+AsF_6 + O_2 \qquad (25)$$

Various reactions of O_2^+ salts are listed in Ref. *36*. Recently, the reaction of $O_2^+BF_4^-$ with xenon has been reported (*54*). At 173°K, oxygen and fluorine were liberated and a white solid formed, which, on the basis of analytical and vibrational spectroscopic data, is claimed to be FXe–BF_2.

B. Other Oxygen Polyatomic Cations

Ozone [IP = 12.3 eV (*55*)] reacts with PtF_6 in the gas phase to give $O_2^+PtF_6^-$; no evidence for $O_3^+PtF_6^-$ was obtained (*56*). Goetschel and co-workers (*57*) reacted a mixture of oxygen fluorides, obtained by the radiolysis of F_2 and O_2 with boron trifluoride at low temperatures, and claim to have made O_4BF_4 and O_6BF_4 although reliable evidence for the existence of these interesting compounds has not been obtained.

C. Sulfur Polyatomic Cations

The nature of the colored solutions obtained on dissolving sulfur in oleum (*58*) has until recently remained a mystery since their discovery by Bucholz (*59*) in 1804. Red, yellow, and blue solutions have been prepared; however, particular attention has been given to the blue solutions. The species responsible for the blue color has been identified by various workers as S_2O_3 (*60*), S_2 (*61*), the radical ion $(X_2S–SX_2)^+$ (*62*), and a species designated S_x (*63*). The confusing evidence concerning the blue compound "S_2O_3" has been reviewed (*64*). Recently, the various colors have been shown to be due to the cations S_{16}^{2+}, S_8^{2+}, and S_4^{2+} (*65–67*).

1. *Preparation*

Sulfur can be quantitatively oxidized by arsenic or antimony pentafluoride to red compounds of composition $S_{16}(AsF_6)_2$ and $S_{16}(SbF_6)_2$ or to the deep blue compounds, $S_8(AsF_6)_2$ and $S_8(Sb_2F_{11})_2$ according to Eq. (26)–(29). In addition the pale yellow compound $S_4(SbF_6)_2$ has been

$$2S_8 + 3AsF_5 \xrightarrow{HF} S_{16}(AsF_6)_2 + AsF_3 \text{ (65, 68)} \quad (26)$$

$$2S_8 + 3SbF_5 \xrightarrow{HF \text{ or } SO_2} S_{16}(SbF_6)_2 + SbF_3 \text{ (65, 69)} \quad (27)$$

$$S_8 + 3AsF_5 \xrightarrow{HF} S_8(AsF_6)_2 + AsF_3 \text{ (65, 68)} \quad (28)$$

$$S_8 + 5SbF_5 \xrightarrow[\text{sealed tube}]{SO_2} S_8(Sb_2F_{11})_2 + SbF_3 \text{ (65, 69)} \quad (29)$$

prepared by the reaction of sulfur (*65, 69*) and SbF_5 at 140°. Solid materials were obtained by Ruff (*9*) and by Peacock (*70*), which were assigned the compositions SbF_5S and $(SbF_5)_2S$, respectively. It is probable, however, that the materials that they obtained were not pure compounds but contained SbF_3 or an $SbF_3 \cdot SbF_5$ complex in addition to cations of sulfur and an anion such as $Sb_2F_{11}^-$. A blue material obtained by the reaction of sulfur and SO_3 has been known for a long time (*64*, *71*) and has been described as a lower oxide of sulfur with the composition S_2O_3. This material must contain S_8^{2+} and is probably $S_8(HS_3O_{10})_2$ (*66*) but may also contain $S_4(S_4O_{13})$.

Sulfur may also be oxidized by $S_2O_6F_2$ in fluorosulfuric acid at 0°C (*65*, *69*). The results of conductometric and cryoscopic measurements carried out on this red solution were consistent with the formation of S_{16}^{2+} according to Eq. (30). Further oxidation by $S_2O_6F_2$ produces a

$$2S_8 + S_2O_6F_2 \longrightarrow S_{16}^{2+} + 2SO_3F^- \qquad (30)$$

blue solution containing S_8^{2+}; however, these solutions are not stable and slowly deposit sulfur on standing. The pale yellow compound $S_4(SO_3F)_2$ has been prepared by carefully reacting $S_2O_6F_2$ with elemental sulfur in sulfur dioxide solvent at low temperatures. This compound is not stable in fluorosulfuric acid as the characteristic peak of the blue S_8^{2+} cation slowly appears and increases in intensity with time. However, a stable colorless solution is obtained in the stronger acid HSO_3F–SbF_5. The absorption spectra of S_{16}^{2+} and S_8^{2+} in HSO_3F, and of S_4^{2+} in HSO_3F–SbF_5 are shown in Fig. 2.

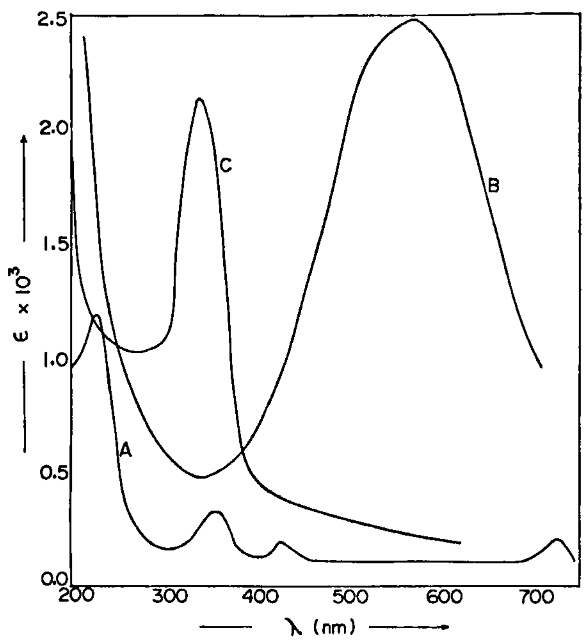


FIG. 2. Absorption spectra of S_{16}^{2+} (A) and S_8^{2+} (B) in HSO_3F and of S_4^{2+} in (C) HSO_3F–SbF_5.

Seel and co-workers (*72*) have reported that $S_2F^+AsF_6^-$ gives a mixture of sulfur polyatomic cations and $SF_3^+AsF_6^-$ on warming to 100°, or at room temperature in the presence of AsF_5.

The deeply colored solutions of sulfur in oleum have been known for a long time (*59*), but it was not until the identification of the sulfur cations S_4^{2+}, S_8^{2+}, and S_{16}^{2+} that the nature of these solutions became clear (*66*). In 95–100% H_2SO_4 sulfur forms a colloidal solution but after 12 hr at 75° the element dissolves as S_8 molecules. In 5% oleum, oxidation is observed and S_{16}^{2+} is formed. In 10% and 15% oleum, sulfur is oxidized first rather rapidly to a mixture of S_{16}^{2+} and S_8^{2+} and then very slowly to SO_2. In 30% oleum, S_{16}^{2+} and S_8^{2+} produced initially are further oxidized to S_4^{2+} and finally to SO_2. In more concentrated oleums (45 and 65%), S_8^{2+} and S_4^{2+} are the initial products, and as S_4^{2+} appears to be rather stable in these solvents further oxidation to SO_2 is very slow. Changes in concentration of the various species with time and with SO_3 concentration are complicated by disproportionation reactions. Thus, S_8^{2+} disproportionates to SO_2 and S_{16}^{2+} in oleum containing less than 15% SO_3, and S_4^{2+} disproportionates to S_8^{2+} and SO_2 in oleum containing less than 40% SO_3.

2. *Structures of* S_{16}^{2+}, S_8^{2+}, *and* S_4^{2+}

No structural data are available for S_{16}^{2+}. The crystal structure of $S_8(AsF_6)_2$ has been determined (*67*); it contains the S_8^{2+} ion which has the structure shown in Fig. 3. It consists of a folded ring with approximately C_s symmetry and has an *endo-exo* conformation. The average bond distance around the ring is 2.04 Å, which is identical with that in the S_8 molecule (*73*, *74*). The three cross-ring distances, as determined in the two crystallographically different S_8^{2+} rings, are S_4–S_6 [2.942(10),

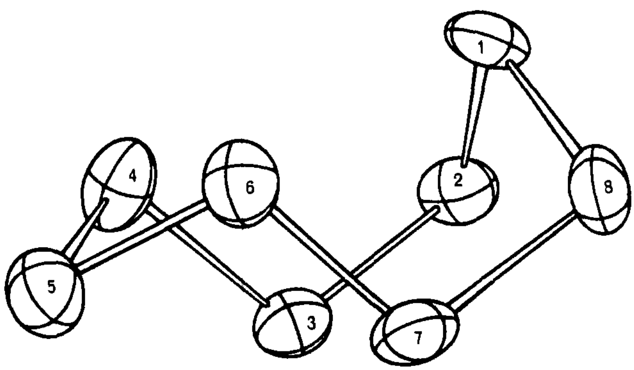
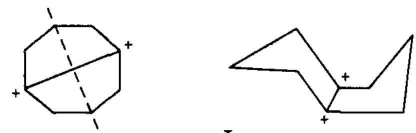
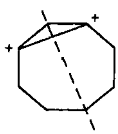


FIG. 3. Structure of S_8^{2+} in $S_8(AsF_6)_2$.

3.053(12) Å], S_3–S_7 [2.832(10), 2.889(12) Å], and S_2–S_8 [3.010(11), 2.866(11) Å], significantly shorter than in the S_8 ring (4.68 Å) or the van der Waals distance of 3.7 Å. These findings strongly suggest that there is weak transannular bonding. It is also noted that there are other sulfur–sulfur bond distances in the ring significantly shorter than the van der Waals distance, e.g., S_5–S_3 [3.082(9), 3.065(10) Å]. The bonding in the ion is, therefore, complex but may perhaps be described by the valence bond structures (I–IV) and in addition others, such as V and VI, where the dashed line indicates the plane of symmetry in the



I



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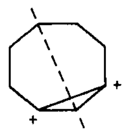
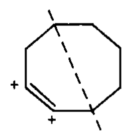
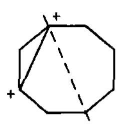


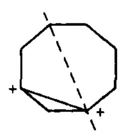
III



IV



V



VI

molecule. The distortion of the ring produced by this cross-ring bonding causes all the angles, which range from 91.5° to 104.3°, to be smaller than the angle of 107.9° found in the S_8 ring.

The ultraviolet and Raman spectra of S_4^{2+} (*65*) are very similar to those of Se_4^{2+} and Te_4^{2+} which have been shown to be planar, suggesting that S_4^{2+} has the same geometry (Tables VIII and IX). The results of a study of the magnetic circular dichroism of solutions of S_4^{2+}, Se_4^{2+}, and Te_4^{2+} also lead to the same conclusion (*75*).

3. *Radical Cations*

Solutions of sulfur in oleum give rise to ESR spectra, but the interpretation of these spectra has been the subject of some controversy in the literature (*62, 76, 77*). No progress was made in the interpretation of these spectra until it had been established that the main species present under various conditions are the sulfur cations S_4^{2+}, S_8^{2+}, and S_{16}^{2+}. It was then shown that solutions of S_8^{2+} in HSO_3F

are paramagnetic and give an ESR spectrum ($g = 2.014$) which is identical with that obtained from blue solutions of sulfur in 60% oleum. Since on cooling these solutions the intensity of the ESR signal decreases, it was proposed that there is an equilibrium between S_8^{2+} and the radical cation S_4^+, i.e.,

$$S_8^{2+} \rightleftharpoons 2S_4^+ \tag{31}$$

This has been confirmed by the observation of the ESR spectrum of a solution of ^{33}S in 60% oleum which was found (*77*) to consist of thirteen lines consistent with the presence of four equivalent sulfur atoms of spin $\frac{3}{2}$. Presumably S_4^+ has a square planar structure the same as S_4^{2+}. The observed g values were reported as 2.0163 for ^{33}S and 2.013 for ^{32}S which are to be compared with the value of $g = 2.014$ reported by Gillespie *et al.* (*65*). Symons and Wilkinson (*78*) have recently given a different interpretation of the spectrum of ^{33}S in oleum but this seems to be inconsistent with all the other information about these solutions. The conclusion that the radical species is S_4^+ also receives some support from the ESR spectra of frozen solutions reported by Giggenbach (*79*) which gave a typical glass spectrum of $g_\perp = 2.0004$ and $g_\parallel = 2.0192$, indicating that the species giving rise to this signal has axial symmetry. This is consistent with the proposed planar structure for S_4^+.

Solutions of sulfur in more dilute oleum, e.g., 15%, give ESR spectra with a second signal ($g = 2.027$). This signal is also obtained from a solution of S_{16}^{2+} in fluorosulfuric acid. It seems reasonable, therefore, to attribute this ESR signal to a radical associated with S_{16}^{2+}, presumably S_8^+, formed by dissociation [Eq. (32)].

$$S_{16}^{2+} \rightleftharpoons 2S_8^+ \tag{32}$$

Consistent with this proposal, it was found that the intensity of the $g = 2.027$ signal decreased on cooling the oleum solutions and at the same time absorption bands at 430, 720, and 935 nm decreased in intensity. Presumably the foregoing equilibrium shifts to the left on cooling the solution, and the bands at 430, 720, and 935 nm as well as the ESR signal at $g = 2.027$ are to be attributed to S_8^+. The g values

TABLE V

THE g VALUES AND ABSORPTION MAXIMA FOR SULFUR CATIONS

Parameters	S_{16}^{2+}	S_8^+	S_8^{2+}	S_4^+	S_4^{2+}
g	—	2.027	—	2.014	—
Absorption max. (nm)	235	430	590	—	330
	335	720	—	—	—
	—	935	—	—	—

and absorption maxima for the various sulfur cations are summarized in Table V.

No ESR spectra have been observed for solutions of S_4^{2+}.

D. Selenium Polyatomic Cations

The colored solutions produced on dissolving elemental selenium in sulfuric acid were first observed by Magnus in 1827 (*80*). Since then a number of workers have investigated the nature of selenium solutions in sulfuric acid, oleum, and sulfur trioxide, providing (*81*) a substantial amount of data but little understanding of the system. Recently, it has been shown that these solutions contain the yellow Se_4^{2+} and green Se_8^{2+} polyatomic cations (*82*).

1. Preparation

Selenium polycations are less electrophilic than their sulfur analogs and give stable solutions in various strong acids (*82*). In fluorosulfuric acid, selenium can be oxidized quantitatively by $S_2O_6F_2$ to give yellow Se_4^{2+} [Eq. (33)]

$$4Se + S_2O_6F_2 = Se_4^{2+} + 2SO_3F^- \tag{33}$$

A photometric titration of selenium and $S_2O_6F_2$ established the oxidation state of the yellow species as $+\frac{1}{2}$; conductometric measurements showed that two fluorosulfate ions are produced per four selenium atoms; and the molecular weight of Se_4^{2+} was established by cryoscopy. The absorption spectrum of the yellow Se_4^{2+} solution in HSO_3F is shown in Fig. 4.

The addition of selenium to the yellow solution up to a 8:1 ratio of Se–$S_2O_6F_2$ did not appreciably affect the conductivity. This indicated that the SO_3F^- ion concentration remained unchanged and that the Se_4^{2+} ion is reduced by selenium according to Eq. (34).

$$Se_4^{2+} + 4Se = Se_8^{2+} \tag{34}$$

Conductivity measurements of selenium in pure fluorosulfuric acid were also consistent with the formation of Se_8^{2+}. The absorption spectrum of the green solution is shown in Fig. 4.

Solutions of Se_8^{2+} in 100% H_2SO_4 may be prepared by heating selenium in the acid at 50° to 60°; the element is oxidized by sulfuric acid according to Eq. (35).

$$8Se + 5H_2SO_4 = Se_8^{2+} + 2H_3O^+ + 4HSO_4^- + SO_2 \tag{35}$$

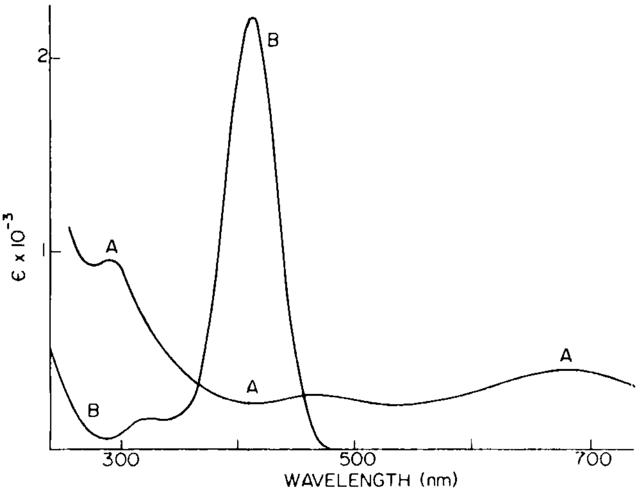


FIG. 4. Absorption spectra of Se_4^{2+} (A) and Se_8^{2+} (B) in HSO_3F.

The cation Se_4^{2+} was obtained on further oxidation of Se_8^{2+} with selenium dioxide:

$$7Se_8^{2+} + 4SeO_2 + 24H_2SO_4 = 15Se_4^{2+} + 8H_3O^+ + 24HSO_4^- \qquad (36)$$

The cations Se_4^{2+} and Se_8^{2+} can also be obtained in disulfuric acid by oxidation of elemental selenium by the solvent, first to Se_8^{2+} and with time to Se_4^{2+} according to Eq. (37) and (38).

$$8Se + 6H_2S_2O_7 = Se_8^{2+} + 2HS_3O_{10}^- + 5H_2SO_4 + SO_2 \qquad (37)$$

$$4Se + 6H_2S_2O_7 = Se_4^{2+} + 2HS_3O_{10}^- + 5H_2SO_4 + SO_2 \qquad (38)$$

Various Se_4^{2+}- and Se_8^{2+}-containing compounds have been prepared by oxidizing selenium with $SeCl_4$ plus $AlCl_3$, sulfur trioxide, oleum, SbF_5, and AsF_5. These preparations are listed in Table VI (*83–87*). In addition to the compounds listed, Paul and co-workers (*88*) have reported the compounds $Se_4S_4O_{13}$, $Se_4S_3O_{10}$, and $Se_4S_2O_7$, prepared by the reaction of elemental selenium and sulfur trioxide for various periods of time. The compounds $Se_4(HS_2O_7)_2$ and $Se_4S_4O_{13}$ have very similar analyses and were both previously incorrectly described as $SeSO_3$ (*89*). The yellow material described by Aynsley, Peacock, and Robinson(*70*) as $Se(SbF_5)_2$, whatever its exact composition, very probably contains the Se_4^{2+} cation. All selenium polyatomic cations are diamagnetic and so far no evidence has been reported for radicals analogous to S_4^+ and S_8^+.

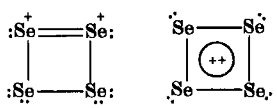
TABLE VI

PREPARATION OF COMPOUNDS CONTAINING POLYATOMIC CATIONS OF SELENIUM

Compound	Reaction	Conditions	References
$Se_4(HS_2O_7)_2$	Se + 65% oleum	50°–60°. Left until yellow-brown. Crystals given on standing	(*83*)
$Se_4S_4O_{13}$	Se + excess SO_3	0°. Left 24 hr	(*83*)
$Se_4(SO_3F)_2$	4Se + $S_2O_6F_2$	Solvent HSO_3F	(*83*)
$Se_4(Sb_2F_{11})_2$	Se + excess SbF_5	Heat at 100°–140° for 6 hr	(*83*)
$Se_4(AsF_6)_2$	Se_8 + 6AsF_5	Solvent SO_2; 80° for 8 days. Yellow solid deposited from green solution	(*84*)
$Se_8(Sb_2F_{11})_2$	Se_8 + 5SbF_5	Solvent SO_2; −23° for 3 days	(*85*)
$Se_8(AsF_6)_2$	Se_8 + 3AsF_5	Solvent HF. Warmed up slowly from −78° to 0° over 3 days	(*85*)
$Se_8(AlCl_4)_2$	Se + $SeCl_4$ + 2$AlCl_3$	Fuse at 250° for 3 hr	(*86, 87*)
$Se_4(AlCl_4)_2$	Obtained from Se–($SeCl_4$–4$AlCl_3$) melts		(*86*)

2. *Structures of* Se_4^{2+} *and* Se_8^{2+}

The crystal structure of $Se_4(HS_2O_7)_2$ (*90, 91*) has shown Se_4^{2+} to be square planar with an Se–Se bond distance of 2.283(4) Å, significantly less than that of 2.34(2) Å found in the Se_8 molecule (*92*), indicating some degree of multiple bonding. Such a result is consistent with a valence bond description of the molecule involving four structures of type VII. Alternatively the structure can be understood in terms of molecule orbital theory. The circle in structure VIII denotes a closed-shell (aromatic?) six-π-electron system. Of the four π molecular orbitals,



VII VIII

the two almost nonbonding (e_g) orbitals and the lower-energy (b_{2u}) bonding orbital are occupied by the six π electrons, leaving the upper antibonding (a_{1g}) orbitals empty. The intense yellow-orange color of Se_4^{2+} has been attributed to the dipole allowed excitation of an electron from an e_g orbital to the lowest empty π orbital (b_{2u}). Stephens (*75*) has shown that the magnetic circular dichroism results are consistent with such a model.

The square planar structure was also found to be consistent with the infrared and Raman spectra of several compounds containing Se_4^{2+} (*93*). A normal coordinate analysis yielded a value of 2.2 mdynes $Å^{-1}$ for the Se–Se stretching constant, which is somewhat greater than the value of 1.67 mdynes $Å^{-1}$ obtained for the single Se–Se bond in $(CH_3)_2Se_2$.

The structure of Se_8^{2+} in $Se_8(AlCl_4)_2$ (*86*, *87*) is similar to that of S_8^{2+} except that the cross-ring distance Se_3–Se_7 is relatively shorter than that found in the sulfur cation, and the other cross-ring distances,

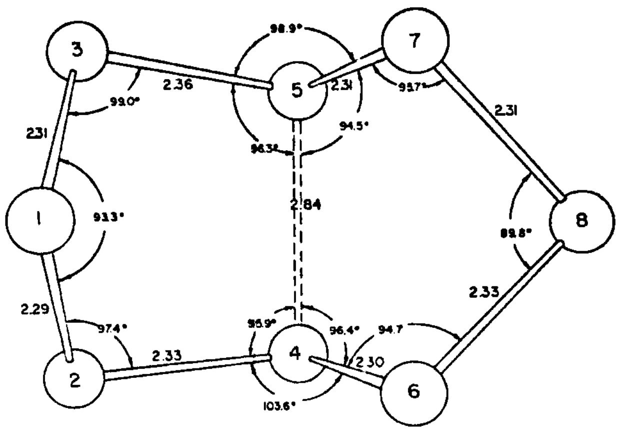
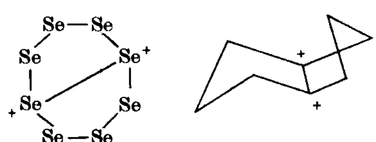


FIG. 5. Projection of Se_8^{2+} structure down the *a* axis.

Se_4–Se_6 and Se_2–Se_8, are relatively long (Fig. 5). The cation Se_8^{2+} is, therefore, reasonably well described by valence bond structure (IX),



IX

although there may be small contributions from structures analogous to structures II to VI proposed for S_8^{2+}. The ring has an endo-exo conformation with approximately C_s symmetry. The bond lengths around the ring vary between 2.29 and 2.36 Å and do not differ significantly from those found in α- and β-selenium, but the bond angles are smaller than in the Se_8 ring. The bond distances and angles in Se_8^{2+} are given in Fig. 5.

E. Tellurium Polyatomic Cations

The red color produced when tellurium dissolves in concentrated sulfuric acid was first observed as long ago as 1798 (*94*), but the origin of this color has remained somewhat of a mystery until very recently. Much more recently Bjerrum and Smith (*95*) and Bjerrum (*96*) have studied the reaction of tellurium tetrachloride with tellurium in molten $AlCl_3$–NaCl. They obtained a purple melt which they concluded contained the species $Te_{2n}{}^{n+}$ (probably $Te_4{}^{2+}$) formed by reaction (39).

$$7Te + Te_4{}^{2+} \longrightarrow 2Te_4{}^{2+} \qquad (39)$$

At about the same time solutions of tellurium in various acids were investigated in detail (*97*, *98*). It was found that red solutions are produced when tellurium is dissolved in sulfuric acid, fluorosulfuric acid, or oleum with the simultaneous production of SO_2, indicating that

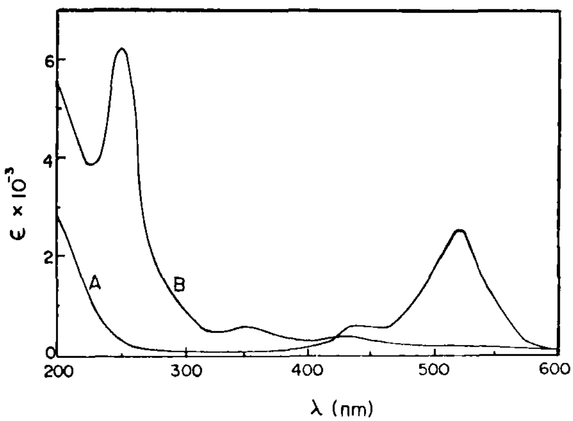


Fig. 6. Absorption spectra of HSO_3F solution of the red tellurium species A and the yellow tellurium species B.

the tellurium is oxidized. The spectra of the solutions (Fig. 6) were found to be identical with those obtained by Bjerrum and Smith from their melts. Conductometric and cryoscopic measurements of the acid solutions led to the conclusion that they contain a species Te_{2n}^{n+} which was certainly not $Te_2{}^+$ but probably $Te_4{}^{2+}$.

Reaction of tellurium with $S_2O_6F_2$ (*98*), SbF_5, and AsF_5 in SO_2 gave the compounds $Te_4(SO_3F)_2$, $Te_4(Sb_2F_{11})_2$, and $Te_4(AsF_6)_2$ and, from Te–($TeCl_4$–$AlCl_3$) melts, compounds $Te_4(AlCl_4)_2$ and $Te_4(Al_2Cl_7)_2$ (*99*) were obtained [Table VII (*98–101*)]. The formulation of the red species

TABLE VII

PREPARATION OF COMPOUNDS CONTAINING POLYATOMIC CATIONS OF TELLURIUM

Compound	Reaction	Conditions	References
$Te_4(Sb_2F_{11})_2$	$Te + SbF_5$	Solvent SO_2. Stirred for several days at $-23°C$. SO_2-soluble products extracted by the solvent	(*98*)
$TeSbF_6$	$Te + SbF_5$	$TeSbF_6$ is insoluble in SO_2, therefore readily separated from $Te_4(Sb_2F_{11})_2$	(*98, 100*)
$Te_4(AsF_6)_2$	$4Te + 3AsF_5$	Solvent SO_2. Stirred at 25°C for 1 day	(*98*)
Te_3AsF_6	$6Te + 3AsF_5$	Conditions as above	(*98*)
$Te(SO_3F)_2$	$4Te + S_2O_6F_2$	Solvent SO_2. Stirred at $-63°C$ and $-23°C$ for 1 day, respectively.	(*98*)
$TeSO_3F$	$4Te + S_2O_6F_2$ (excess)	Compound is unstable above $-20°C$.	(*98*)
$Te_4(AlCl_4)_2$, $Te_4(Al_2Cl_7)_2$, $Te_6(AlCl_4)_2$	Obtained from $Te–(TeCl_4–4AlCl_3)$ melts		(*99*)
$Te_4S_3O_{10}$	$Te + SO_3$	0°C; excess SO_3; 24 hr	(*101*)
$Te_2S_3O_{10}$	$Te + SO_3$	Room temp.; excess SO_3; several days	(*100, 101*)

as Te_4^{2+} was finally confirmed by the determination of the crystal structures of these latter two compounds (*102*).

When the acid solutions are warmed above room temperature or in the case of solution in 45% oleum at room temperature the color of the solution changes slowly from red to orange and to yellow. The same change in color is produced by the addition of an oxidizing agent such as $S_2O_6F_2$ or peroxodisulfate. Absorption spectra and cryoscopic and conductometric measurements on the fluorosulfuric acid solutions established that the yellow species is Te_n^{n+} and that it could not be Te_2^{2+} and was probably Te_4^{4+} although higher molecular weights, such as Te_6^{6+} and Te_8^{8+}, were not excluded with certainty (*98*). Paul and co-workers (*103*) have, however, concluded from absorption spectra and from cryoscopic and conductometric measurements that the yellow species is Te_2^{2+}. A similar conclusion was made by Bjerrum (*104*) from spectrometric measurements of $TeCl_4$ and elementary tellurium in $KAlCl_4$ melts buffered with KCl–$ZnCl_2$. The equilibrium (*40*) was reported to occur under these conditions. The possibility that there are

$$3Te(II) \rightleftharpoons Te_2^{2+} + 3Te(II) \rightleftharpoons Te_2^{2+} + Te(IV) \qquad (40)$$

various Te_n^{n+} species, depending on the nature of the solvent or accompanying ions, cannot be ruled out. Yellow solids of empirical formula $TeSO_3F$, $TeSbF_6$, and $Te_2S_3O_{10}$ have been obtained from the reactions of tellurium with $S_2O_6F_2$, SbF_5, and oleum, respectively (Table VII). A crystal structure of a Te_n^{n+} salt is badly needed to help resolve this problem.

The tellurium analog of Se_8^{2+} and S_8^{2+} has not been reported; however, a gray solid of empirical formula Te_3AsF_6 has been prepared (*98*) by reacting tellurium with a stoichiometric amount of arsenic pentafluoride in liquid SO_2. The compound is diamagnetic and is, therefore, probably $Te_6^{2+}(AsF_6)_2^-$. In phase diagram studies of the system Te–($TeCl_4$–$4AlCl_3$), Corbett *et al.* (*99*) found the phase $(Te_3AlCl_4)_n$ and were able to grow black crystals by vapor phase transport. The compound is diamagnetic, and the density and dimensions of the unit cell indicate that $n = 1$ or 2; hence, the compound is reasonably formulated as $Te_6(AlCl_4)_2$. Some evidence for a lower oxidation state of tellurium had been previously obtained by Bjerrum and Smith (*95*) from experiments in which they had added more than seven parts of tellurium to one part of $TeCl_4$ in molten $AlCl_3$–NaCl.

Structure of Te_4^{2+}

The structure of Te_4^{2+} has been determined (*102*) from the crystal structures of $Te_4(AlCl_4)_2$ and $Te_4(Al_2Cl_7)_2$. In both cases the Te_4^{2+} ion lies on a center of symmetry and is almost exactly square planar. The tellurium–tellurium distance of 2.66 Å is significantly shorter than the tellurium–tellurium distance of 2.864 Å within the spiral chain in elemental tellurium (*105*). This is consistent with a structure exactly analogous to that for Se_4^{2+} in which each bond has 25% double bond character. The Raman spectra of Te_4^{2+} in solution and the solid state are analogous to those of Se_4^{2+} and S_4^{2+} but shifted to lower frequency (Table VIII). The magnetic circular dichroism (*75*) and visible and

TABLE VIII

VIBRATIONAL FREQUENCIES OF THE S_4^{2+}, Se_4^{2+}, AND Te_4^{2+} IONS

Vibrational mode	S_4^{2+}	Se_4^{2+}	Te_4^{2+}
$\nu_1(A_{1g})$ (cm^{-1})	584	327	219
$\nu_2(B_{1g})$ (cm^{-1})	530	319	219
$\nu_3(E_u)$ (cm^{-1})	460	306	—
$\nu_4(B_{2g})$ (cm^{-1})	330	192	139

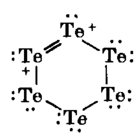
TABLE IX

COMPARISON OF ABSORPTION SPECTRA OF Te_4^{2+}, Se_4^{2+}, AND S_4^{2+} CATIONS

	$_{max}$ (nm)	
Cation	Strong	Weak
Te_4^{2+}	510	420
Se_4^{2+}	410	320
S_4^{2+}	330	280

ultraviolet spectrum (Table IX) of solutions of Te_4^{2+} were also similar to those of Se_4^{2+} as expected on the basis of their structural similarity.

No structural information is available for Te_n^{n+} or Te_6^{2+}. It is interesting to note, however, that, if Te_n^{n+} is in fact Te_4^{4+}, it is isoelectronic with Sb_4 and would presumably have the same tetrahedral



X

structure. It is also tempting to speculate that Te_6^{2+} might have the cyclic structure (X) or possibly six resonance structures of this type.

F. REACTIONS OF GROUP VI POLYATOMIC CATIONS

The reactions of Group VI polyatomic cations are as yet almost completely uninvestigated, but this will no doubt be an area of activity in the future. The only reaction that has so far been studied is that of tetrafluoroethylene with various Group VI polyatomic cations in a solid-gas reaction and in SO_2. The results are given in Table X (*106–108*). It is possible that initially C_2F_4 acts as a diradical toward the centers of unsaturation and very weak bonds in the various polyatomic cations; e.g., the long S–S and Se–Se bonds in S_8^{2+} and Se_8^{2+}, respectively, and the double bond in Te_4^{2+}, to form active intermediates which may abstract fluoride ion from AsF_6^-. In sulfur dioxide solution the reaction products are more complicated and, in addition to the products in the neat reactions, OSF_2 and carbonyl fluorides are formed [e.g., C_2F_5Se-$SeCF_2COF$], suggesting that the solvent itself takes part in the reaction.

TABLE X

REACTION OF C_2F_4 WITH VARIOUS GROUP VI POLYATOMIC CATIONS

Compound	Conditions	Products[a]	Reference
$S_8(AsF_6)_2$	a. Room temp.; ambient pressures of C_2F_4	$(C_2F_5)_2S_x$ (x = 2–6)	*(106)*
	b. Solvent SO_2; room temp.; 3 atm pressure C_2F_4	$(C_2F_5)_2S_x$ (x = 2–3)	
		$C_2F_5S_xCF_3$	
		$C_2F_5S_xCF_2COF$	
$S_{16}(AsF_6)_2$	Room temp.; ambient pressures C_2F_4	$(C_2F_5)_2S_x$ (x = 2–6)	
$Se_8(AsF_6)_2$	a. Room temp.; excess C_2F_4 in pressure reactor	$(C_2F_5)_2Se_x$ (x = 2, 3)	*(107)*
	b. In SO_2 solution; room temp.; about 4 atm pressure C_2F_4	$(C_2F_5)_2Se_x$ (x = 2, 3)	
		$C_2F_5Se_2C_2F_5$	
		$C_2F_5Se_xCF_2COF$	
$Te_4(AsF_6)_2$	a. 100°C; excess C_2F_4 in pressure reactor	$(C_2F_5)_2Te_x$ (x = 1, 2)	*(108)*
		$C_2F_5Te_xC_4F_9$	
	b. SO_2 solvent; 100°C; excess C_2F_4 in pressure reactor	$(C_2F_5)_2Te_x$ (x = 1, 2)	
		$C_2F_5Te_xC_4F_9$	
		$C_2F_5TeC_3F_6COF$	

[a] In addition to these products, arsenic trifluoride and unidentified solids were obtained.

IV. Polyatomic Cations of Group V

A. Bismuth Polyatomic Cations

1. *Preparation and Structure of* Bi_9^{5+}

The discovery of bismuth polycations arose out of an investigation into the nature of "BiCl", first prepared by reduction of bismuth trichloride by bismuth metal by Eggink (*110*) in 1908. More recently, Hershaft and Corbett (*109*), obtained black crystals of this material from the melt and by single crystal X-ray diffraction showed that the unit cell contained $4Bi_9^{5+}$, $8BiCl_5^{2-}$, and $2Bi_2Cl_8^{2-}$, i.e., it has the empirical composition Bi_6Cl_7. Recently the cation Bi_9^{5+} has also been

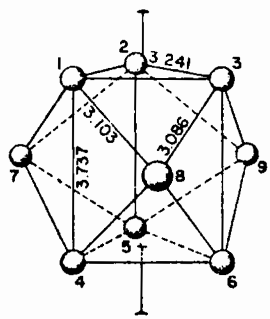


FIG. 7. Structure of Bi_9^{5+}.

identified in the compound $Bi_{10}HfCl_{18}$ (*111*) which was prepared by the reduction of a 3:2 mixture of hafnium tetrachloride and bismuth trichloride with elemental bismuth. By X-ray crystallography this compound was shown to be $Bi^+Bi_9^{5+}$ $(HfCl_6^{2-})_3$. The structure of the Bi_9^{5+} cation is shown in Fig. 7. It is a tricapped trigonal prism which ideally has D_{3h} symmetry but in this case is slightly distorted to give C_{3h} symmetry. The bonding (*112*) in this ion has been treated using D_{3h} symmetry orbitals obtained from the 6p atomic orbitals in a linear combination of atomic orbitals–molecular orbital (LCAO-MO) calculation. The stability and diamagnetism of the cation was explained by the closed-shell MO configuration of 22p electrons in eleven bonding MO's.

2. *Preparation of* Bi_5^{3+} *and* Bi_8^{2+}

Bjerrum and Smith have established the identity of Bi^+, Bi_5^{3+} (*113*, *114*), and Bi_8^{2+} (*115*) in fused salts. The formulas Bi^+ and Bi_5^{3+} were determined by studying the equilibria (41)–(43). Equilibrium

(41) was studied in melts of $AlCl_3$–NaCl eutectic, and equilibria (42) and (43) in molten $ZnCl_2$–KCl eutectic as solvent. The cation Bi_8^{2+} was also prepared and identified in $AlCl_3$–NaCl melts by reduction of Bi^{3+} according to Eq. (44) (*115*). Spectrophotometric measurements established

$$6Bi^+(soln) \rightleftharpoons Bi_5^{3+}(soln) + Bi^{3+}(soln) \quad (41)$$

$$2Bi(liq) + Bi^{3+}(soln) \rightleftharpoons 3Bi^+(soln) \quad (42)$$

$$4Bi(liq) + Bi^{3+} \rightleftharpoons Bi_5^{3+}(soln) \quad (43)$$

$$22Bi(metal) + 2Bi^{3+}(soln) = 3Bi_8^{2+}(soln) \quad (44)$$

that equilibrium (44) is displaced strongly to the right, so that the oxidation state was readily established as 0.25 by the uptake of bismuth by a known amount of $BiCl_3$. In molten $NaAlCl_4$ saturated with NaCl as solvent, the Bi_8^{2+} was shown to be in equilibrium with Bi^+ and bismuth metal. Spectrophotometric measurements on various mixtures yielded the complete reaction stoichiometry and definitely fixed the formula as Bi_8^{2+}.

The compounds $Bi_5(AlCl_4)_3$ and $Bi_8(AlCl_4)_2$ were prepared (*116*, *117*) by reaction of $BiCl_3$–$AlCl_3$ with a stoichiometric quantity of bismuth and with an excess quantity of bismuth, respectively, in liquid $NaAlCl_4$. The compounds are diamagnetic and have electronic spectra very similar to those of Bi_8^{2+} and Bi_5^{3+} in solution. Trigonal bipyramidal (D_{3h}) and square antiprismatic (D_{4h}) structures have been predicted for Bi_5^{3+} and Bi_8^{2+} on the basis of LCAO-MO calculations (*116*), although direct evidence is lacking.

Reports of Bi_3^{3+} (*118*) and Bi_4^{4+} (*119*, *120*) have been shown to be incorrect (*116*, *121*).

B. The Polyatomic Cation Sb_n^{n+}

Antimony metal has been oxidized by arsenic pentafluoride (*122*) to the compound $SbAsF_6$ according to Eq. (45).

The compound $SbAsF_6$ may contain the $(Sb^+)_n$ cation, but it would be difficult on the basis of analysis alone to rule out other stoichiometries such as $Sb_5^{4+}(AsF_6^-)_4$ where the antimony is in an oxidation state close to but not equal to +1.

Metallic antimony dissolves slowly in fluorosulfuric acid (*123*) at room temperature according to Eq. (46) to give the compound $SbSO_3F$ which has been isolated as a pure solid.

$$2Sb + 3AsF_5 \xrightarrow{SO_2} 2SbAsF_6 + AsF_3 \quad (45)$$

$$2Sb + 4HSO_3F \longrightarrow 2Sb(SO_3F) + H_3O^+ + SO_3F^- + SO_2 + HF \quad (46)$$

C. Other Polyatomic Cations of Group V

The cations Sb_4^{2+}, Sb_8^{2+} (*124*), As_4^{2+}, As_2^{2+} (*125*), P_4^{2+}, and P_8^{2+} (*126*) have been reported as products of the reaction of the elements with $S_2O_6F_2$ in HSO_3F or with oleum. However, the ultraviolet spectra reported for these species are very similar to those found for S_{16}^{2+}, S_8^{2+}, or S_4^{2+}, and it seems very probable that antimony, arsenic, and phosphorus reduce HSO_3F and $H_2S_2O_7$ to elemental sulfur, which is then oxidized to S_{16}^{2+}, S_8^{2+}, or S_4^{2+}. Indeed, it has been demonstrated that elemental sulfur is one of the products of the reduction of oleum by antimony (*123*). Thus there is at present no reliable evidence for any polyatomic cations of P, As, or Sb, with the exception of $(Sb^+)_n$.

V. Polyatomic Cations of Group IIb

A. Hg_2^{2+}, Cd_2^{2+}, Zn_2^{2+}

The mercurous ion Hg_2^{2+} is by far the most stable of the known polyatomic cations, and its existence in acidic aqueous solution and in a variety of simple crystalline salts, e.g., Hg_2X_2 (X = F, Br, Cl, I) is well documented (*127*). The corresponding cadmium ion Cd_2^{2+} is less well established but evidence for the compound $Cd_2(AlCl_4)_2$ has been obtained from a study of the Cd–$CdCl_2$–$AlCl_3$ phase diagram (*128*). Evidence has been obtained for the cation Zn_2^{2+} (*129*) in solutions of zinc in zinc chloride and in zinc chloride–cerium chloride melts, although compounds containing this cation have not been isolated. The Raman spectra of solutions containing Hg_2^{2+}, Cd_2^{2+}, or Zn_2^{2+} show peaks at 169 (*130*) [more recently 182 (*131*)], 183 (*132*), and 175 (*129*) cm^{-1}, respectively, which have been attributed to the metal–metal stretching vibrations. Force constants of 2.52 (*132*), 1.68 (*132*), and 0.6 (*129*) mdyn $Å^{-1}$ have been estimated for Hg_2^{2+}, Cd_2^{2+}, and Zn_2^{2+}, respectively. The value for Hg_2^{2+} is probably somewhat higher than 2.52 mdyn $Å^{-1}$ as it was based on the earlier 169 cm^{-1} value of the Hg–Hg stretching frequency. It has been suggested (*132*) that the higher Hg metal–metal bond strength in Hg_2^{2+} is a consequence of the higher electron affinity of Hg^+ relative to Cd^+ (first IP Hg = 10.43 eV, Cd = 8.99 eV). However, although zinc has an ionization potential [9.39 eV] intermediate between mercury and cadmium, Zn_2^{2+} has a very low force constant (0.6 mdyn).

B. Hg_3^{2+}

Although the Hg_2^{2+} ion has been known for a very long time, it is only very recently that evidence for other ions of the general formula

Hg_n^{2+} has been obtained. The compound $Hg_3(AlCl_4)_2$ (*133*, *134*) has been prepared by reacting a 1:2:2 molar mixture of $HgCl_2$, Hg, and $AlCl_3$ at 240° for 6 days. The absorption spectra of a mixture of Hg_2^{2+} and Hg in molten $AlCl_3$–NaCl at 175° gave an absorption due to a mercury species of lower oxidation state than Hg_2^{2+} which was attributed to Hg_3^{2+}. Polarograms for the reduction of Hg^{2+} in molten $AlCl_3$–NaCl show three waves consistent with the reaction scheme:

$$2Hg^{2+} + 2e^- = Hg_2^{2+} \quad (47)$$

$$3Hg_2^{2+} + 2e^- = 2Hg_3^{2+} \quad (48)$$

$$Hg_3^{2+} + 2e^- = 3Hg \quad (49)$$

Equilibrium constants for the reactions $Hg^{2+} + Hg_3^{2+} = 2Hg_2^{2+}$ and $Hg_2^{2+} + Hg = Hg_3^{2+}$ have been obtained (*134*) by linear sweep voltammetry and chronopotentiometry for several $AlCl_3$–NaCl composition ratios at various temperatures.

The yellow compound $Hg_3(AsF_6)_2$ has been prepared in sulfur dioxide solution (*131*, *136*) either by oxidizing mercury with AsF_5,

$$3Hg + 3AsF_5 \longrightarrow Hg_3(AsF_6)_2 + AsF_3 \quad (50)$$

or by reacting mercurous hexafluoroarsenate with mercury,

$$Hg_2(AsF_6)_2 + Hg \longrightarrow Hg_3(AsF_6)_2 \quad (51)$$

The compound $Hg_3(Sb_2F_{11})_2$ can also be prepared by the similar reaction of mercury with SbF_5 in SO_2 solution:

$$3Hg + 5SbF_5 \longrightarrow Hg_3(Sb_2F_{11})_2 + SbF_3 \quad (52)$$

The Raman spectrum of $Hg_3^{2+}(AsF_6)_2$ in sulfur dioxide solution shows in addition to peaks attributable to AsF_6^- and the solvent, a single strong polarized band at 118 cm^{-1} which was assigned to a Hg–Hg stretch indicating that Hg_3^{2+} has the linear structure Hg^+–Hg–Hg^+.

The structure of $Hg_3(AsF_6)_2$ has been determined by X-ray crystallography and the Hg_3^{2+} ion has been found to be linear and symmetric. The mercury–mercury distance was found to be 2.552(4) Å (*135*). The crystal structure of $Hg_3(AlCl_4)_2$ has also been determined (*136*). In this case the two mercury–mercury bond distances were found to be almost equal [2.551(1) and 2.562(1) Å], but the ion is not quite linear having a bond angle of 174.4°. The mercury–mercury bond distance of 2.55 Å in both compounds is somewhat longer than the range of 2.49 to 2.54 Å reported for the Hg–Hg bond lengths in several halides (*137*) and salts of Hg_2^{2+} (*138–143*). The rather short Hg···Cl distance of 2.54 Å (cf. Hg–Cl = 2.43 Å in Hg_2Cl_2) indicates considerable covalent interaction between the Hg_3^{2+} "ion" and the $AlCl_4^-$.

Accordingly, Ellison *et al.* (*136*) have preferred to describe the compound as molecular rather than ionic.

C. Hg_4^{2+}

By using more mercury than is necessary to prepare Hg_3^{2+} in the reaction with AsF_5 in SO_2 solution, the dark red crystalline compound $Hg_4(AsF_6)_2$ can be obtained:

$$4Hg + 3AsF_5 \longrightarrow Hg_4(AsF_6)_2 + AsF_3$$

A determination of the structure of this compound by X-ray crystallography has shown that the Hg_4^{2+} ion has a centrosymmetric almost linear structure with the following dimensions (*144*):

$$\mathrm{Hg} \xrightarrow[\quad]{2.57\ \text{Å}} \mathrm{Hg} \xrightarrow[\quad]{2.70\ \text{Å}} \mathrm{Hg} \text{ ——— } \mathrm{Hg}$$

$$176^\circ$$

D. $Hg_n^{0.35n+}$

When mercury is allowed to react with a solution of arsenic pentafluoride in SO_2 at room temperature, a remarkable reaction is observed in which the mercury crystallizes over a period of 10 to 15 min to a golden-yellow solid with a striking metallic appearance. If excess AsF_5 is present the solid eventually dissolves to give a yellow solution of Hg_3^{2+}. When a limited amount of AsF_5 is used (i.e., $AsF_5/Hg = 1:2$) the gold solid, which is quite insoluble in SO_2, can be obtained in a pure state. When this compound was first analyzed, it was believed (*145*) to have the composition Hg_3AsF_6 and to have been formed according to the following reaction:

$$6Hg + 3AsF_6 \xrightarrow{SO_2} \text{“}Hg_3AsF_6\text{”} + AsF_3 \tag{53}$$

Supporting this assumption, it was found possible to prepare the compound by reacting $Hg_2(AsF_6)_2$ with the appropriate amount of mercury according to Eq. (54). However, the determination of the structure of

$$Hg_2(AsF_6)_2 + 4Hg \longrightarrow 2Hg_3AsF_6 \tag{54}$$

this compound by X-ray crystallography (*146*) has shown that it, in fact, has the composition $Hg_{2.85}AsF_6$ and that it has a remarkable structure in which the octahedral AsF_6^- ions are stacked in such a manner that the fluorines occupy three-quarters of the sites of a cubic close-packed lattice and so that there are channels running through the lattice in two mutually perpendicular directions. Within these channels are infinite chains of mercury atoms, each with an average formal charge of $+0.35$, and with an average mercury–mercury distance of 2.64(1) Å (see Fig. 8). The crystals have a conductivity of the order of magnitude of that expected for a metal. It is noteworthy that this interesting compound contains covalently bonded AsF_6^- ions, metallically bonded $Hg_n^{0.35n+}$ chains, and ionic bonding between the metallic chains and the AsF_6^- ions. Each mercury chain constitutes a one-dimensional metal.

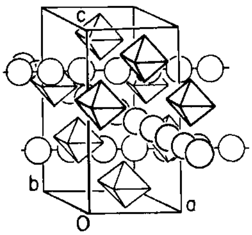


FIG. 8. Structure of $Hg_{2.86}AsF_6$.

VI. Polyatomic Cations of Other Elements

We have not discussed the evidence for polyatomic cations formed in the mass spectrometer or as transient reaction intermediates; instead we have concentrated on recent work on those polyatomic cations that exist as stable entities in solution or in the solid state. We may add that evidence has also been given for the formation of Pb_2^{2+} (*147*), Mg_2^{2+} (*148*), Ca_2^{2+} (*149*), Sr_2^{2+} (*150*), and Ba_2^{2+} (*150*) on addition of the respective element to the corresponding MCl_2 melt at high temperatures, and ESR evidence has been presented for Ag_4^+ or Ag_4^{3+} (*151*), Ag_2^+, Cd_2^{3+} (*152*), and Hg_2^{3+} or Hg_2^+ (*153*).

VII. Conclusion

Salts of homopolyatomic cationic clusters now constitute a well-established class of compound—there are at least twenty-six fairly well-characterized examples. It is probable that many other elements will also be shown to form polyatomic cations. As yet reactions of these species have been little studied, and there is obviously a wide open field here awaiting exploration. Many structures of known cations, as well as those that have not yet been prepared, remain to be investigated, and there is a need for theories that can predict the stability and geometry of these cations and provide a description of the bonding.

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