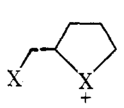
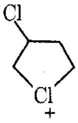
Recently we have prepared halonium ions which were halogen substituted in the side chain (**48**)[30] or in the ring (**49** and **50**).[31]



48, X = Cl, Br



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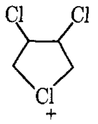

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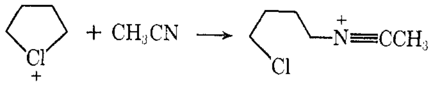
The nmr spectra of all ions mentioned are of interest because of the strong deshielding effect of positive halogen which leads to peaks at approximately δ 5 (methylene next to positive chlorine) and/or δ 6 (methine next to positive chlorine).

It should be mentioned that Olah and coworkers have now reported the preparation of many alkyl halonium ions, including $CH_3ClCH_3^+Sb_2F_{11}^-$ and $CH_3ICH_3^+$-SbF_6^-, as stable solids at room temperature![32] The cyclic halonium ions reviewed in this Account, accordingly, are merely the heterocyclic members of a potentially enormous class of reactive compounds. We may anticipate that rapid developments will occur in the structural elaboration of these ions and in the exploitation of their chemical properties, of which their high reactivity as alkylating agents (exemplified in the reaction of eq 5; *cf*. ref 31 and 32) has been found to be notable.



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Polycations of Group VI

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Cation formation has normally been associated with the metallic elements, but over the past few years evidence has accumulated which shows that it is a fairly common occurrence among nonmetals as well, at least insofar as polycations of the type A_m^{n+} are concerned. These polycations are important in terms of their stereochemistry and bonding and constitute a novel class of compounds of intrinsic interest. For the transition metals homonuclear groupings are well known in the "cluster" compounds which, however, have ligands attached to the metal cluster, *e.g.*, $[Mo_6Cl_8]^{4+}$. In the nonmetal cations A_m^{n+} lone pairs of electrons take the place of ligands.

It has long been known that the mercurous ion is not Hg^+, but Hg_2^{2+},[1,2] and recently it has been shown that other metallic elements form similar cations. Thus, evidence has been presented for the formation of Cd_2^{2+},[3] Zn_2^{2+},[4,5] Pb_2^{2+},[5] Mg_2^{2+},[6] Ca_2^{2+},[7] Sr_2^{2+},[8] and Ba_2^{2+} [8] on addition of the respective element to the corresponding MCl_2 melt. Various bismuth polycations have been identified, and in the process many confusing results have been rationalized. The material thought to be BiCl has been shown by an X-ray study to contain Bi_9^{5+} in addition to $BiCl_5^{2-}$ and $Bi_2Cl_8^{2-}$.[9] The Bi^+,[10] Bi_5^{3+},[10] and Bi_8^{2+} [11] ions have been identified in melts and the compounds $Bi_5(AlCl_4)_3$[12] and $Bi_8(AlCl_4)_2$[12] isolated. Recently evidence has been given for a cation containing antimony in the 1+ oxidation state.[13] Esr evidence has been presented for the formation of Ag_4^+ or Ag_4^{3+},[14] Ag_2^+,[15] and Cd_2^{3+}.[15]

There has long been evidence for positive oxidation states of iodine[16] and the I_3^+ and I_5^+ ions are now well established, although "I^+" has been shown to be I_2^+.[17]

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Table I
Preparative Routes to O_2^+ Compounds

Product	Reaction	Conditions	Ref
O_2PtF_6	$F_2 + O_2 + Pt$ (sponge)	425–450°; flow system	29
O_2PtF_6	$F_2O + Pt$ (sponge)	Above 400°; flow system	29
O_2PtF_6	$F_2 + PtCl_2, PtCl_4, PtBr_4, PtI_4$	Above 400°; glass flow system	29
O_2PtF_6	$O_2 + PtF_6$	Tensimetric titration at room temperature	29
O_2PF_6, O_2AsF_6	$O_2F_2 + PF_5, AsF_5$	Excess O_2F_2; −162°	25
O_2SbF_6	$O_2F_2 + SbF_5$	−80°	25
O_2BF_4, O_2PF_6	$O_2F_2 + BF_3, PF_5$	Excess BF_3, PF_5, −126°	25, 27, 31
O_2BF_4	$O_4F_2 + BF_3$	Excess BF_3, −138°	31
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	32
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; exposed to sunlight.	24

The evidence for other recently characterized group VII polycations, *i.e.*, I_4^{2+}, Br_2^+, Br_3^+, and Cl_3^+, has been reviewed.[18]

This Account is concerned with recent work on the group VI polycations which have received considerable investigation during the last few years, during which time at least nine such cations have been characterized and isolated in the form of crystalline solids. The unusual colors of solutions of sulfur, selenium, and tellurium in strong acid solvents, *e.g.*, sulfuric acid and oleum, have been known for over 150 years, but the nature of these solutions remained obscure until it was demonstrated recently that the colors are due to polyatomic cations.

The O_2^+ Cation

Preparation. The existence of O_2^+ in the gas phase at low pressures has been well established.[19] However, it was not until 1962 that a compound containing this ion was identified.[20] This compound, a reaction product of the fluorination of platinum, or platinum salts at high temperature, in a glass or silica apparatus, was first thought to be an oxyfluoride of platinum, $PtOF_4$,[21] but improved analysis showed the new compound to have the empirical formula O_2PtF_6.[20] It was then prepared by direct oxidation of molecular oxygen by platinum hexafluoride at room temperature. Bartlett speculated that if molecular oxygen (IP 12.2 eV) could be oxidized by platinum hexafluoride, then so could xenon (IP 12.13 eV). Subsequently, Bartlett[22] prepared the first compound of the so-called inert gases, $XePtF_6$, by the reaction of xenon with platinum hexafluoride.

Claims have been made that a dioxygenyl salt was prepared prior to 1962.[23] This work was reviewed in 1966,[23] with extensive reference to sources that are not readily available in the literature. Table I lists the various methods of preparing dioxygenyl compounds. The most convenient route appears to be the photochemical synthesis of $O_2^+AsF_6^-$ (SbF_6^-) from oxygen, fluorine, and arsenic (antimony) pentafluoride.[24]

Physical Properties. O_2PtF_6 is red, due to the PtF_6^- ion, while the other compounds are colorless. Young[25] noted that violet areas developed on the surface of the colorless salt O_2SbF_6 on cooling to −80°, and Shamir[24] found the same color appeared with addition of excess pentafluoride. Various violet colors were observed in some of the chemical reactions of the oxygenyl compounds referred to in ref 23. The origin of these colors is not known. The O_2BF_4 and O_2PF_6 salts dissociate at room temperature, but the other compounds are stable. O_2PtF_6 was sublimed at 100°.

The magnetic behavior of O_2^+ in O_2PtF_6 over the temperature range 77 to 298°K is similar to that of nitric oxide, showing the presence of one unpaired electron[26] ($^2\pi$ ground state). The esr spectra of O_2BF_4[27] and O_2AsF_6[24] have single absorptions at $g = 1.97 \pm 0.10$ and 1.998 ± 0.002, respectively.

The Raman spectra of O_2AsF_6 and O_2SbF_6 gave direct evidence for the presence of O_2^+ with a strong absorption at about 1860 cm^{-1}.[28] This may be compared with the value of 1876 cm^{-1} determined from the electronic band spectrum of gaseous O_2^+.

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.[29] 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 owing to disorder of the O_2^+ ion in the structure.[30]

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$O_2^+BF_4^-$ decomposes at a moderate rate at 0° to give O_2, F_2, and BF_3. Kinetic data and ^{18}F tracer studies led to the conclusion that the mechanism of the decomposition involves the equilibrium

$$O_2BF_4(s) \rightleftharpoons O_2F(g) + BF_3(g)$$

followed by a bimolecular decomposition of O_2F.[31] It is possible that the chemistry of O_2^+ has been extensively studied,[23] although this information is not yet part of the general literature.

Sulfur Polycations

The nature of the colored solutions obtained on dissolving sulfur in oleum has remained somewhat of a mystery ever since their discovery by Bucholz in 1804.[33] Red, yellow, and blue solutions have been prepared, particular attention being given to the blue solutions. The species responsible for the blue color has been variously identified as S_2O_3,[34] S_2,[35] the radical ion $[X_2S{-}SX_2]^+$,[36] and a species designated S_x.[37] The confusing evidence concerning the blue compound "S_2O_3" has been reviewed.[38] The presence, but not the identity, of species in addition to the blue entity in solutions of sulfur in oleum is well established.[37] Recently this problem has been reinvestigated, and the various colors have been shown to be due to the cations S_{16}^{2+}, S_8^{2+}, and S_4^{2+}.[39-42]

The S_{16}^{2+} Cation. Sulfur can be quantitatively oxidized by arsenic or antimony pentafluoride to red compounds of composition $S_{16}(AsF_6)_2$ or $S_{16}(SbF_6)_2$, according to eq 1 and 2.

$$2S_8 + 3AsF_5 \xrightarrow{\text{HF}} S_{16}(AsF_6)_2 + AsF_3\text{[39,40]} \tag{1}$$

$$2S_8 + 3SbF_5 \xrightarrow[\text{or SO}_2]{\text{HF}} S_{16}(SbF_6)_2 + SbF_3\text{[40,41]} \tag{2}$$

Sulfur has also been oxidized with $S_2O_6F_2$ in fluorosulfuric acid at 0°. Conductometric and cryoscopic measurements carried out on this red solution were consistent with the formation of S_{16}^{2+} according to eq 3.[40]

$$2S_8 + S_2O_6F_2 \longrightarrow S_{16}^{2+} + 2SO_3F^- \tag{3}$$

The absorption spectrum of this solution is shown in Figure 1.

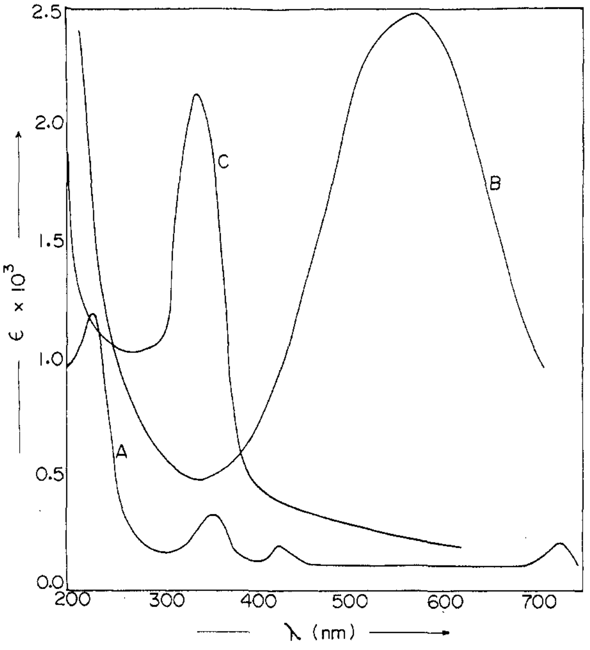

Figure 1. Absorption spectra of S_{16}^{2+} (A), S_8^{2+} (B), and S_4^{2+} (C) in solution in HSO_3F.

Magnetic susceptibility measurements on solid $S_{16}(AsF_6)_2$ and concentrated solutions of S_{16}^{2+} in fluorosulfuric acid showed it to have a very small paramagnetism.[39] Esr studies of solutions of sulfur in oleum indicated that a signal at $g = 2.027$ can be associated[42] with a species that is always present together with the S_{16}^{2+} ion, and it is probable that this is the paramagnetic S_8^+ ion, existing in equilibrium with S_{16}^{2+}.

The S_8^{2+} Cation. Compounds containing the deep blue S_8^{2+} cation have been synthesized by quantitative oxidation of sulfur by arsenic[39,40] or antimony pentafluorides[40,41] according to eq 4 and 5.

$$S_8 + 3AsF_5 \xrightarrow{\text{HF}} S_8(AsF_6)_2 + AsF_3 \tag{4}$$

$$S_8 + 5SbF_5 \xrightarrow[\text{sealed tube}]{SO_2} S_8(Sb_2F_{11})_2 + SbF_3 \tag{5}$$

Oxidation of sulfur may also be effected by $S_2O_6F_2$ in fluorosulfuric acid to produce a blue solution containing S_8^{2+}.[40] The absorption spectrum of this solution is shown in Figure 1. However, these solutions are not stable and slowly deposit sulfur on standing.

Completely unambiguous evidence for S_8^{2+} has been provided by the X-ray study of a single crystal of $S_8(AsF_6)_2$.[43] The structure is given in Figure 2; it consists of a folded ring with approximate C_s symmetry and having an *endo,exo* conformation. The average S–S bond distance around the ring is 2.04 Å, which is identical with that in the S_8 molecule.[44,45] The average bond angle is 102° excluding the two end angles which are smaller and have an average value of 93°. There is a relatively long bond of length 2.83 Å across the middle of the ring (S_3–S_7), and the other cross-ring distances (S_2–S_6 and S_4–S_6) are somewhat shorter than the van der Waals contact distance. Thus the mole-

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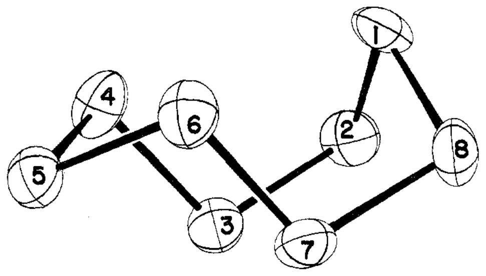
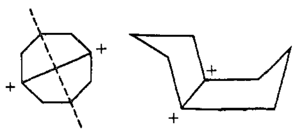


Figure 2. Structure of the S_8^{2+} ion.

cule may be described by the valence bond structure **1** and possibly others in addition, such as **2**, **3**, and **4**,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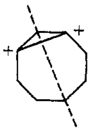
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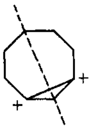
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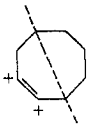
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where the dashed line indicates the plane of symmetry in the molecule. The structure is very similar to that of Se_8^{2+}.[46]

The solid $S_8(AsF_6)_2$ and the concentrated blue solutions are very slightly paramagnetic[39,40] and give esr spectra ($g = 2.014$).[42] It appears that S_8^{2+} is in equilibrium with a small concentration of a paramagnetic species, which it has been proposed is S_4^{+}.

The blue compound "S_2O_3" thought to be a lower oxide of sulfur[38] must contain S_8^{2+} and may be $S_8(HS_3O_{10})_2$.[42]

The S_4^{2+} Cation. 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 temperature,[41] and $S_4(SbF_6)_2$ has been prepared by the reaction of sulfur and SbF_5 at 140°. Solid materials were obtained earlier by Ruff (SbF_5S)[47] and by Peacock [$(SbF_5)_2S$],[48] from the reaction of SbF_5 with sulfur, but the exact nature of these solids is uncertain. It is possible that they were not pure compounds but contained SbF_3. The ultraviolet and Raman spectra[40] of S_4^{2+} are very similar to those of the Se_4^{2+} ion (Table II), suggesting that S_4^{2+} has the same structure as Se_4^{2+}, namely square planar. A study of the magnetic circular dichroism of solutions of S_4^{2+} and Se_4^{2+} leads to the same conclusion.[49] The compounds $S_4(SO_3F)_2$ and $S_4(SbF_6)_2$ are diamagnetic and do not give esr spectra. Table III lists the preparative routes to compounds containing sulfur polycations.

Solutions of Sulfur in Oleum. The reaction of sulfur with sulfuric acid and oleum has been studied by ultraviolet spectroscopy.[42] 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. Increase in the SO_3 concentration causes further oxidation to S_8^{2+} and to S_4^{2+} in oleum having more than 15% SO_3. None of these solutions is completely stable, and oxidation continues slowly to give SO_2 as the final product. The changes in the concentrations of the various sulfur cations in these solutions are also somewhat 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 30% SO_3.

Table II

	λ_{max}, nm		Vibrational frequencies, cm^{-1}			
Cation	Strong	Weak	$\nu_1(A_{1g})$	$\nu_2(B_{1g})$	$\nu_3(E_u)$	$\nu_4(B_{2g})$
S_4^{2+}	330	280	584	530	460	330
Se_4^{2+}	410	320	327	319	306	192
Te_4^{2+}	510	420	219	219	...	139

Selenium Polycations

In 1827[50] Magnus observed that sulfuric acid dissolved selenium to give a green solution. Over the years many workers[51] have investigated the nature of selenium solutions in sulfuric acid, oleum, and sulfur trioxide, providing much data but little real understanding of the system. Recently the problem has been extensively reinvestigated, and it has been shown that these solutions contain the polyatomic cations Se_4^{2+} and Se_8^{2+}.[52]

Oxidation of Selenium in Highly Acidic Solvents.[52] *a. Fluorosulfuric Acid Solutions.* Fluorosulfuric acid dissolves elemental selenium to form a green solution. The reaction goes faster with unpurified commercial fluorosulfuric acid containing sulfur trioxide impurity. Peroxydisulfuryl difluoride oxidizes selenium in fluorosulfuric acid to give green, yellow, and finally colorless solutions as the quantity of $S_2O_6F_2$ is increased. A photometric titration of selenium and $S_2O_6F_2$ established the oxidation state of the yellow species as $^1/_2+$, consistent with the equation

$$4Se + S_2O_6F_2 = Se_4^{2+} + 2SO_3F^- \qquad (6)$$

Conductometric measurements in fluorosulfuric acid showed that two fluorosulfate ions are produced per four selenium atoms. The molecular weight of Se_4^{2+} was determined by cryoscopy. The absorption spectrum of the yellow Se_4^{2+} solution in HSO_3F is shown in Figure 3.

The addition of selenium to the yellow solution up to a ratio of Se:$S_2O_6F_2$ of 8:1 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 7.

$$Se_4^{2+} + 4Se \longrightarrow Se_8^{2+} \qquad (7)$$

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Table III

Preparation of Compounds Containing Polycations of Sulfur

Product	Reaction	Conditions	Ref
$S_{16}(AsF_6)_2$	$2S_8 + 3AsF_5$	Solvent HF; slowly warmed from −78° to 0°	39, 40
$S_{16}(SbF_6)_2$	$2S_8 + 3SbF_5$	Solvent HF; 25°	40, 41
$S_8(AsF_6)_2$	$S_8 + 3AsF_5$	Solvent HF; slowly warmed from −78° to 0°	39, 40
$S_8(Sb_2F_{11})_2$	$S_8 + 5SbF_5$	Solvent SO_2; reaction in a sealed tube at 25°	40, 41
$S_4(SbF_6)_2$	S_8 + excess SbF_5	Heated at 140° for several days	40, 41
$S_4(SO_3F)_2$	S_8 + excess $S_2O_6F_2$	Solvent SO_2; temperature slowly raised from −63 to 25°	40, 41

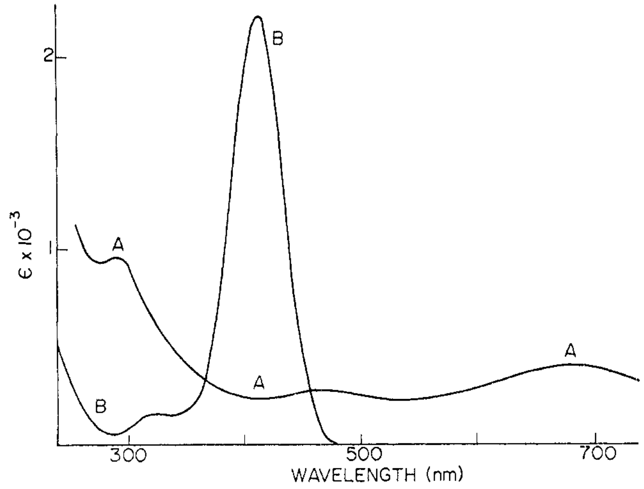

Figure 3. Absorption spectra of Se_8^{2+} (A) and Se_4^{2+} (B) in solution in HSO_3F.

Conductivity measurements of selenium in pure fluorosulfuric acid were also consistent with the formation of Se_8^{2+}. The absorption spectrum of the green Se_8^{2+} solution is shown in Figure 3.

b. Sulfuric Acid Solutions. Selenium does not dissolve in 95% sulfuric acid, but on addition of potassium persulfate green, yellow, or colorless solutions are obtained. With 100% sulfuric acid at 50–60° diamagnetic green solutions can be prepared. Conductivity measurements established the overall oxidation state of the green species as $^1/_4+$, and cryoscopic measurements showed that seven particles are produced in solution for every eight atoms of selenium. This is consistent with eq 8, as SO_2 has a very low solubility in sulfuric acid

$$8Se + 5H_2SO_4 = Se_8^{2+} + 2H_3O^+ + 4HSO_4^- + SO_2 \quad (8)$$

and is therefore not included in the particle count.

The green solutions were oxidized with selenium dioxide, and from conductometric, spectrophotometric, and cryoscopic titrations the equivalence point was established at the Se:SeO_2 ratio of 1:0.071, consistent with eq 9.

$$7Se_8^{2+} + 4SeO_2 + 24H_2SO_4 = 15Se_4^{2+} + 8H_3O^+ + 24HSO_4^- \quad (9)$$

c. Disulfuric Acid Solutions. Selenium initially gives a green solution in disulfuric acid at room temperature. The solution is not stable, however, and further oxidation occurs to give a yellow solution. The results of cryoscopic and conductometric measurements on the green solutions were consistent with the formation of Se_8^{2+} according to eq 10, and the results for the

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

stable yellow solutions were consistent with the formation of Se_4^{2+} according to eq 11.

$$4Se + 6H_2S_2O_7 \longrightarrow Se_4^{2+} + 2HS_3O_{10}^- + 5H_2SO_4 + SO_2 \quad (11)$$

Selenium polycations (Se_n^{2+}, Se_n^+, etc.) have also been suggested by Lundkvist[53] to account for the conductivity of solutions of selenium in $SeCl_2$.

Table IV

Preparation of Compounds Containing Polycations of Selenium

Compound	Reaction	Conditions	Ref
$Se_4(HS_2O_7)_2$	Se + 65% oleum	50–60°; left until yellow-brown; crystals given on standing	54
$Se_4S_4O_{13}$	Se + excess SO_3	0°; left 24 hr	54
$Se_4(SO_3F)_2$	$4Se + S_2O_6F_2$	Solvent HSO_3F	54
$Se_4(Sb_2F_{11})_2$	Se + excess SbF_5	Heated at 100–140° for 6 hr	54
$Se_4(AsF_6)_2$	$8Se + 6AsF_5$	Solvent SO_2, 80° for 8 days; yellow solid deposited from green solution	61
$Se_8(Sb_2F_{11})_2$	$8Se + 5SbF_5$	Solvent SO_2, −23° for 3 days	55
$Se_8(AsF_6)_2$	$8Se + 3AsF_5$	Solvent HF; warmed slowly from −78 to 0° over 3 days	55
$S_8(AlCl_4)_2$ $Se_4(AlCl_4)_2$	Obtained from Se–($SeCl_4$–$4AlCl_3$) melts		46

Compounds Containing the Se_4^{2+} and Se_8^{2+} Ions. A number of solid compounds of Se_4^{2+} and Se_8^{2+} have been prepared by oxidizing selenium with sulfur trioxide, oleum, SbF_5, or AsF_5. Information on these preparations is summarized in Table IV. The presence of the Se_4^{2+} and Se_8^{2+} cations in these compounds was confirmed by comparison of the Raman spectra of the solids and the absorption spectra of their solutions in oleum or HSO_3F with those obtained previously for solutions of Se_4^{2+} and Se_8^{2+} in these solvents (Figure 3 and Table II).[54,55] $Se_4(HS_2O_7)_2$ and $Se_4S_4O_{13}$ have very

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(53) M. Lundkvist, *Acta Chem. Scand.*, **22**, 287 (1968).

(54) J. Barr, D. B. Crump, R. J. Gillespie, R. Kapoor, and P. K. Ummat, *Can. J. Chem.*, **46**, 3607 (1968).

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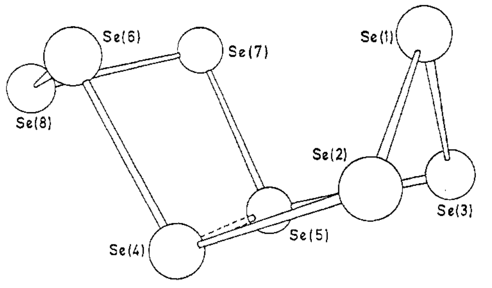
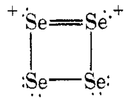


Figure 4. Structure of the Se_8^{2+} ion.

similar analyses and were both previously incorrectly described as $SeSO_3$.[56] From phase diagram studies[57] on the systems Se–($SeCl_4$–$4AlCl_3$), the compounds $Se_4(AlCl_4)_2$ and $Se_8(AlCl_4)_2$ have been identified, and the crystal structure of the latter compound has been reported.[46] The yellow compound of empirical formula $Se(SbF_5)_2$ described by Aynsley, Peacock, and Robinson[48] has not been confirmed, but it seems very probable that, whatever its exact composition, it also contains the Se_4^{2+} ion.

The Structures of Se_4^{2+} and Se_8^{2+}. An X-ray study of $Se_4(HS_2O_7)_2$ has shown that Se_4^{2+} is square planar,[58,59] with an Se–Se bond length of 2.28 Å compared with the Se–Se distance of 2.34 Å in the Se_8 molecule. This square-planar structure is also consistent with the infrared and Raman spectra of several compounds containing Se_4^{2+}[60,61] (Table IV), and a normal coordinate analysis yielded a value of 2.2 mdyn Å^{-1} for the Se–Se stretching constant, which is somewhat greater than the value of 1.67 mdyn Å^{-1} obtained for the single Se–Se bond in $(CH_3)_2Se_2$. The square-planar arrangement is also consistent with the magnetic circular dichroism of the ion in solution.[49] The short Se–Se bond length and the high force constant both indicate a bond order of somewhat greater than unity.

The structure of Se_4^{2+} can be described by valence bond theory in terms of four resonance structures equivalent to **5** or by MO theory by the structure **6**, where the circle denotes a closed-shell ("aromatic?") six-π-electron system.[58] Of the four π molecular or-



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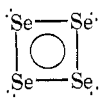


6

bitals, 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}) orbital empty.

The structure of Se_8^{2+} in $Se_8(AlCl_4)_2$ (Figure 4) is very similar to that of S_8^{2+} and consists of a folded ring in the *endo,exo* conformation with approximate 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. Of particular significance is the short cross-ring distance Se_4–Se_5 of 2.84 Å, which is considerably less than the van der Waals contact separation of approximately 3.8 Å. The other cross-ring distances do not appear to be significantly shorter than the van der Waals distance, and thus the structure is probably best described by the valence bond structure **7**, although there may be a small contribution from structures analogous to **2**, **3**, and **4** proposed for S_8^{2+}.

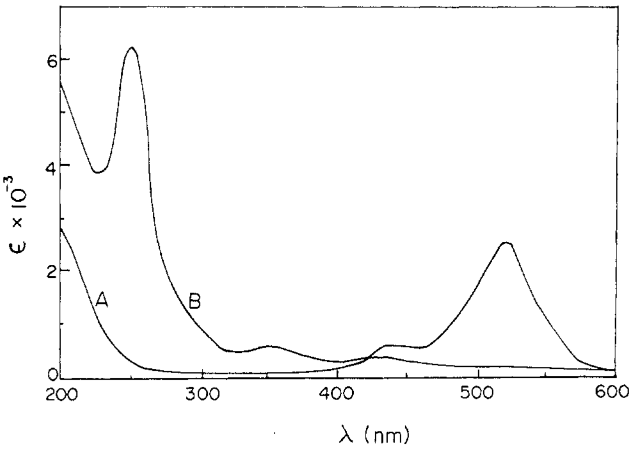
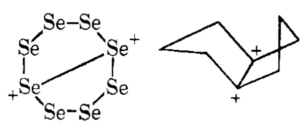


Figure 5. Absorption spectra of solutions of Te_4^{2+} (A) and Te_n^{n+} (B) in HSO_3F.



7

Tellurium Polycations

In 1798 it was reported[62] that elemental tellurium reacted with concentrated sulfuric acid to yield a red solution. More recently, Bjerrum and Smith[63] and Bjerrum[64] have studied the reaction of tellurium tetrachloride with tellurium in molten $AlCl_3$–NaCl. They obtained a purple melt which they concluded contained Te_{2n}^{n+} (probably Te_4^{2+}). Awad[65] has postulated Te_2^+ and Te^+ to explain his results on the anodic dissolution of tellurium in nonoxidizing acids.

Tellurium dissolves in fluorosulfuric acid[66] to give a red solution of identical visible–ultraviolet spectrum with that obtained by Bjerrum and Smith in molten $AlCl_3$–NaCl (Figure 5). Conductometric and cryoscopic measurements showed that tellurium is in the $^1/_2+$ oxidation state and that the ion contains eight or fewer tellurium atoms.

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(59) I. D. Brown, D. B. Crump, and R. J. Gillespie, *Inorg. Chem.*, **10**, 2319 (1971).
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(61) R. J. Gillespie and P. K. Ummat, unpublished results.
(62) M. H. Klaproth, *Phil. Mag.*, **1**, 78 (1798).
(63) N. J. Bjerrum and G. P. Smith, *J. Amer. Chem. Soc.*, **90**, 4472 (1968).
(64) N. J. Bjerrum, *Inorg. Chem.*, **9**, 1965 (1970).
(65) S. A. Awad, *Electrochim. Acta*, **13**, 925 (1968).
(66) J. Barr, R. J. Gillespie, R. Kapoor, and G. P. Pez, *J. Amer. Chem. Soc.*, **90**, 6855 (1968).

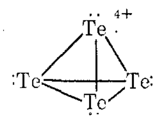
Table V

Preparation of Compounds Containing Polycations of Tellurium

Compound	Reaction	Conditions	Ref
$Te_4(Sb_2F_{11})_2$	$Te + SbF_5$	Solvent SO_2; stirred for several days at −23°; SO_2-soluble products extracted by the solvent	68
$TeSbF_6$	$Te + SbF_5$	$TeSbF_6$ is insoluble in SO_2, therefore readily separated from $Te_4(Sb_2F_{11})_2$	67, 68
$Te_4(AsF_6)_2$	$4Te + 3AsF_5$	Solvent SO_2; stirred at 25° for 1 day	68
Te_3AsF_6	$6Te + 3AsF_5$	Conditions as above	68
$Te_4(SO_3F)_2$	$4Te + S_2O_6F_2$	Solvent SO_2; stirred at −63° and −23°, respectively, for 1 day	68
$TeSO_3F$	$4Te + S_2O_6F_2$ (excess)	Compound is unstable above −20°	67, 68
$Te_4(AlCl_4)_2$ $Te_4(Al_2Cl_7)_2$ $Te_6(AlCl_4)_2$	Obtained from $Te-(TeCl_4-4AlCl_3)$ melts		56

The red solids, $Te_4(Sb_2F_{11})_2$, $Te_4(SO_3F)_2$, $Te_4(AsF_6)_2$, $Te_4(AlCl_4)_2$, and $Te_4(Al_2Cl_7)_2$, have been prepared[56,67,68] (Table V). The Raman spectrum of the tellurium cation is essentially the same in the solids and in solution (Table II). The ultraviolet, visible, and Raman spectra of the solids and their solutions and the magnetic circular dichroism of solutions of Te_4^{2+}[49] were found to be very similar to those for Se_4^{2+}, strongly suggesting that Te_4^{2+} also has a square-planar structure (Table II). This has very recently been confirmed by an X-ray crystallographic study of $Te_4(AlCl_4)_2$ and $Te_4(Al_2Cl_7)_2$[69] in which the Te–Te bond length in the square Te_4^{2+} was found to be 2.67 Å.

Tellurium can be oxidized by $S_2O_6F_2$ in fluorosulfuric acid to the yellow Te_n^{n+}.[67,68] Solids of empirical formula $TeSbF_6$, $TeSO_3F$, and $Te_2S_3O_{10}$ have been prepared.[67,68] These compounds, and concentrated solutions of Te_n^{n+}, are diamagnetic, ruling out the possible formulas Te^+, Te_3^{3+}, etc. Cryoscopic measurements on Te_n^{n+} in fluorosulfuric acid showed that the cation is not Te_2^{2+}, but could not distinguish with certainty between Te_4^{4+}, Te_6^{6+}, and Te_8^{8+}. Possible structures are 8, 9, and 10. The absorption spectrum of a solution of this ion in fluorosulfuric acid is given in Figure 5.



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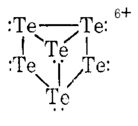

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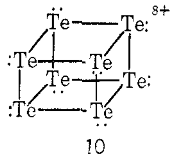

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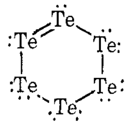
Table VI

Polycations of Group VI

Oxidation state				
1+	1/2+	1/3+	1/4+	1/8+
	O_2^+			
	S_4^{2+}		S_8^{2+}	S_{16}^{2+}
	Se_4^{2+}		Se_8^{2+}	
Te_n^{n+}	Te_4^{2+}	Te_6^{2+}		

A gray solid of empirical formula Te_3AsF_6 has been prepared[68] by treating tellurium with the stoichiometric amount of arsenic pentafluoride in liquid SO_2. The compound is diamagnetic, and is therefore probably $Te_6^{2+}(AsF_6^-)_2$. In the phase diagram studies of the system $Te-(TeCl_4-4AlCl_3)$, Corbett, *et al.*,[57] found the phase $(Te_3AlCl_4)_n$, and they were able to grow black crystals of this material 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 $Te_6(AlCl_4)_2$. Evidence for a lower oxidation state of tellurium has been previously obtained by Bjerrum and Smith[65] from experiments in which they added more than seven parts of tellurium to one part of $TeCl_4$ in molten $AlCl_3$–NaCl. There is as yet no evidence on the structure of Te_6^{2+}; the six-membered ring containing a double bond (**11**) is a possibility, or possibly six resonance structures of this type.



11

Conclusions

A list of the polycations of group VI that have been prepared to date is given in Table VI.

It would appear that the pattern of group VI polycation formation follows general group trends. The high π-bond energy and low σ-bond energy of oxygen favor O_2^+ formation rather than the dimer O_4^{2+}. The reverse is the case for sulfur; the high σ-bond energy relative to π-bond strength perhaps explains why elemental sulfur forms S_8 molecules rather than gaseous S_2, and also why S_4^{2+} is formed rather than S_2^+. The more metallic nature of tellurium is reflected in the formation of Te_n^{n+}, the species with the highest positive charge per atom of the group VI polycations.

It is clear that polycations of the main group elements are no longer just a chemical curiosity restricted to the odd isolated example but are probably a fairly general occurrence. There probably will be considerable development of this new field in the near future.

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