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THE FLUORIDE ION AFFINITIES OF GeF_4 AND BF_3 FROM THERMODYNAMIC AND STRUCTURAL DATA FOR $(SF_3)_2GeF_6$, ClO_2GeF_5 AND ClO_2BF_4

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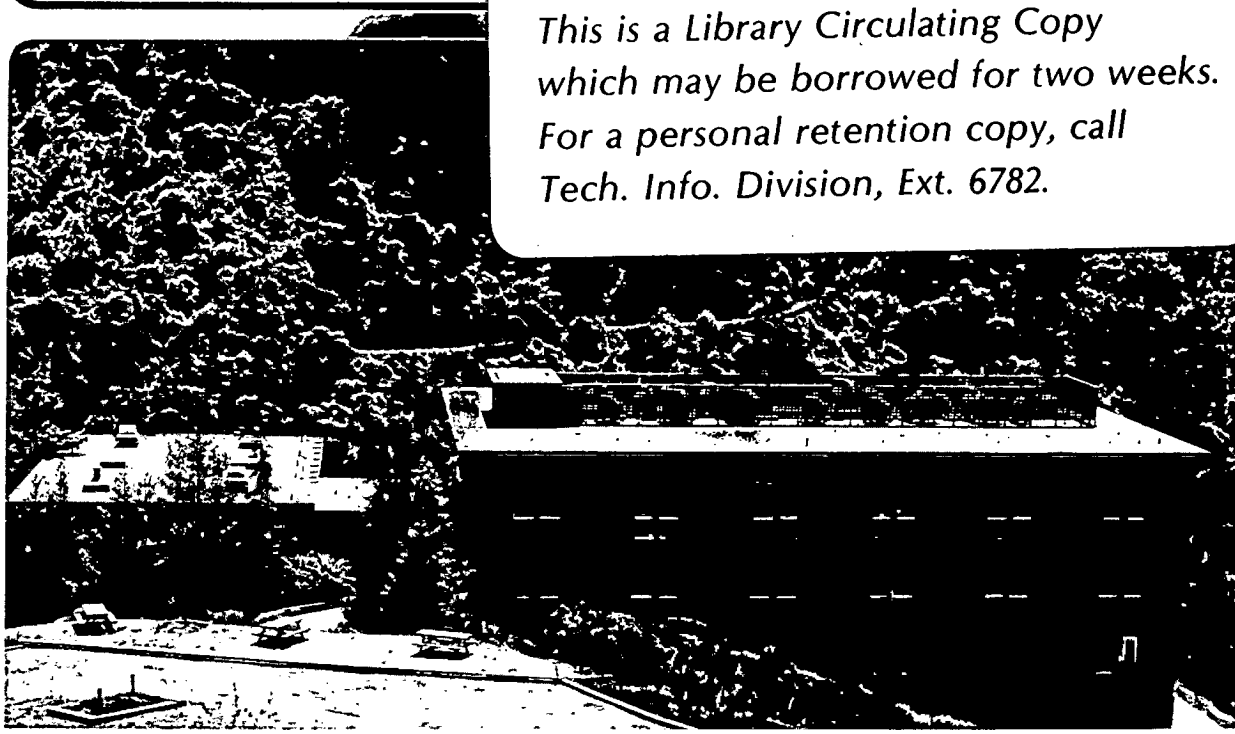

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The Fluoride Ion Affinities of GeF_4 and BF_3 from Thermodynamic and Structural Data for $(SF_3)_2GeF_6$, ClO_2GeF_5 and ClO_2BF_4

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ABSTRACT

$(SF_3)_2GeF_6$ is orthorhombic with a = 6.142(1); b = 9.593(1); c = 7.458(1) Å; V = 439.4(2) Å^3; ρ_{calc} = 2.756. Full matrix least squares refinement using 299 independent observations (MoK$_{\bar{\alpha}}$, graphite monochromator) in space group Pmnn (No. 58) yielded weighted R = 0.025 (unweighted 0.016) from which SF_3^+ ions are seen to have $\sim C_{3v}$ symmetry with S-F = 1.515(2), 1.519(2) Å; F-S-F angle = 96.2(1)°. Each SF_3^+ makes close contact with one F atom from each of three GeF_6^{2-} ions to give a distorted octahedron of F about S. The GeF_6^{2-} ions are almost octahedral with GeF = 1.783(1), 1.787(1) Å and cis F-Ge-F angles within 3σ of 90°, each F ligand being 2.37 to 2.42 Å from an S atom of an SF_3^+. Lattice energy calculation gives $\Delta H°(2SF_{3(g)}^+ + GeF_{6(g)}^{2-} = (SF_3^+)_2GeF_{6(s)}^{2-}) = -383(12)$ kcal mole^{-1}. From dissociative pressure dependence on temperature: $\Delta H°[(SF_3)_2GeF_{6(s)} = 2SF_{4(g)} + GeF_{4(g)}] =$ 42.9(6) kcal mole^{-1}, $\Delta S°$ = 125(2) cal mole^{-1}. Similarly $\Delta H°(ClO_2GeF_5 =$

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$ClO_2F_{(g)} + GeF_{4(g)}) = 29.1(4)$ kcal mole^{-1}, $\Delta S° = 90(1)$ cal mole^{-1}K^{-1}. Calculation of $\Delta H°(ClO_2^+{}_{(g)} + GeF_5^-{}_{(g)} = ClO_2^+GeF_5^-{}_{(s)})$ gives -146(5) kcal mole^{-1}. The derived enthalpy changes are $\Delta H°(GeF_{4(g)} + F^-_{(g)} = GeF^-_{5(g,\ polymer)})$. = -98(7) and $\Delta H°(GeF_{4(g)} + 2F^-_{(g)} = GeF^{2-}_{6(g)})$ = -82(18) kcal mole^{-1}.

ClO_2BF_4 is monoclinic with a = 5.522(1); b = 8.646(1); c = 9.549(2); β = 98.01(1)°; V = 451.4(2) Å^3; ρ_{calc} = 2.269. The structure was refined in space group Cc (No. 9) to yield a weighted R = 0.032 (unweighted 0.023) from 577 independent reflections. All four fluorine atoms of the tetrahedral BF_4^- ion form van der Waals' contacts to the chlorine atoms of neighboring ClO_2^+ ions. The closest of these contacts are nearly perpendicular to the plane defined by the centers of the chlorine and oxygen atoms. From measurements of the dissociation pressure of $ClO_2^+BF_4^-$ the previously reported value[1] of $\Delta H°(ClO_2F_{(g)} + BF_{3(g)} = ClO_2BF_{4(s)})$ = -24(1) kcal mole^{-1} has been confirmed. Lattice energy calculations have provided for evaluation of the following enthalpy changes: $\Delta H°(BF_{3(g)} + F^-_{(g)} = BF_{4(g)})$ = -92(6), $\Delta H°(SF_{4(g)} = SF^+_{3(g)} + F^-_{(g)})$ = 211(8), and $\Delta H°(UF_{6(g)} + e^- = UF^-_{6(g)})$ = -133(6) kcal mole^{-1}.

Introduction

The discovery[2] of what appears to be a thermodynamic threshold governing the intercalation of graphite by fluoro anions, MF_x^-, has required the evaluation of the thermodynamic stability of a number of such species. Since germanium tetrafluoride and fluorine are intercalated, in combination, by graphite[3] to form both GeF_5^- and GeF_6^{2-}, the first and second fluoride-ion affinities of that molecule are each of interest. Evaluation of the fluoride ion affinity of boron trifluoride by Altschuler[4] yielded a value of -71 kcal

mole^{-1}. This has been accepted by several authors[5,6] as the basis for other fluoride ion affinities and electron affinities. Sharpe[7], however, has preferred a value of -91 kcal mole^{-1}, based upon the data of Bills and Cotton[8]. Although this latter value is in harmony with other fluoride ion affinities and electron affinities, its confirmation was clearly desirable to provide a firm basis for correction of affinities based upon the lower value. This paper describes the studies which have provided these fluoride ion affinities.

The salts $ClO_2^+GeF_5^-$ and $(SF_3^+)_2GeF_6^{2-}$, each of which dissociates to stable component species at easily accessible temperatures, have provided for the determination of the following enthalpy changes:

$$\Delta H^\circ(ClO_2GeF_{5(s)} \rightarrow ClO_2F_{(g)} + GeF_{4(g)}) \quad (1)$$

$$\Delta H^\circ[(SF_3)_2GeF_{6(s)} \rightarrow 2\ SF_{4(g)} + GeF_{4(g)}] \quad (2)$$

The salt $ClO_2^+BF_4^-$ also dissociates extensively at ordinary temperatures, and the enthalpy change:

$$\Delta H^\circ(ClO_2BF_{4(s)} \rightarrow ClO_2F_{(g)} + BF_{3(g)}) \quad (3)$$

has been reported[1] to be -24(1) kcal mole^{-1}. This finding has been confirmed in the present study.

The crystal structures of the salts have been determined, ClO_2GeF_5 being reported in the accompanying paper[9], and the $(SF_3)_2GeF_6$ and ClO_2BF_4 structures in this paper. From that structural information, lattice energies for the latter two salts have been derived after the method of Bertaut[10] as modified by Templeton[11]. These provide enthalpy changes for the processes:

$$\Delta H^\circ(2SF_{3(g)}^{+} + GeF_{6(g)}^{2-} \rightarrow (SF_3)_2GeF_{6(s)}) \quad (4)$$

$$\Delta H^\circ(ClO_{2(g)}^{+} + BF_{4(g)}^{-} \rightarrow ClO_2BF_{4(s)}) \quad (5)$$

The lattice enthalpy for ClO_2GeF_5:

$$\Delta H^\circ(ClO_{2(g)}^{+} + GeF_{5(g)} \rightarrow ClO_2GeF_{5(s)}) \quad (6)$$

has been estimated from a simple linear empirical relationship between lattice energy and the reciprocal of the cube root of the formula unit volume.

The enthalpy change:

$$\Delta H^\circ(ClO_2F_{(g)} \rightarrow ClO_2^{+} + F_{(g)}^{-}) \quad (7)$$

is known from previously reported data[12,13,14], hence the values of

$$\Delta H^\circ(GeF_{4(g)} + F_{(g)}^{-} \rightarrow GeF_{5(g)}^{-}) \quad (8)$$

$$\Delta H^\circ(BF_{3(g)} + F_{(g)}^{-} \rightarrow BF_{4(g)}^{-}) \quad (9)$$

are obtained directly from the complete thermodynamic cycles. In the case of the $(SF_3)_2GeF_6$ salt however, the enthalpy change:

$$\Delta H^\circ(SF_{4(g)} \rightarrow SF_{3(g)}^{+} + F_{(g)}^{-}) \quad (10)$$

was uncertain. This uncertainty derived from disagreement on the value of

$$\Delta H^\circ(BF_{3(g)} + F_{(g)}^{-} \rightarrow BF_{4(g)}^{-}) \quad (9)$$

to be used to complete the cycle for the salt $SF_3^{+}BF_{4(s)}^{-}$. The crystal structure of this salt is accurately known[15] and the enthalpy change:

$$\Delta H^\circ(SF_3BF_{4(s)} \rightarrow SF_{4(g)} + BF_{3(g)}) \quad (11)$$

has been evaluated in three independent studies[16,17,18]. Since the reported electron affinity[19] of UF_6 had been based on the erroneous values for (9), an independent evaluation of

$$\Delta H^\circ(UF_{6(g)} + e^- \rightarrow UF^-_{6(g)}) \qquad (12)$$

has been derived from the thermodynamic data available[20], for the salt $NO^+UF^-_{6(s)}$. This also checks the lattice energy evaluations.

Experimental Section

Preparations and Structures. $(SF_3)_2GeF_6$: SF_4 and GeF_4 were brought together in a 2:1 molar ratio to produce a colorless solid $2SF_4.GeF_4$ which was purified by sublimation at room temperature. The apparatus, handling techniques, and starting material preparations are described in the accompanying paper.[9] Single crystals were grown by sublimation in quartz X-ray capillaries at 30-35°. Precession photographs indicated space group Pnn2 or Pnnm. A crystal mounted on a CAD-4 four circle diffractometer provided a data set collected in the manner previously described[9]. Because of the ready dissociation of this compound, data were gathered at -97±7°. They are given in Table I.

The structure was successfully refined, as described elsewhere[9], in the centric space group Pmnn (#58). Full matrix least squares refinement with anisotropic thermal parameters gave final convergence with weighted R = .025, unweighted R = .016, e.s.d.o.u.w. = 1.463 for 42 variables and 299 independent observations. The largest parameter shift in the final

refinement cycle was < 0.1σ. A final difference Fourier gave no peaks with density greater than 0.141 $e^-/Å^3$. Positional and thermal parameters for $(SF_3)_2GeF_6$ are given in Table II.

The sulfur and germanium coordination environments in the $(SF_3)_2GeF_6$ structure are shown in Figure 3. While the space group requires C_s symmetry at S and C_{2v} symmetry at Ge, the SF_3^+ ion has essentially C_{3v} symmetry with all S-F bonds of equal length and all F-S-F angles equal within one standard deviation; the GeF_6^{2-} ion is almost a regular octahedron with all Ge - F bond lengths equal within 1σ and with F-Ge-F angles differing from 90° by about 3σ. Each sulfur atom makes close contacts with one F atom from each of three different anions, and so the cation-anion coordination in $(SF_3)_2GeF_6$ is 6:3, with each fluorine atom in the GeF_6^{2-} octahedron making a bridging contact (2.37 - 2.42 Å) to a sulfur atom. Fluorine atoms in the SF_3^+ ion make only van der Waals' contacts (≥ 2.65 Å) with other fluorine atoms in the structure. The bridging by fluorine in this structure resembles that found[15] in SF_3BF_4, where the coordination is 3:3. The dimensions of SF_3^+ in $SF_3^+BF_4^-$ and $(SF_3^+)_2GeF_6^{2-}$ are not significantly different, and as has been remarked earlier[15], the F - S - F bond angle has the same value as that of F - P - F in the isoelectronic relative PF_3. Bond lengths and angles for $(SF_3)_2GeF_6$ are given in Table III.

<u>ClO_2BF_4</u>: ClO_2F and BF_3 were combined in a 1:1 molar ratio. The pale yellow solid product was purified by sublimation and handled in a manner similar to $(SF_3)_2GeF_6$. Single crystals were grown in quartz

capillaries at 25-30°. Precession photographs indicated space group C2/c or Cc. Data were gathered successfully at room temperature (Table I).

Refinement, in the acentric space group Cc (#9), with anisotropic thermal parameters, gave final convergence with weighted R = .032, unweighted R = .023, e.s.d.o.u.w. = 1.828 for 72 variables and 577 independent observations. The largest parameter shift in the final refinement cycle was 0.1σ. The largest peak in the final difference Fourier was 0.274 $e^-/Å^3$. Positional and thermal parameters for ClO_2BF_4 are given in Table IV.

Upon examination of the data, it was found that three reflections gathered consecutively, the $\bar{2}2\bar{1}$, $\bar{2}20$ and $\bar{2}21$, showed the worst fit of F_{obs} to F_{calc}. Intensities of these reflections were apparently not fully counted due to misorientation and were omitted from the final refinement.

A stereoview (Fig. 4) shows the coordination about the Cl atom in ClO_2BF_4. Selected bond lengths and bond angles are given in Table V. The closest Cl···F contacts (F_1, 2.534(2), and F_3, 2.580(1)Å) are those approximately normal to the plane defined by the ClO_2^+. The other two Cl···F contacts (F_2, 2.704(2), and F_4, 2.731(2)) are in that plane. All four Cl···F contacts, together with the Cl-O bonds, complete a grossly distorted octahedral coordination about the Cl atom. The additional ligands perpendicular to the ClO_2 plane are similarly placed to those in the $ClO_2^+GeF_5^-$ structure[9], where there are two crystallographically distinct ClO_2^+. The in-plane Cl···F contacts are different in $ClO_2^+BF_4^-$ from each of the two arrangements in $ClO_2^+GeF_5^-$. Evidently the Cl···F contacts

perpendicular to the ClO_2^+ plane are more significant than the others. The BF_4^- ions are almost tetrahedral.

Dissociation pressure measurements for $ClO_2^+GeF_5^-$ and $(SF_3^+)_2GeF_6^{2-}$

Vapor pressure measurements were made using a Monel diaphragm gauge as described by Cromer[21]. Each sample (1-2g.) was sublimed into a thin-walled quartz bulb partially collapsed to increase the surface area for good thermal contact. This was attached via Monel compression fittings to the gauge as shown in Figure 1.

The null point (no pressure difference across the nickel diaphragm) was established by closing A and C and opening B and D. For vapor pressure readings, the sample system and gauge were fully immersed in a water bath. Valve B was closed, A and C were opened, and E and D were adjusted to find the null point at each bath temperature at equilibrium, the pressure being determined from a mercury column. The sample was pumped out briefly between pressure readings, which were reproducible within 1 or 2 torr at low temperature (0-10°C) and within 4 or 5 torr at higher temperatures (25-35°C). Log P vs. 1/T data for ClO_2GeF_5 and $(SF_3)_2GeF_6$ are given in Table VI. Since for ClO_2GeF_5 $K_p = [P_{ClO_2F}]$

$[P_{GeF_4}] = \frac{1}{4}P^2$, and for $(SF_3)_2GeF_6$ $K_p = [P_{SF_4}]^2[P_{GeF_4}] = 4P^3/27$, we have from the van't Hoff relation, $d(\ln K_p)/d(1/T) = -\Delta H°/R$:

$$ClO_2GeF_{5(s)} = ClO_2F_{(g)} + GeF_{4(g)} \qquad \Delta H° = 29.1(4) \text{ kcal/mole}, \quad \Delta S° = 90(1) \text{ cal/mole°K}$$

$$(SF_3)_2GeF_{6(s)} = 2SF_{4(g)} + GeF_{4(g)} \qquad \Delta H° = 42.9(6) \text{ kcal/mole}, \quad \Delta S° = 125(2) \text{ cal/mole°K}$$

The identities of the gaseous species in equilibrium with the solids were established by infrared spectroscopy.

Lattice Energy Calculations

Electrostatic Terms

The electrostatic energy of a lattice of atoms of zero polarizability may be calculated exactly by the method of Bertaut[10], provided the position and charge of each atom in the structure is known. This method involves the infinite sum in reciprocal space:

$$U_{elec} = \frac{18\pi R^2}{V} \sum_{hkl} |F(hkl)|^2 \frac{(\sin\alpha - \alpha\cos\alpha)^2}{\alpha^8} - \frac{3}{5R} \sum_j q_j^2$$

where $F(hkl) = \sum_j q_j \exp(2\pi i \underline{h}\cdot\underline{r}_j)$, $\alpha = 2\pi R/d_{hkl}$,

q_j is the charge on atom j, $\underline{h} \cdot \underline{r}_j = hx_j + ky_j + lz_j$, where (x_j, y_j, z_j) are the fractional coordinates of atom j, R is one-half the shortest interatomic distance in the crystal, d_{hkl} is the distance between lattice planes hkl, and V is the volume of the unit cell. In practice the sum must be terminated at some finite value of h, k, and l, and to estimate the error introduced thereby, the modification introduced by Templeton[11] has been used. In all calculations the termination of the series was chosen so as to insure that this error was no greater than

0.2 kcal/mole. Fractional charges were assigned to atoms using the electronegativity equalization procedure of Jolly and Perry[22]. Variation of these charges, within reasonable limits, produced small (1-3%) variations in the electrostatic part of the lattice energy; this is as expected since the multipolar interactions of complex ions in ionic crystals only amount to a few percent of the total lattice energy.[23]

London Energy Terms

The dipole-induced dipole dispersion energy (U_{dd}) is given by

$$U_{dd} = \frac{-3}{2} \sum_{i \neq j} \alpha_i \alpha_j \varepsilon_i \varepsilon_j \, r_{ij}^{-6} / (\varepsilon_i + \varepsilon_j)$$

where α and ε are respectively the polarizability and characteristic energy of the ion. The dipole-induced quadrupole energy (U_{dq}) is likewise given by a summation in r_{ij}^{-8}; it is however generally 10 - 15% of U_{dd}. We take U_{dq} to be 12% of U_{dd}.

The Closed-Shell Repulsion Term

A number of approaches to the calculation of closed shell repulsion energies may be found in the literature. Ladd and Lee[24] have successfully used the expression:

$$U_r = B \exp(-r_o/\rho)$$

where B is a constant eliminated by the criterion of energy minimization, r_o the shortest interatomic distance, and ρ a parameter usually determined from compressibility data. In the absence of such data, Born and Mayer's equation[25] may be used:

$$U_r = b \sum_{i \neq j} (1 + q_i/n_i + q_j/n_j) \exp[(\bar{r}_i + \bar{r}_j - r_{ij})/\rho]$$

Here n is the number of electrons in the outer shell of the ion, q is the charge of the ion, $\bar{r}$ is its "basic radius", r_{ij} is the distance between ions i and j, and b and ρ are constants (10^{-12} erg molecule^{-1} and 0.32 - 0.36 Å, respectively). The range of variation of the parameter ρ is smaller when this expression for U_r is used. The Born-Mayer expression was used exclusively in the present calculations.

The Zero Point Vibrational Energy and $\int C_p dT$ Terms

A complete lattice enthalpy at 298 K must include the enthalpy of cooling the gaseous ions to 0 K, the enthalpy of warming the crystal from 0 K to 298 K, and the zero point vibrational energy of the crystal.

For crystals containing relatively massive ions (SF_3^+, UF_6^-, GeF_6^{2-}, etc.), the zero point energy (U_z) is small (0.2 - 0.4 kcal mole^{-1}). For crystals containing lighter ions this term is more important and may be estimated from Waddington's correlation[26] of S^o_{298} with U_z. The specific heat (C_p) of the crystal is taken to be 3R per ion; C_p is taken to be 5/2 R for monatomic, 7/2 R for diatomic, and 4R for nonlinear polyatomic ions in the gas phase.

Derivation of Parameters

The assignment of polarizabilities, characteristic energies, and basic radii to the atoms in a crystal is not straightforward. Although readily accepted values for these quantities for alkali and halide ions are available, serious errors (vide infra) can arise if the values of α, $\bar{r}$, and ε of fluoride ions are applied to fluorine atoms in a complex ion or molecule. The present approach has been, instead, to calculate the lattice energies of the molecular fluoride crystals UF_6 and SiF_4 (ignoring M - F interactions in the calculation of the repulsion energy, since the

forces giving rise to it are of extreme short range). The sublimation enthalpies (and hence the lattice energies) are known for these compounds, and ε_F and $\bar{r}_F$ are derived parametrically, using the energy minimization criterion, if values are assumed for α_F, α_M, and ε_M. The last two terms are of reduced parametric importance since M - F interactions account for only a small fraction of the dispersion energies of these compounds. The average of the values derived for ε_F, 46.90 (SiF_4) and 52.24 (UF_6) eV molecule^{-1}, and $\bar{r}_F$, 1.053 (SiF_4) and 1.079 (UF_6) Å, are used in subsequent calculations. These quantities are derived in the Appendix.

Calculations

The derived fluorine parameters were applied to calculations for the salts $SF_3^+BF_4^-$, $NO^+UF_6^-$, $(SF_3^+)_2GeF_6^{2-}$, $ClO_2^+BF_4^-$, and $K^+BF_4^-$. If the central atom in the anion is assumed to make no contribution to U_r, the lattice energy of the salt and the basic radius of the central atom in the cation may be calculated by minimizing the lattice energy with respect to variation in a crystallographic dimension r; r is chosen as the cube root of the unit cell volume, and so dM/dr = 0, where M is the Madelung constant. The following details for the salt $SF_3^+BF_4^-$ exemplify this approach:

From $(dU_L/dr)_{r=r_o} = 0$, we have

$$U_{elec} + 6U_{dd} + 8U_{dq} = b[\exp(2\bar{r}_S/\rho)\ \Sigma_{\underline{A}} + \exp((\bar{r}_S + \bar{r}_F)/\rho)\ \Sigma_{\underline{B}} + \exp(2\bar{r}_F/\rho)\ \Sigma_{\underline{C}}]$$

where $\Sigma_{\underline{A},\underline{B},\underline{C}} = \sum_{i \neq j} (1 + q_i/n_i + q_j/n_j) r_{ij}/\rho \exp(-r_{ij}/\rho)$

$\underline{A}$ refers to the sum over S - S, $\underline{B}$ over S - F, and $\underline{C}$ over F - F interactions. As pointed out by previous workers[27], this equation is quadratic in $\exp(\bar{r}_S/\rho)$, and so we obtain $\bar{r}_S$ and hence U_r from Born and Mayer's equation.

Calculation of the dispersion energy terms U_{dd} and U_{dq} requires that ε and α be assigned to the central atom of the cation (S in SF_3^+, Cl in ClO_2^+, NO^+, and K^+). The polarizability of cationic sulfur and chlorine atoms should be less than that of the neutral argon atom[28], 1.6 Å^3, and slightly larger than that of K^+, for which a preferred value[29] of 1.029 Å^3 has been given. We take these to have a polarizability of 1.2 Å^3 and NO^+ (which occupies about the same valume as a K^+ ion in its salts) to have a polarizability of 1.0 Å^3. The characteristic energy is taken as 9/10 of the second ionization potential of the free atom.

Table VII shows the calculated lattice enthalpies for $SF_3^+BF_4^-$, $NO^+UF_6^-$, $(SF_3^+)_2GeF_6^{2-}$, $ClO_2^+BF_4^-$, and $K^+BF_4^-$, and the derived basic radii for $S^{+.94}$, $Cl^{+1.1}$, NO^+, and K^+. In these calculations a value of ρ = 0.333 Å was chosen, since this is the preferred value for the alkali fluorides[27]. Variation of ρ between 0.333 and 0.360 produced a variation of 1.5 kcal mole^{-1} in the lattice enthalpy calculated for $SF_3^+BF_4^-$. Likewise a variation of $U_{dd} + U_{dq}$ by 25% (= 9.5 kcal mole^{-1}) produced a change in the calculated lattice enthalpy of only 2.4 kcal mole^{-1}, because of a compensating change induced in U_r.

For $ClO_2^+GeF_5^-$ the method of calculation of the lattice enthalpy outlined above cannot be applied since the anion rearranges from a monomer in the gas phase to a cis-bridged polymer in the crystal. The lattice energy of this salt may be estimated from its formula-unit volume. Since the lattice energy of a simple A^+B^- salt is dominated by the coulombic term (the repulsion energy and the dispersion energy terms being largely mutually canceling over a fairly wide range of formula-unit volumes), a roughly linear correlation between the lattice energy and $M/(r_{A^+-B^-})$ is expected, where M is the

Madelung constant and $r_{A^+-B^-}$ is the shortest cation - anion distance in the crystal. Kapustinskii has shown[30], however, that $M/(r_{A^+-B^-})$ is relatively invariant with transformation from one structural type to another for the same ions A^+ and B^-; and so one should expect a linear correlation between the lattice energy and the inverse of the average primitive unit cell edge, i.e., the cube root of the formula-unit volume in the crystal. This linear correlation is shown in Fig. 2. The correlation is particularly good among members of a given structural family, e.g., NaCl or CsCl. Where the dispersion energy term is expected to be large, because of highly polarizable or strongly coordinating ions (e.g., TlCl, ClO_2BF_4, SF_3BF_4), a positive deviation is seen. The lattice enthalpy of $ClO_2^+GeF_5^-$ is therefore calculated simply from the U_L vs. $V^{-1/3}$ plot, allowing the same positive deviation as for $ClO_2^+BF_4$, to give $\Delta H°_L(ClO_2GeF_5) = 146(5)$ kcal mole^{-1}.

Results and Discussion

Fluoride Ion Affinities

Boron trifluoride -- The enthalpy change for the reaction:

$$ClO_2F_{(g)} + BF_{3(g)} = ClO_2BF_{4(s)}$$

had been reported[1] to be -24 (1) kcal mole^{-1}. This value has been confirmed by our measurements. Since $\Delta H°_L(ClO_2BF_4) = 149(5)$ kcal, then we have from $\Delta H°_f(ClO_2F) = -8.0(5)$ kcal[12], $\Delta H°_f(ClO_2) = 24.5(8)$ kcal[13], $ClO_2 = ClO_2^+ + e^-$ ($\Delta H° = +246.6(23)$ kcal[14]), and $\Delta H°_f(F^-) = -62(1)$ kcal, that for $BF_{3(g)} + F^-_{(g)} = BF^-_{4(g)}$, $\Delta H° = -92(6)$ kcal mole^{-1}. This is in agreement with the value calculated by Sharpe[7] from the data originally published by Bills and Cotton[8], but disagrees with the often cited value

of -71 kcal which derives[5] from the enthalpy change for the reaction $KBF_{4(s)} = KF_{(s)} + BF_{3(g)}$.

Uranium hexafluoride -- The electron affinity of UF_6 has been evaluated at 113 kcal mole^{-1} by Beauchamp and coworkers[19] from measurement of the enthalpy of the reaction:

$$UF^-_{6(g)} + BF_{3(g)} = BF^-_{4(g)} + UF_{5(g)} \qquad \Delta H° = +37\ (4)\ \text{kcal}$$

Substituting the revised value of -92 kcal for $\Delta H°(BF_{3(g)} + F^-_{(g)} = BF^-_{4(g)})$ in place of the -71 assumed by Beauchamp, et al. and using -62 kcal for the heat of formation of F^-, we obtain $E(UF_6) = 135$ kcal.

Since $\Delta H°(NO_{(g)} + UF_{6(g)} = NOUF_{6(s)}) = -52$ kcal[20], from the ionization potential of NO (+213 kcal) and our calculated lattice enthalpy for $NOUF_6$ (132 kcal) we obtain $E(UF_6) = 133$ kcal. This agreement of the cyclotron resonance and lattice energy evaluations of $E(UF_6)$ points to the correctness of the -92 kcal value for $\Delta H°(BF_{3(g)} + F^-_{(g)} = BF^-_{4(g)})$ and also indicates that the lattice energy evaluations are reliable.

Sulfur tetrafluoride -- We may now calculate $\Delta H°(SF_{4(g)} = SF^+_{3(g)} + F^-_{(g)}) = +211(8)$ kcal from $\Delta H°_L(SF_3BF_4) = 144(5)$, $\Delta H°(BF_{3(g)} + F^-_{(g)} = BF^-_{4(g)}) = -92(6)$ and $\Delta H°(SF_{4(g)} + BF_{3(g)} = SF_3BF_{4(s)}) = -25(1)$ kcal.

The first fluoride ion affinity of GeF_4 is obtained from $\Delta H°(ClO_2F_{(g)} = ClO^+_{2(g)} + F^-_{(g)}) = +217(3)$, $\Delta H°(ClO_2F_{(g)} + GeF_{4(g)} = ClO_2GeF_{5(s)}) = -29(1)$, and $\Delta H°_L(ClO_2GeF_5) = 146(5)$ kcal mole^{-1}. Thus $\Delta H°(GeF_{4(g)} + F^-_{(g)} = GeF^-_{5(g,\ polymer)}) = -100(6)$ kcal mole^{-1}.

From $\Delta H°(2SF_{4(g)} = 2SF^+_{3(g)} + 2F^-_{(g)}) = 422(16)$, $\Delta H°(2SF_{4(g)} + GeF_{4(g)} = (SF_3)_2GeF_{6(s)}) = -43(1)$, and $\Delta H°_L[(SF_3)_2GeF_6] = -383(12)$ kcal mole^{-1}, the double fluoride ion affinity $\Delta H°(GeF_{4(g)} + 2F^-_{(g)} = GeF^{2-}_{6(g)}) = -82(18)$ kcal mole^{-1} is obtained.

Thus the first fluoride ion affinity of GeF_4 to form the polymeric ion $(GeF_5)_n^{n-}$ exceeds that of BF_3 by 8 kcal $mole^{-1}$. Because of the smaller volume of BF_4^- relative to the uni-negative unit of $(GeF_5)_n^{n-}$, the more favorable lattice energy of the former approximately offsets the higher fluoride ion affinity of GeF_4 at least in salts with small cations. In cases where cations are large and the values of the lattice energies of the $(GeF_5)_n^{n-}$ and BF_4^- salts are therefore closer, the thermodynamic stability of the $(GeF_5)_n^{n-}$ salts must exceed those of the corresponding fluoroborates.

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Appendix

For the compounds SiF_4 and UF_6 we have:

$$U_r = b(1 + 2q_F/n_F)\exp(2\bar{r}_F/\rho) \sum_{i\neq j} \exp(-r_{ij}/\rho)$$

$$U_{dq} \simeq 0.12\ U_{dd}$$

The lattice energy (U_L) is given by:

$$U_L = U_{elec} + U_{dd} + U_{dq} - U_r - U_z$$

Since $(dU_L/dr)_{r=r_o} = 0$, we have

$$U_{elec} + 6U_{dd} + 8U_{dq} = b(1 + 2q_F/n_F)\exp(2\bar{r}_F/\rho) \sum_{i\neq j} r_{ij}/\rho \exp(-r_{ij}/\rho)$$

Substituting $U_{dq} = 0.12\ U_{dd}$, we obtain

$$U_r = \left[\frac{U_L + U_z - .8391\ U_{elec}}{\sum_{i\neq j} (.1609 r_{ij}/\rho - 1)\exp(-r_{ij}/\rho)}\right] \sum_{i\neq j} \exp(-r_{ij}/\rho)$$

$$\bar{r}_F = \rho/2\ \ell n \left[\frac{U_L + U_z - .8391\ U_{elec}}{b(1 + 2q_F/n_F) \sum_{i\neq j} (.1609 r_{ij}/\rho - 1)\exp(-r_{ij}/\rho)}\right]$$

We note that U_r (and thus $U_{dd} + U_{dq}$) is independent of the constant b and thus depends only on the choice of ρ, the calculated electrostatic energy, and the measured sublimation enthalpy. However, $\bar{r}_F$ depends on both b and ρ.

The crystal structures of SiF_4 and UF_6 are accurately known[31,32], and the polarizabilities, characteristic energies, and fractional charges assigned to each atom are shown in Table V. From these we obtain U_{elec} = 1.1(1) kcal mole^{-1} for SiF_4 and 2.0(1) kcal mole^{-1} for UF_6; the heats of sublimation are 6.2 kcal mole^{-1} (at 177K) for SiF_4[33] and 11.8 kcal mole^{-1} (at 298K) for UF_6.[34] The calculated values of ε_F and $\bar{r}_F$ (using a polarizability of 0.80 Å^3 for F) are shown for three choices of ρ in Table VIII. Since the characteristic energy of an atom is related to its ionization potential, it is not surprising that the derived value of ε_F for these (nearly electroneutral) fluorine atoms is significantly higher than that calculated by Mayer[35] for the fluoride ion in the alkali fluorides. $\bar{r}_F$ is likewise slightly smaller than the fluoride ion value determined by Jenkins and Pratt[27]. The agreement between the parameters derived from the SiF_4 and UF_6 calculations is reasonably good; when the lattice energy of SF_3BF_4 was calculated using the two sets of parameters, the calculations differed by 1.3 kcal/mole. Average values of $\bar{r}_F$ and ε_F are adopted for subsequent calculations. Oxygen parameters $\bar{r}_O$ and ε_O are calculated from the OsO_4 structure[36] (for which the heat of sublimation[37] is 11.6 kcal at 300K and U_{elec} = 2.5(1) kcal mole^{-1}), assuming a polarizability of 0.90 Å^3 for the O atoms. Thus we obtain $\bar{r}_O$ = 1.144 Å and ε_O = 58.5 eV molecule^{-1}. The values of α and ε assigned to the central atom in the anion again have little impact on the result of the calculation.

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23. In these calculations we have taken the charge distributions of the individual atoms to be spherical. However, since the atoms are polarizable, they will in fact have multipolar charge distributions arising from the non-spherical arrangement of their (charged) near neighbors. The interactions of these multipoles will contribute another term to the electrostatic part of the lattice energy, which should be greater for NO^+, ClO_2^+, and SF_3^+ salts than for simple alkali halide salts. We have evaluated the largest of these, the dipole-monopole interaction term, for SF_3BF_4, by allowing each atom to become a permanent dipole (by virtue of its polarizability and the field created by the other point charges in the ion); the energy of this interaction is found to be $\sim$ 0.1 kcal $mole^{-1}$. While this model is crude, it nevertheless provides an estimate of the order of magnitude of such interactions, which is indeed small.

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Table I Crystal Data for $(SF_3)_2GeF_6$ and ClO_2BF_4

	$(SF_3)_2GeF_6$	ClO_2BF_4
crystal dimensions:	.022 x .018 x .020 cm	.04 x .02 x .02 cm
space group	Pmnn (non-standard setting of Pnnm, #58)	Cc (#9)
vol. ($Å^3$):	439.4(2)	451.4(3)
ρ(calc'd):	2.756	2.269
cell dimensions:	a = 6.142(1), b = 9.593(1), c = 7.458(1)Å	a = 5.522(1), b = 8.646(1), c = 9.549(a)Å, β = 98.0(1)°
radiation:	MoKα, graphite monochrometer (λ = .71073Å)	
2θ range:	3 - 45°	
scane mole:	θ - 2θ	
scane rate:	variable, maximum 50 sec.	
background:	.25 x Δθ, where Δθ = .50 + .347 tanθ	
hkl range:	±h, +k, +ℓ	±h, +k, ±ℓ
reflections measured:	687	684
orientation standards:	$(\bar{4}11)$, $(\bar{1}61)$, (006) every 250 reflections no reorintation	$(\bar{3}1\bar{6})$, $(1\bar{5}\bar{4})$, $(\bar{1}1\bar{6})$ every 50 reflections frequent reorintation
intensity standards:	$(\bar{4}11)$, $(\bar{1}61)$, (006) every 250 reflections no decay correction	$(11\bar{2})$, (060), $(\bar{1}3\bar{5})$ every 100 reflections non-linear isotropic decay correction applied
absorption coefficient (μcalc):	43.27 cm^{-1}	
transmission:	47.4% min., 64.7% max.	---

TABLE II

Positional and Thermal Parameters for $(SF_3^+)_2GeF_6^{2-}$

Atom	X	Y	Z	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
GE	0.5000(0)	0.5000(0)	0.000(0)	0.0083(1)	0.00307(5)	0.00541(8)	0.0000(0)	0.0000(0)	-0.0007(1)
S	0.0000(0)	0.25615(8)	0.0651(1)	0.0112(2)	0.00354(8)	0.0077(2)	0.0000(0)	0.0000(0)	0.0012(2)
F1	0.1842(2)	0.1547(1)	0.0267(2)	0.0189(4)	0.0057(2)	0.0132(3)	0.0074(5)	0.0060(6)	0.0002(3)
F2	0.0000(0)	0.1437(2)	0.3475(3)	0.0178(5)	0.0055(2)	0.0090(3)	0.0000(0)	0.0000(0)	0.0056(5)
F3	0.5000(0)	0.1757(2)	0.3819(3)	0.0193(5)	0.0071(2)	0.0074(3)	0.0000(0)	0.0000(0)	-0.0039(5)
F4	0.2946(2)	0.4160(1)	0.1298(2)	0.0133(3)	0.0066(2)	0.0088(2)	-0.0045(4)	0.0035(5)	0.0019(3)

The Form of the Anisotropic Thermal Parameter is:

$$\exp\left(-\left[B(1,1)h^2 + B(2,2)k^2 + B(3,3)\ell^2 + B(1,2)hk + B(1,3)h\ell + B(2,3)k\ell\right]\right)$$

Table III. Bond Lengths and Angles for $(SF_3^+)_2GeF_6^{2-}$

Ge - F2	1.787(1)	S - F3	1.515(2)
Ge - F4	1.783(1)	S - F4	2.420(1)
S - F1	1.519(1)		
S - F2	2.367(2)		

F2 - Ge - F4	89.83(5)
F1 - S - F1	96.23(10)
F1 - S - F2	82.86(6)
F1 - S - F3	96.12(8)
F1 - S - F4	179.22(7), 83.51(5)
F2 - S - F3	178.47(8)
F2 - S - F4	96.38(4)
F3 - S - F4	84.63(5)
F4 - S - F4	96.75(6)

TABLE IV

Positional and Thermal Parameters for $ClO_2^+BF_4^-$

Atom	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl	0.000	-0.7352(6)	0.250	0.0213(2)	0.0101(1)	0.0065(1)	-0.0005(2)	0.0020(2)	-0.0008(1)
O1	-0.0377(5)	0.0756(2)	0.2990(3)	0.0335(7)	0.0117(3)	0.0128(3)	0.0043(3)	-0.0028(8)	-0.0048(4)
O2	-0.0747(4)	-0.1995(2)	0.3237(2)	0.0347(7)	0.0132(3)	0.0110(3)	-0.0074(8)	0.0081(8)	0.0044(5)
B	0.4884(6)	0.0675(3)	0.0152(4)	0.0167(8)	0.0098(3)	0.0061(3)	0.001(1)	0.0003(1)	-0.0012(6)
F1	0.6348(4)	-0.0580(2)	0.0578(2)	0.0369(7)	0.0139(2)	0.0128(2)	0.0120(6)	-0.0113(8)	-0.0025(4)
F2	0.2652(4)	0.0549(2)	0.0626(2)	0.0273(6)	0.0208(3)	0.0114(2)	-0.0037(7)	0.0097(6)	0.0062(4)
F3	0.4492(3)	0.0723(2)	-0.1310(2)	0.0286(6)	0.0193(3)	0.0067(2)	-0.0020(6)	-0.0001(6)	-0.0001(3)
F4	0.6048(3)	0.2003(2)	0.0680(2)	0.0368(6)	0.0132(3)	0.0125(2)	-0.0075(6)	0.0037(7)	-0.0072(4)

Table V. $C\ell O_2^+BF_4^-$ - Bond Lengths and Angles

DISTANCES

Cℓ - O1	1.397(2)	B - F1	1.380(3)
Cℓ - O2	1.390(2)	B - F2	1.376(4)
Cℓ - F1	2.534(2)	B - F3	1.383(3)
Cℓ - F2	2.704(2)	B - F4	1.377(3)
Cℓ - F3	2.580(1)		
Cℓ - F4	2.731(2)		

ANGLES

O1 - Cℓ - O2	119.0(1)	F1 - C - F2	87.07(6)
O1 - Cℓ - F1	93.0(1)	F1 - C - F3	159.69(6)
O1 - Cℓ - F2	87.9(1)	F1 - C - F4	78.18(5)
O1 - Cℓ - F3	91.6(1)	F2 - C - F3	73.34(5)
O1 - Cℓ - F4	158.2(1)	F2 - C - F4	71.97(5)
O2 - Cℓ - F1	98.4(1)	F3 - C - F4	90.40(5)
O2 - Cℓ - F2	152.01(8)	F1 - B - F2	110.8(2)
O2 - Cℓ - F3	96.62(9)	F1 - B - F3	108.9(2)
O2 - Cℓ - F4	82.25(8)	F1 - B - F4	108.9(2)
		F2 - B - F3	108.3(2)
		F2 - B - F4	109.9(2)
		F3 - B - F4	110.1(2)

TABLE VI

ℓnK_p vs. $\frac{1}{T}$ for $ClO_2^+GeF_5^-$ and $(SF_3^+)_2\ GeF_6$

$ClO_2^+\ GeF_5^-$

ΔH^0 = 29.1(4) kcal
ΔS^0 = 90(1) cal/K

$\frac{1}{T} \times 10^3\ (K^{-1})$	$-\ell nK_p$(obs)	$-\ell nK_p$(calc)
3.562	7.09	7.05
3.512	6.29	6.32
3.464	5.57	5.61
3.412	4.92	4.85
3.355	3.93	4.02
3.304	3.29	3.27
3.262	2.68	2.65

$(SF_3^+)_2\ GeF_6$

ΔH^0 = 42.9(6) kcal
ΔS^0 = 125(2) cal/K

$\frac{1}{T} \times 10^3\ (K^{-1})$	$-\ell nK_p$(obs)	$-\ell nK_p$(calc)
3.661	15.97	16.01
3.593	14.62	14.55
3.529	13.19	13.17
3.473	11.98	11.96
3.416	10.60	10.73
3.288	8.02	7.97

Table VII. Lattice Enthalpies and Basic Radii

	SF_3BF_4	$NOUF_6$	ClO_2BF_4	KBF_4	$(SF_3)_2GeF_6$
U_{elec} (kcal)	147.8	137.8	154.2	160.6	413.3
U_{dd} (kcal)	37.14	26.21	35.13	22.37	72.73
U_{dq} (kcal)	4.46	3.15	4.22	2.68	8.73
U_r (kcal)	46.27	36.24	45.01	35.54	113.58
U_z (kcal)	0.2	0.2	0.3	0.5	0.2
U_L (0 K, kcal)	142.9	130.7	148.2	149.7	381.0
ΔH_L° (298K, kcal)	144.1	131.6	149.4	149.9	382.8
$\bar{r}$ (Å)	$\bar{r}_S = 1.147$	$\bar{r}_{NO} = 1.262$	$\bar{r}_{C\ell} = 1.150$	$\bar{r}_K = 1.193$	$\bar{r}_S = 1.170$

(for all calculations $\rho = 0.333$ Å, $\bar{r}_F = 1.066$ Å)

SF_3^+: $q_s = {}^+.9442$, $q_F = {}^+.0186$

BF_4^-: $q_B = {}^+.1420$, $q_F = {}^-.2855$

UF_6^-: $q_U = {}^+.5846$, $q_F = {}^-.2641$

ClO_2^+: $q_{C\ell} = {}^+1.083$, $q_O = {}^-.0415$

GeF_6^{2-}: $q_{Ge} = {}^+.3148$, $q_F = {}^-.3858$

	F	O	S	Cℓ	B	U	Ge	K	NO
α(Å^3)	0.80	0.90	1.20	1.20	0.05	2.50	0.75	1.03	1.00
ε(eV)	49.57	58.53	21.06	21.42	22.63	15.00	14.34	28.63	28.60

Table VIII. Lattice Energy Calculations for SiF_4, UF_6, and OsO_4

	ρ = .333 Å			ρ = .345 Å		ρ = .360 Å	
	SiF_4	UF_6	OsO_4	SiF_4	UF_6	SiF_4	UF_6
$U_{dd}+U_{dq}$(kcal)	16.62	29.37	27.64	17.84	31.59	19.60	34.69
U_z (kcal)	0.5	0.2	0.5	0.5	0.2	0.5	0.2
U_r (kcal)	11.40	19.91	18.63	12.62	22.13	14.38	25.23
ε_F (eV)	46.90	52.24	-	51.00	56.53	56.98	63.32
ε_0 (eV)	-	-	58.53	-	-	-	-
$\bar{r}_F$ (Å)	1.053	1.079	-	1.053	1.077	1.055	1.079
$\bar{r}_F$ (Å)	-	-	1.144	-	-	-	-

$$\left.\begin{array}{l} SiF_4:\ q_F = {}^-.1710,\ q_{Si} = {}^+.6840 \\ UF_6:\ q_F = {}^-.2210,\ q_U = {}^+1.3260 \end{array}\right\}\ \alpha_F = 0.80\ \text{Å}^3$$

$$OsO_4:\ q_0 = {}^-.2915,\ q_{Os} = {}^+1.1660\ \Big\}\ \alpha_0 = 0.90\ \text{Å}^3$$

	Si	U	Os
α(Å^3)	1.20	2.50	2.00
ε(eV)	14.7	15.0	15.3

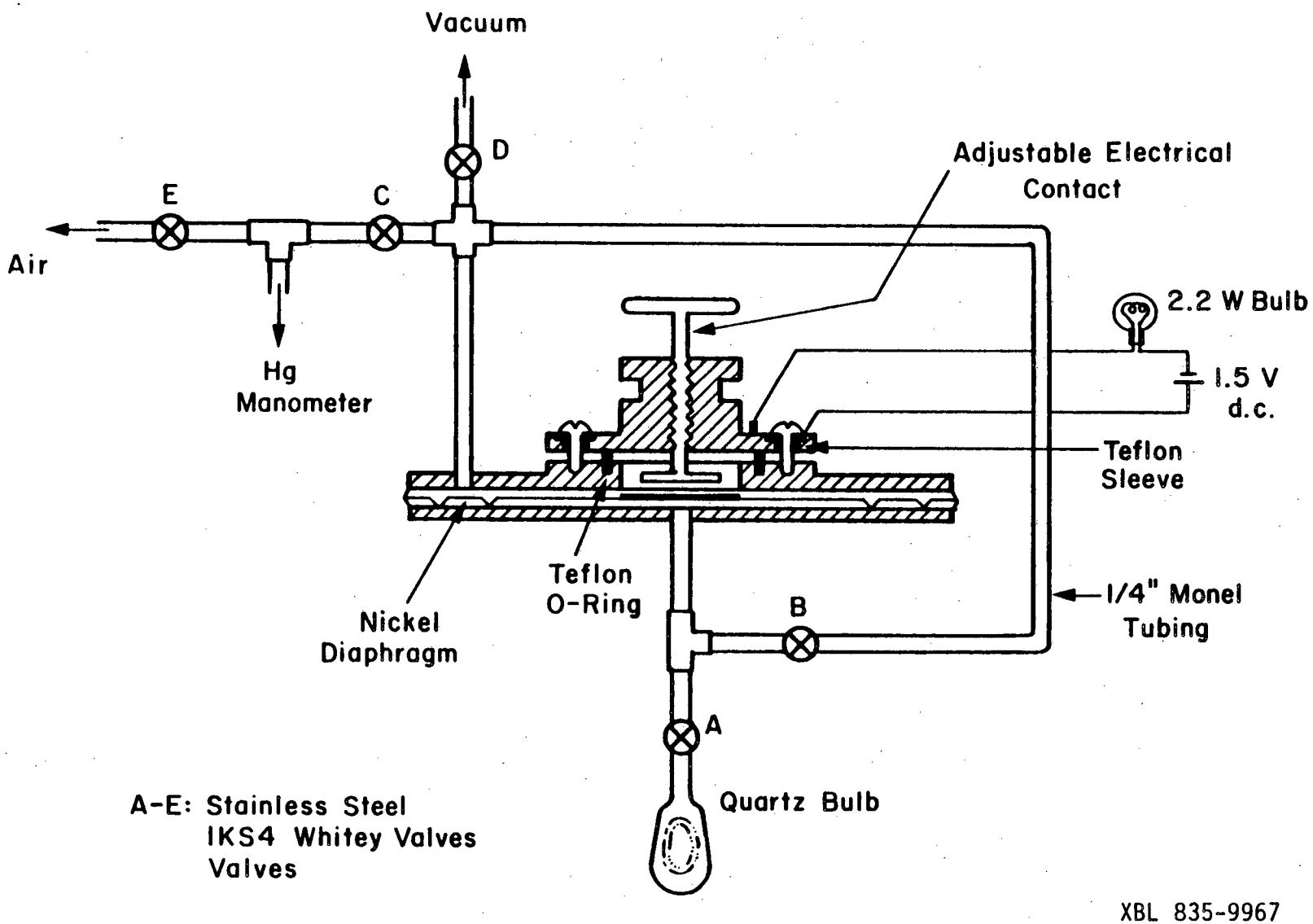


Figure 1. Apparatus for vapor pressure measurements

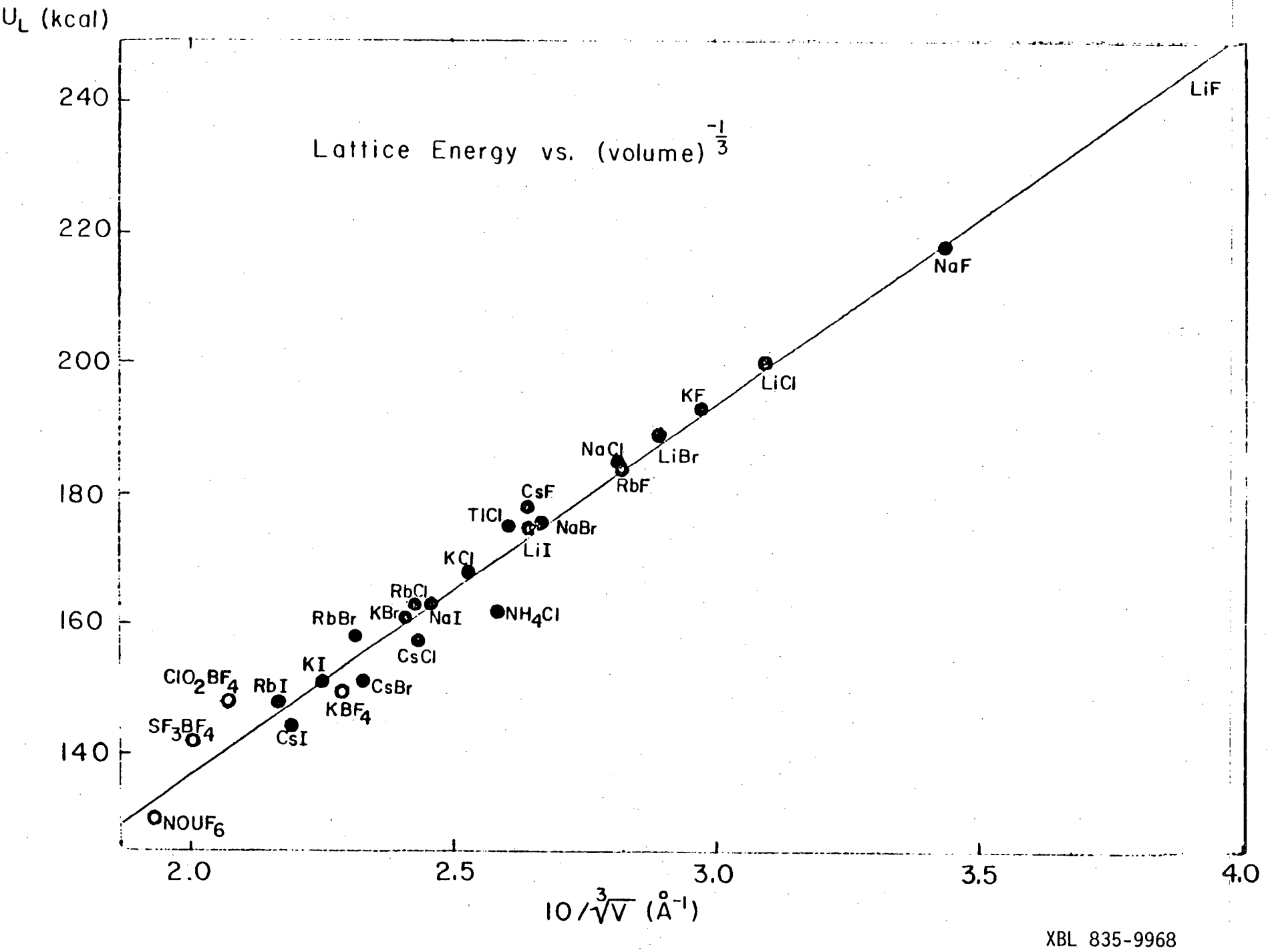
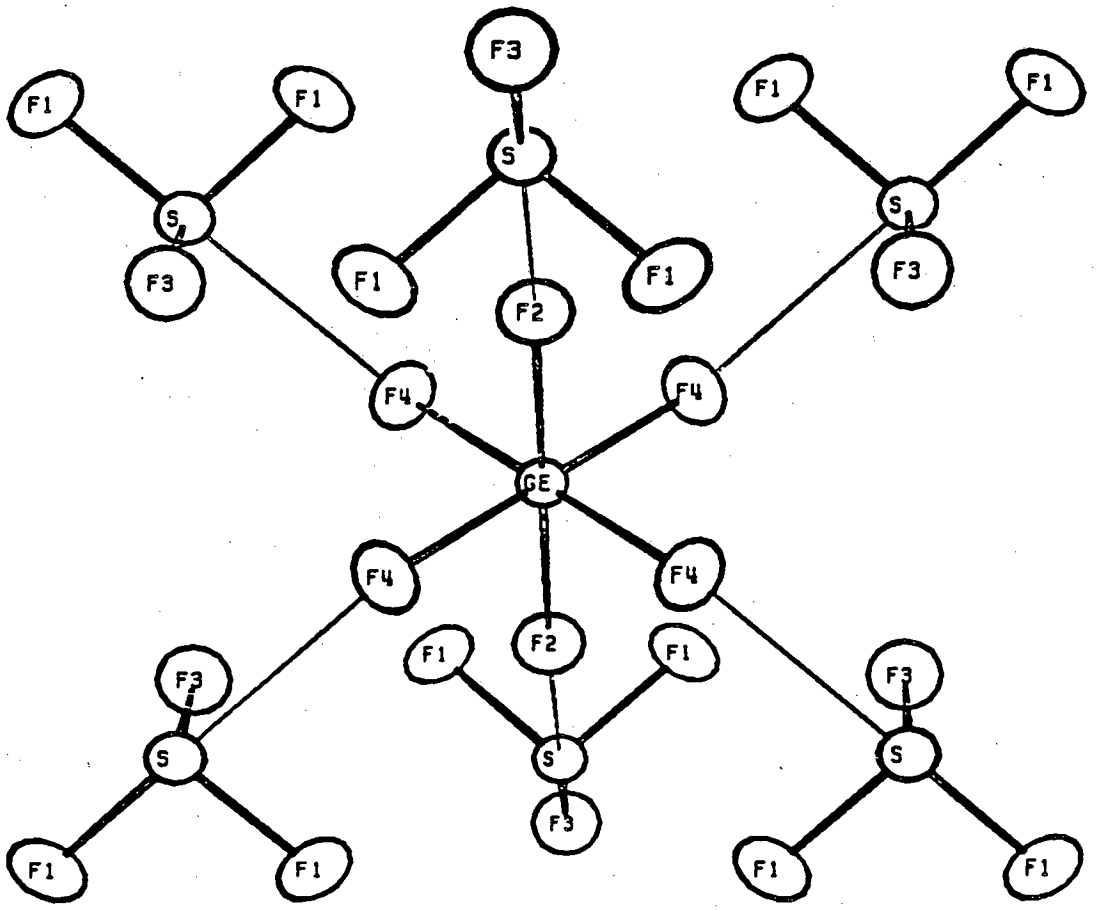
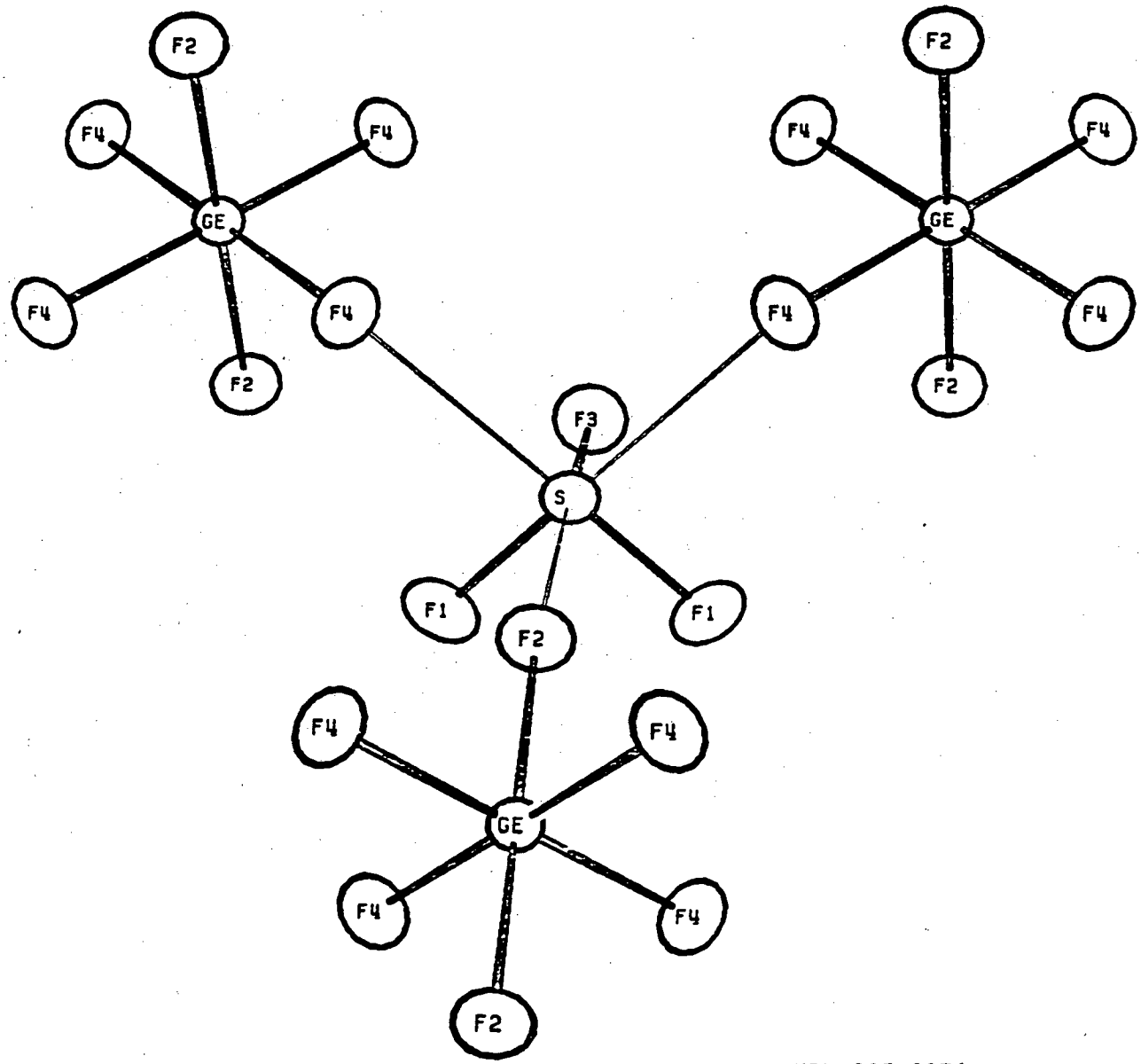


Figure 2. Lattice Energies vs. (molecular volume)$^{-1/3}$. Open circles--this work; shaded circles--ref. 31.



XBL 835-9975

Figure 3a. Ge Coordination Environment in $(SF_3^+)_2GeF_6^{2-}$



XBL 835 9974

Figure 3b. S Coordination Environment in $(SF_3^+)_2GeF_6$

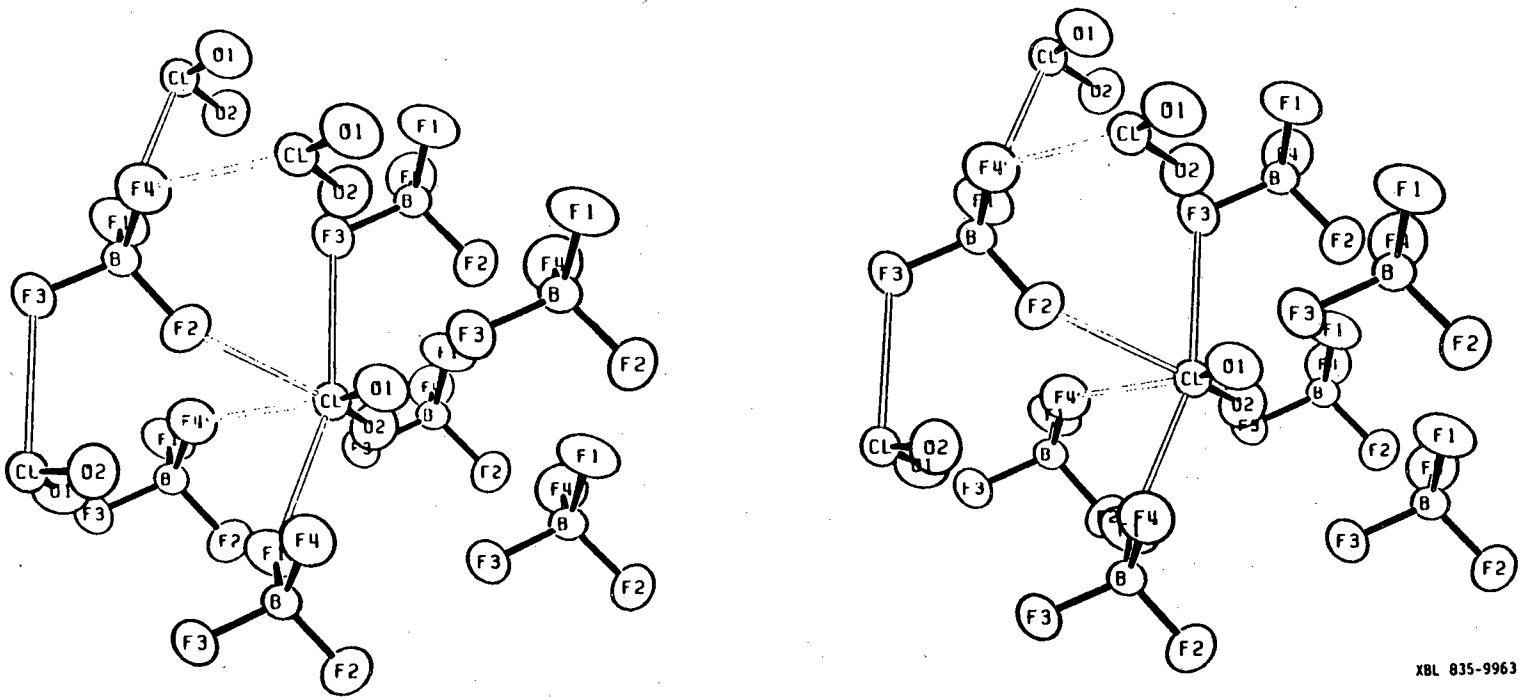


Figure 4. Stereoview Showing Coordination Environment in ClO_2BF_4

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