cobalt(III) couples,[41] it does appear that the greater part of variations in potentials of these couples as the ligands are changed does arise from the concomitant variation in ligand field stabilization energies.

The nitro complex deviates significantly from the above pattern. The discrepancy may arise partly from the use of incorrect values of Dq^z for this ligand.[35] However, it seems more likely that the above treatment is no longer even approximately true when the ligands X are not predominantly σ donors.

Acknowledgments.—We are indebted to Professor R. R. Schroeder for many useful discussions and for his suggestions concerning technique and apparatus. It is a pleasure to acknowledge some stimulating discussions with Professor Daryle H. Busch and to thank Professor Busch for making details of some of his work available to us prior to publication.

[41] J. J. Kim and P. A. Rock, *Inorg. Chem.*, **8**, 563 (1969).

CONTRIBUTION NO. 2886 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY,
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Bismuth(I) Tetrachloroaluminate. A Spectrophotometric Study of Its Equilibrium Formation in the Gas Phase[1]

BY RICHARD A. LYNDE AND JOHN D. CORBETT*

Received October 23, 1970

A new absorption band at 723 nm in the ternary system Bi(l)–BiCl$_3$(g)–AlCl$_3$(g) is shown to originate from BiAlCl$_4$(g). A value of -28.1 ± 0.5 kcal mol^{-1} for $\Delta H°_{1050}$ for the reaction BiCl(g) + AlCl$_3$(g) = BiAlCl$_4$(g) is obtained from spectral data obtained between 650 and 900° together with known data pertaining to the BiCl and AlCl$_3$ reactants. An estimated value of -42.8 ± 4 eu for $\Delta S°$ gives $K_p(1050°\mathrm{K}) = 3.1 \times 10^{-4}$ and $\epsilon = 5.4 \times 10^4$ l. mol^{-1} cm^{-1}. Species of the type Bi$_x$AlCl$_4$, $x > 1$, are eliminated on the basis of entropy considerations and the implausibly large values of ϵ obtained. The enthalpy change for the above reaction can be accounted for well in terms of known data and a simple ionic model for Bi$^+$-AlCl$_4^-$. Several new, low-intensity bands for BiCl were observed between 1350 and 1620 nm.

Introduction

The simple bismuth(I) oxidation state has a relatively limited stability in condensed systems. The Bi$^+$ ion has been well established in dilute solution in BiCl$_3$[2,3] and in NaAlCl$_4$[4] but the simple ion evidently polymerizes at higher concentration to form Bi$_4^{4+}$ [2,3] (or Bi$_3^+$ [5]) in chloride media and Bi$_5^{3+}$ and Bi$_8^{2+}$ with tetrachloroaluminate anions.[6,7] The so-called "BiCl" which separates from concentrated solutions of metal in liquid BiCl$_3$ has been shown to be a complex structure with the stoichiometry BiCl$_{1.167}$, *viz.*, (Bi$_9^{5+}$)$_2$(BiCl$_5^{2-}$)$_2$(Bi$_2$Cl$_8^{2-}$).[8] The only example of a Bi$^+$ ion in a solid compound is in the recently discovered Bi$^+$(Bi$_9^{5+}$)(HfCl$_6^{2-}$)$_3$.[9]

The simple monochloride BiCl has a well-documented existence in the vapor phase as a minor product on reduction or decomposition of BiCl$_3$. The BiCl band system at 450 nm was first observed and correctly identified by Saper,[10] while the thermodynamics of the equilibrium of gaseous BiCl with BiCl$_3$(g) and liquid metal have been studied by Cubicciotti by transpiration techniques.[11,12]

A spectral examination of the gaseous products in the Bi–BiCl$_3$ system was originally undertaken in order to determine whether there were unreported BiCl transitions in the visible or near-ir region. This possibility was raised[13] by a tentative application of the theory of p^2 ↔ p^2 intraconfigurational transitions which was developed for Bi$^+$ in NaCl–AlCl$_3$ melts.[14] When such new features were not readily discernible, the study was extended to include the Bi–BiCl$_3$–AlCl$_3$ system in order to examine the possible formation of reduced bismuth tetrachloroaluminate species in the gas phase which might be important in the transport reaction of Bi$_5$(AlCl$_4$)$_3$(s).[15] Quantitative studies on the formation of gaseous adducts with aluminum chloride have been reported for neodymium(III)[16] and uranium(IV)[17] chlorides and, more recently, for calcium, magnesium, manganese, cobalt, and nickel dichlorides.[18] The principal driving force for such reactions is presumably the rather large chloride ion affinity of AlCl$_3$, ~78 ± 7 kcal/mol.[19]

Experimental Methods

Materials.—The bismuth employed and the preparation of the trichloride were previously described.[7] The salt after three vacuum distillations was white and free of carbonaceous impurities. The aluminum trichloride was prepared from high-purity aluminum and "transistor grade" HCl as before.[20] All transfers

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[1] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] L. E. Topol, S. T. Yosim, and R. A. Osteryoung, *J. Phys. Chem.*, **65**, 1511 (1961).

[3] C. R. Boston, G. P. Smith, and L. C. Howick, *ibid.*, **67**, 1849 (1963).

[4] N. J. Bjerrum, C. R. Boston, and G. P. Smith, *Inorg. Chem.*, **6**, 1162 (1967).

[5] J. D. Corbett, *Inorg. Chim. Acta*, **2**, 22 (1968).

[6] N. J. Bjerrum and G. P. Smith, *Inorg. Chem.*, **6**, 1968 (1967).

[7] J. D. Corbett, *ibid.*, **7**, 198 (1968).

[8] A. Hershaft and J. D. Corbett, *ibid.*, **2**, 979 (1963).

[9] R. M. Friedman and J. D. Corbett, *Chem. Commun.*, 422 (1971).

[10] P. G. Saper, *Phys. Rev.*, **37**, 1710 (1931).

[11] D. Cubicciotti, *J. Phys. Chem.*, **64**, 791 (1960).

[12] D. Cubicciotti, *ibid.*, **71**, 3066 (1967).

[13] G. P. Smith, private communication.

[14] H. L. Davis, N. J. Bjerrum, and G. P. Smith, *Inorg. Chem.*, **6**, 1172 (1967).

[15] D. A. Lokken and J. D. Corbett, unpublished research.

[16] H. A. Øye and D. M. Gruen, *J. Amer. Chem. Soc.*, **91**, 2229 (1969).

[17] D. M. Gruen and R. L. McBeth, *Inorg. Chem.*, **8**, 2625 (1969).

[18] E. W. Dewing, *Met. Trans.*, **1**, 2169 (1970).

[19] R. H. Wood and L. A. Orazio, *Inorg. Chem.*, **5**, 682 (1966).

[20] R. A. Potts, R. D. Barnes, and J. D. Corbett, *ibid.*, **7**, 2558 (1968).

were made in an argon-filled drybox, and both the salt storage ampoules and the spectral cells were sealed off under vacuum.

Apparatus.—Spectra of isothermal gaseous mixtures were obtained with a Cary 14 recording spectrophotometer modified for use with reverse optics. The major features of this and the furnace assembly have been described before.[21] The cylindrical, fused-silica cells (Pyrocell Manufacturing Co., Inc., Westwood, N. J.), of 2.2-cm diameter and 10.0- or 15.0-cm length, were supported in a holder constructed from two disks of 2.5-cm Marinite, held parallel and 7 cm apart by alundum rods placed around their periphery. This arrangement avoided the attack of cells by oxidation products of the stainless steel holder employed earlier. The two 10-cm end units of the surrounding furnace were normally controlled 30° higher than the central 20-cm portion to prevent condensation on the cell windows, a procedure which resulted in the temperature of the cell windows being 5–7° higher than that at the center. The overall uncertainty in the effective cell temperature is estimated to have been $\pm(3\text{–}5)°$ but the deviation was probably relatively constant.

Data Collection.—The empty cells exhibited no absorption in the region of interest (300–1800 nm at 200–1000°). The $BiAlCl_4$ transition centered at 723 nm was superimposed on the smoothly decreasing, low-energy tail of an intense BiCl band located near 460 nm. At the temperatures and concentrations used for quantitative measurements on $BiAlCl_4$ the BiCl band attained $A = 2$ at 500–540 nm. The small background absorbance under the $BiAlCl_4$ peak was determined by fitting a flexible draftsman's spline to the smooth background on either side of the peak, the interpolation being over only 180 nm or 15 cm on the chart.

The pressures of the gaseous species were established from the weights (± 0.2 mg or $\leq 0.67\%$) of the $AlCl_3$ and $BiCl_3$ added to cells of known volume together with literature data on the formation of bismuth monochloride[11,12] from Bi and $BiCl_3$ and on the dissociation of Al_2Cl_6 to $AlCl_3$.[17,22] Under the conditions of the present study 1–33% of the initial $BiCl_3$ reacted to form bismuth(I) products and the aluminum chloride was predominantly the monomer. Equilibrium was evidently attained very rapidly after temperature alteration

Significant cell attack and severe scattering of the light beam was noted above 650° in runs containing $AlCl_3$, similar to that reported by Øye and Gruen[17] above 627°. The cumulative effect of the attack at 900° was such as to render a cell useless after one to three runs with $P_{AlCl_3} \approx 2$ atm or four to six runs with $P_{AlCl_3} < 1$ atm.

Results and Discussion

Spectra.—Aluminum trichloride exhibits no features in the spectral range of interest, 325–1800 nm. The spectrum of bismuth trichloride consists of a very strong absorption at <240 nm and a less intense overlapping band at 296 nm. For the conditions of the quantitative experiments performed, the $BiCl_3$ absorbance reached 2.0 near 370 nm, rising so rapidly that a quantitative spectral determination of the equilibrium concentration of $BiCl_3$ thereby was not feasible. Addition of $AlCl_3$ did not change the $BiCl_3$ spectrum. The complex 392- and 450-nm band systems known for bismuth monochloride[23] were readily observed in the Bi–$BiCl_3$ system.

A new broad and symmetric band with λ_{max} 723 nm appeared superimposed on the edge of the BiCl and $BiCl_3$ bands in the Bi–$BiCl_3$–$AlCl_3$ system at temperatures above 400–450°, Figure 1. The half-width (594 cm^{-1}) remained constant (within 5%) on varying the amounts of the reactants, and the new band could be fit very well by a Gaussian distribution of energy, suggesting it arose from a single transition. The experimental absorbance data at the band maximum (corrected for background) are given in Table I as a function of calculated BiCl and $AlCl_3$ pressures present.

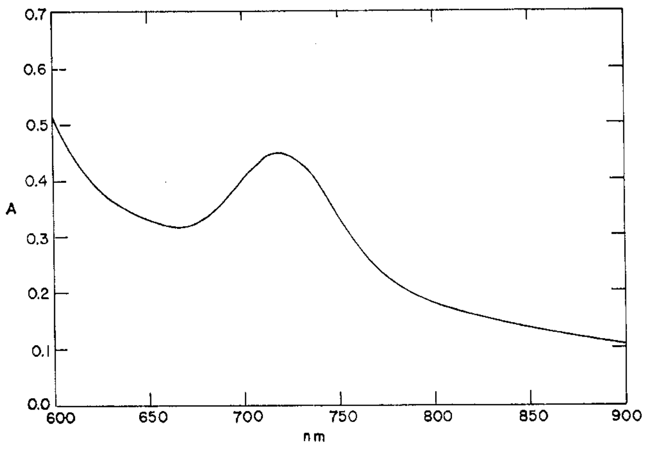

Figure 1.—The spectrum of the gaseous Bi–$BiCl_3$–$AlCl_3$ system ($P_{BiCl_3} = 0.554$ atm, $P_{AlCl_3} = 0.653$ atm, path length 10.0 cm, temperature 654°).

TABLE I

CALCULATED PRESSURES OF $BiCl_3$, BiCl, AND $AlCl_3$ AND VALUES OF A_{723}

Ref no.	Temp, °K	P_{BiCl_3}, atm	10^2P_{BiCl}, atm	$10P_{AlCl_3}$, atm	A_{723}[a]
1	926	0.18_0	1.54	12.3	0.242
2	922	1.33_4	2.81	12.8	0.470
	975	1.40_0	5.99	17.0	0.544
3	923	1.03_3	2.61	12.4	0.452
	974	1.08_2	5.54	16.4	0.498
4	924	3.72_8	1.89	1.86	0.050
	973	3.86_6	3.78	2.089	0.051
5	925	1.56_5	1.44	0.69	0.018
6	928	0.554	2.29	6.53	0.208
	975	0.575	4.47	7.91	0.215
7	927	0.484	2.16	11.7	0.344
	974	0.502	4.25	14.9	0.360
8	925	1.21_6	2.82	7.20	0.276
9	923	1.01_6	2.59	8.18	0.288
10	923	0.410	1.93	5.23	0.143
	971	0.425	3.76	6.27	0.149
	1023	0.437	7.36	7.22	0.161
	1075	0.440	13.4	8.00	0.157
	1122	0.434	21.7	8.59	0.147
11	923	0.446	1.99	4.39	0.121
	972	0.464	3.99	5.21	0.127
	1022	0.477	7.50	5.63	0.127
	1073	0.482	13.5	6.47	0.128
	1123	0.476	22.6	6.94	0.119
	1173	0.456	35.8	7.35	0.115
12	924	0.703	2.31	4.81	0.158
	973	0.733	4.69	5.77	0.162
	1026	0.758	9.21	6.60	0.162
	1074	0.773	16.1	7.22	0.160
	1125	0.775	27.1	7.78	0.146
	1172	0.763	41.6	8.22	0.139

[a] For 10.0-cm path length.

A second new feature first observed with the Bi–$BiCl_3$–$AlCl_3$ system at temperatures above 650° consisted of five weak ($\epsilon \lesssim 10$) bands in the near-ir spectrum (~1620, 1555, 1490, 1420, and 1350 nm) each of which exhibited regular fine structure (*e.g.*, ~20- and 15-cm^{-1} separation in the 1555- and 1490-nm bands, respectively). These features were later observed in the Bi–$BiCl_3$ system and shown to vary as $[BiCl_3]^{1/3}$, as expected for BiCl. Further work will be necessary before more can be asserted concerning their origin.

Product Identification.—The observation of the new band only in the ternary system Bi(l)–$BiCl_3$(g)–$AlCl_3$(g) likewise limits the possible products to those formed from all three reactants. Further, the logical

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[21] J. D. Corbett and R. A. Lynde, *Inorg. Chem.*, **6**, 2199 (1967).

[22] "JANAF Thermochemical Tables," Dow Chemical Co., Thermal Research Laboratory, Midland, Mich., 1960.

[23] R. B. Singh and K. N. Upadhya, *Curr. Sci.*, **35**, 484 (1966).

association reactions yielding $Bi_xCl_y(AlCl_3)_z$ species are restricted in complexity by entropy considerations. For these reasons the products considered possible were limited to those in which $y = 2$ or 1 and in which only Cl, $AlCl_4$, or Al_2Cl_7 units were present, meaning $z = 1, 2, 3,$ or 4. For $x = 1$ these correspond to simple bismuth(I) or bismuth(II) compounds. Although polybismuth cases ($x > 1$) cannot be distinguished by these means since excess condensed metal was always present, the potential effect of this event on the entropy change makes them less likely, as will be considered later.

A Beer's law test of each of these possible reaction stoichiometries was performed assuming ϵ_{723} was constant and that K_p for the formation of the product was sufficiently small that concentrations of $AlCl_3$, Al_2Cl_6, $BiCl_3$, and BiCl calculated without this reaction were not significantly changed. Distinctly nonlinear results were obtained for other than the $[BiCl_3]^{1/3}[AlCl_3]$ relationship which corresponds to the reaction

$$^2/_3Bi(l) + ^1/_3BiCl_3(g) + AlCl_3(g) = BiAlCl_4(g) \qquad (1)$$

The plot of A_{723} *vs.* this function over a 40-fold range for the latter for data obtained at 650° is shown in Figure 2.

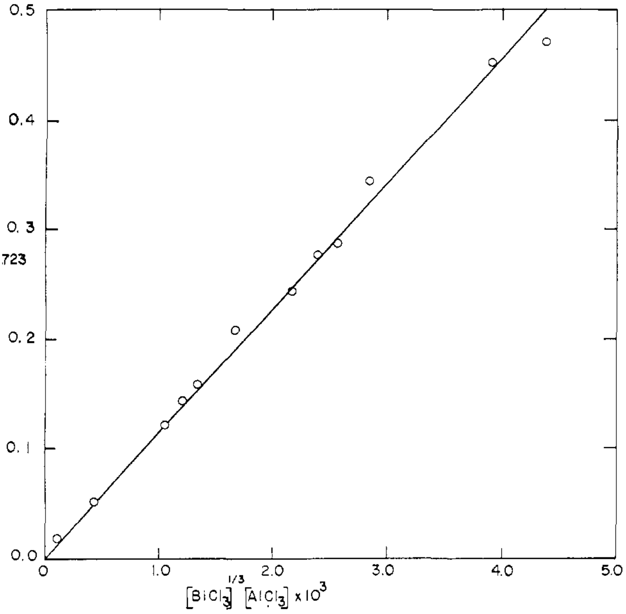

Figure 2.—Absorbance at 723 nm *vs.* $[BiCl_3]^{1/3}[AlCl_3]$ at 650° (concentrations in moles per liter).

If other reaction products are present, they must be at relatively small concentrations and be spectroscopically undetectable in the regions studied.

Thermodynamic Calculations.—The reaction of most interest

$$BiCl(g) + AlCl_3(g) = BiAlCl_4(g) \qquad (2)$$

is obtained from reaction 1 with $BiCl_3$ reactant by the inclusion of the equilibrium

$$^2/_3Bi(l) + ^1/_3BiCl_3(g) = BiCl(g) \qquad (3)$$

Known data[11,12] for reaction 3 have already been utilized in compiling Table I since account must be taken of the substantial fraction of BiCl formed. The apparent equilibrium constant K_a ($=K_p/\epsilon$) for equilibrium 2 is

$$K_a = \frac{A_{723}RT/b}{P_{BiCl}P_{AlCl_3}}$$

where b is the path length. The deduction of the reaction enthalpy according to the second law is shown in Figure 3 for data from three runs over the range of 650–900°. (Data from other runs near 650 and 700° given in Table I are not plotted since close adherence to Beer's law makes the data substantially superimpose at each temperature.) The linear least-squares description of the data shown yields a value of −28.1 ± 0.5 kcal/mol for $\Delta H°$ at 1050°K, the midpoint of the range. A statistical estimate for $\Delta(H°_{1050} - H°_{298})$ gives −30.4 kcal mol^{-1} for $\Delta H°_{298}$.

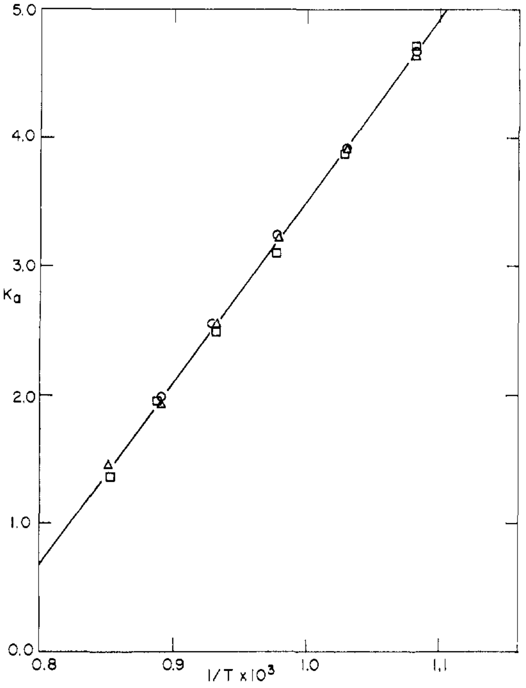

Figure 3.—Temperature variation of ln K for $BiAlCl_4$ formation: ○, run 10; △, run 11; □, run 12.

A value for $\Delta S°_{1050}$ was estimated by statistical means in order to determine other quantities for equilibrium 2. The entropies of BiCl(g) and $AlCl_3$(g) were calculated directly using data available in the literature.[22–24] The product of the moments of inertia of $BiAlCl_4$(g) was estimated for a model with the bismuth atom on a face of a tetrahedral $AlCl_4$ entity with a Bi–Cl bond distance of 3.1 Å. Following the approach of Stull and Prophet[25] an average of 250 cm^{-1} for the 12 vibrational frequencies of $BiAlCl_4$(g) was estimated from the frequencies of BiCl(g), $AlCl_3$(g), and $BiCl_3$(g).[22,23,26–29] The electronic entropy was assumed to be zero. The resultant $S°_{1050}$ for $BiAlCl_4$(g), 130.7 ± 4 eu, together with data for the other species yields $\Delta S°_{1050} = -42.8 \pm 4$ eu for reaction 2. From this $K_{p,1050} = 3.1 \times 10^{-4}$ atm^{-1} and $\epsilon(723\ nm) = 5.4 \times 10^4$ l. mol^{-1} cm^{-1}. The $BiAlCl_4$(g) pressure was <0.1% of the smaller of the two reactant pressures under all of the experimental conditions, consistent with an earlier assumption. The oscillator strength of 0.30 obtained for the $BiAlCl_4$

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[24] D. R. Hershbach and V. W. Laurie, *J. Chem. Phys.*, **35**, 458 (1961).

[25] D. R. Stull and H. Prophet in "The Characterization of High-Temperature Vapors," J. L. Margrave, Ed., Wiley, New York, N. Y., 1967, p 359 ff.

[26] R. P. Oertel and R. A. Plane, *Inorg. Chem.*, **8**, 1188 (1969).

[27] J. K. Wilmshurst, *J. Mol. Spectrosc.*, **5**, 343 (1960).

[28] P. W. David and R. A. Oetjen, *ibid.*, **2**, 253 (1958).

[29] J. T. Kenney and F. X. Powell, *J. Phys. Chem.*, **72**, 3094 (1968).

transition is about 10^2 that observed for the most allowed transition of Bi^+ in melts.[14]

Note was made earlier of the fact that the presence of excess liquid bismuth in these experiments meant that equilibrium measurements could not distinguish $BiAlCl_4$ from Bi_xAlCl_4. This could include in particular the attractive Bi_3^+ which has been suggested to be stable in solution in $BiCl_3$.[5] However incorporation of the two additional metal atoms would make the entropy change for the formation reaction more negative by roughly 24 eu according to the same estimation methods just used for $BiAlCl_4$. This change would yield a K_p of 1.9×10^{-6} and a preposterous value for ϵ, $>10^9$ l. mol^{-1} cm^{-1}. Even the Bi_2AlCl_4 alternative appears to give an unreasonable result for ϵ and so it is concluded that only $BiAlCl_4$ will satisfy the experimental data.

Spectroscopic investigations of the gas phase in the ternary system were also carried out at lower temperatures (400–600°) but these generally gave unsatisfactory results, evidently because of partial condensation to the very stable, reduced tetrachloroaluminate melts.[7] With decreasing temperature the values of K_a deduced become increasingly erratic and low when compared with those expected according to parameters deduced at higher temperatures, but no observable differences in the spectra measured were noted other than in overall intensity. At a given temperature, deviations from absorbances calculated according to the high-temperature data were found to correlate well with the total moles of the two trichlorides added, a reasonable result for a system undergoing partial and roughly congruent condensation together with reduction by the excess metal present.

Although the conversion of some metal chlorides to their gaseous tetrachloroaluminate salts is large and accompanied by substantial alteration in volatility,[16-18] BiCl remains the major component even in the presence of more than 1 atm of $AlCl_3$. Much of this may be attributed to the extra stability of BiCl associated with covalency. The value of 71.8 ± 1 kcal mol^{-1} for ΔH°_{298} for its dissociation to atoms,[12] together with standard ionization and affinity data and the coulomb energy of the simple ion pair at 2.83[12] to 3.1 Å,[8,9] indicates the real molecule is of the order of 40–50 kcal mol^{-1} more stable than the ionic model. On the other hand the stability of $BiAlCl_4$ can apparently be satisfactorily accounted for with a simple ionic entity, adding to the above data for the formation of gaseous Bi^+ and Cl^- the chloride ion affinity of $AlCl_3$, -78 ± 7 kcal mol^{-1},[19] and the coulomb energy of a model ion pair. For the last the tetrahedral $AlCl_4$ unit with the usual Al–Cl distances of 2.12 Å[15] is employed since substantial angular distortion is not likely with Cl–Cl distances already reduced to 3.45 Å (compared with twice the van der Waals radius of ~3.6 Å). The Bi^+ ion is again placed on a triangular face of the anion at Bi–Cl distances of 3.1 Å.[8,9] For the point charge calculation employed the inherent charge asymmetry of the Al–Cl bonds and the charge polarization of the anion caused by the cation cannot both be uniquely established. However, plausible combinations yield the coulomb energy of the ion pair (-109 ± 7 kcal mol^{-1}) necessary to account for observed data, for example, charges on aluminum, each of the three chlorine atoms next to Bi^+, and the fourth chlorine atom of +1, −0.55, −0.35 or +0.33, −0.42, −0.08, respectively. Although the estimation methods are drastically simplified, the results are gratifying. Measurements of the moment of inertia of $BiAlCl_4$ and of the stability of simple and more ideal examples such as $NaAlCl_4(g)$ would be illuminating.

CONTRIBUTION NO. 2865 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY,
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The Crystal Structure of Octaselenium(2+) Tetrachloroaluminate, $Se_8^{2+}(AlCl_4^-)_2$[1]

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Received December 22, 1970

The crystal structure of the compound $Se_8(AlCl_4)_2$ formed in the pseudobinary Se–($SeCl_4$ + 4$AlCl_3$) system has been determined from three-dimensional X-ray diffraction data. The crystals are orthorhombic (space group $Pca2_1$) with $a = 14.92$ (2), $b = 10.67$ (1), and $c = 13.22$ (1) Å and four $Se_8(AlCl_4)_2$ units per cell. The model was derived by Patterson and Fourier methods and refined to a conventional R index of 0.077 by full-matrix least squares (Se anisotropic, Al and Cl isotropic) on 721 observed reflections $>2\sigma(I)$. The structure consists of approximately tetrahedral $AlCl_4^-$ ions and Se_8^{2+} ions of novel geometry. The angles in the $AlCl_4^-$ groups average 109.5°, and the Al–Cl distances, 2.12 Å. The Se_8^{2+} ion (approximate symmetry C_s) has a [3.3.0] bicyclic structure derived from an eight-membered ring in the endo,exo configuration through shortening of one transannular separation to form a weak Se–Se bond at 2.84 Å, which compares with 2.29–2.36 Å about the ring and in the element. The structure of Se_8^{2+} is discussed in relation to those of S_4N_4, Se_4N_4, and Se_8.

Introduction

Earlier successes in preparing new polybismuth cations as their tetrachloroaluminate salts[2] led to an examination of the analogous tellurium and selenium systems and to the preparation of five new polyatomic compounds of these elements.[3] In this study rather poor liquidus data characterized one of the selenium compounds as having a Se:$AlCl_4$ ratio in the neighborhood of 4, and infrared data seemed to support rather

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(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) J. D. Corbett, *Inorg. Chem.*, **7**, 198 (1968).

(3) D. J. Prince, J. D. Corbett, and B. Garbisch, *ibid.*, **9**, 2731 (1970).