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A study of the preparation, structure, and properties of compounds containing polynuclear cations of bismuth. An investigation of anion effects

by

Robert Mark Friedman

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INTRODUCTION

Following World War Two science was deluged with financial support because of the realization of the impact that fundamental research can have on technology. The study of molten salts was the recipient of much attention owing to their unique physical properties, e.g., high thermal stability, low vapor pressure, wide range of accessible temperatures, good electrical conductivity, and low viscosity.

Interest in the use of molten salts in nuclear reactors as solvents for fissionable materials or as a heat exchange medium, industrial concern about the mechanism of corrosion, and the low current yields in electrometallurgical processes provided the impetus for basic investigations into the nature of the solution of metals in their molten salts. Several theories, differing mainly in the character of the solute species, arose to explain the phenomenon. The three most popular solution models were: A.) the dissolution of metal atoms such as found in the vapor phase, B.) the solution of "ion pairs" with solvated electrons occupying anion sites in the quasi-lattice of the melt, and C.) the formation of a reduced solute cation by an oxidation-reduction reaction between the metal and the melt cations. None of these hypotheses alone was capable of explaining all of the observed data. It was sometimes necessary to choose a combination of models to explain all of the physiochemical properties of a single system, i.e., a different model for a different property.

One of the more intricate systems to be investigated was the bismuth-bismuth trichloride system. It had long been known (1) that when bismuth dissolved in its trichloride a black solid was formed with the approximate composition BiCl. Although simple monomeric BiCl was observed and identified (2) in the gas phase in 1931, it was found necessary to invoke polymerization to explain the diamagnetism of the solid isolated by Corbett (3). The properties of dilute solutions of the metal in the molten halide were intensively studied. The liquidus of the BiCl-$BiCl_3$ portion of the phase diagram (4) was interpreted (3) in terms of a $(BiCl)_4$ solute, whereas precise cryoscopic measurements (5) suggested the presence of $(BiCl)_2$ or Bi_2^{2+}. Vapor pressures (6) over solutions containing up to 24 mole % metal were accounted for by considering alternatively metal atoms (6), tetramers of the form $(BiCl)_4$ (7), or a mixture of $(BiCl)_2$ and Bi_2 (8) to be present. A reexamination of the phase diagram of the bismuth-bismuth trichloride system (9) essentially confirmed the earlier work by Sokolova (4) on the liquid-solid region. The metal and salt were found to be completely miscible above 780°.[1] In

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[1] All temperatures are in degrees Centigrade unless otherwise noted.

determining the features of the two liquid region, the occurrence of retrograde solubility of bismuth on the salt-rich side of the miscibility gap was discovered; the solubility of bismuth in its trichloride decreased from 45% at 320° to 28% at about 550°. The initial decrease in solubility followed by its increase as the temperature was increased to the consolute temperature was interpreted as the resultant of two processes, one predominant at lower temperatures and the other predominant at higher temperatures; for example, the solution of bismuth as a polymeric subhalide at lower temperatures followed by decomposition at higher temperatures. Polarographic measurements (10) on very dilute solutions gave results consistent with a Bi^+ solute species, while EMF concentration cells (11) showed Bi^+ to be present below 0.6 mole % metal with polymerization to a species such as Bi_4^{4+} at higher metal concentrations. A spectrophotometric study (12) established the presence of two chromophores in the range 0.01 to 6 mole % metal. An unambiguous identification of the solute species was not possible, but the simplest equilibrium consistent with the data (13), $4Bi^+ \rightleftarrows Bi_4^{4+}$, was in agreement with the EMF measurements.

Corbett and McMullan (14) prepared $BiAlCl_4$, analogous to BiCl, by adding aluminum chloride to the metal-metal halide binary system. They found complete conversion to the "acid-stabilized" salt at 260° in contrast with the 46% conversion to BiCl in the binary. The compound melted at 253°. It was maroon in bulk and reddish-brown as a powder, but darkened rapidly in air. An X-ray diffraction study (15) indicated the probable space group as R3c for $BiAlCl_4$. The radial pair distribution functions of the melt and of the powder of this composition were interpreted in terms of an equilateral triangle of bismuth atoms separated by 3.04 Å (16). Based on the assumed stoichiometry the investigators concluded that the correct formulation of the compound should be $(Bi_3)^{3+}(AlCl_4^-)_3$. The probable existence of polynuclear cations of bismuth appeared to be established both in the melt and the solid state.

The unravelling of the crystal structure of bismuth monochloride (17) revealed a greater breadth and complexity in the chemistry of bismuth. The existence of a discrete Bi_9^{5+} ion with two types of chlorobismuthate(III) anions resulted in an overall stoichiometry of $BiCl_{1.167}$. A rationalization of this strange beast was proposed by Corbett and Rundle (18) through an extended Huckel LCAO-MO model utilizing a 6p atomic orbital basis set on each bismuth. The success of this simple model to provide a reasonable description of the electronic structure of this unusual cation encouraged its application to similar problems.

Previous workers had proposed the existence of Bi_3^{3+} ions in solid and molten $BiAlCl_4$. Corbett (19) noted that this ion did not have a reasonable bonding scheme for a diamagnetic compound since molecular orbitals with symmetries a_1', a_2'', and e' were all strongly bonding; thus, Bi_3^+, with eight bonding electrons, would be predicted. This ion would also be compatible with the X-ray diffraction results as well as studies of dilute solutions of bismuth in bismuth trichloride. In the dilute solution studies one could not distinguish between the family of solutes ($Bi_3^+ \cdot nBi^{+3}$); hence, Bi_3^+ and Bi_4^{4+}, previously proposed to fit the data, would be equivalent.

Investigation of the $Bi-BiCl_3 \cdot 3AlCl_3$ system uncovered two new compounds, $Bi_5(AlCl_4)_3$ and $Bi_4(AlCl_4)$, and a glass phase which remained uncharacterized (19). Concurrently a spectrophotometric study of the dilute solutions of bismuth and bismuth trichloride in $NaCl-AlCl_3$ and $KCl-ZnCl_2$ solvents revealed the presence of Bi^+, Bi_5^{3+}, and Bi_8^{2+} ions (20,21). Corbett noted the spectral resemblance between the above solid compounds and the two polymeric ions present in the melt and concluded that they were present in the solid phases. Using the simple Huckel molecular orbital procedure and the observed diamagnetism of the compounds he predicted the trigonal bipyramid, D_{3h} symmetry, and the Archimedean antiprism, D_{4d} symmetry, to be the geometries of the Bi_5^{3+} and the Bi_8^{2+} ions, respectively. The other reasonable geometries for five and eight atom polyhedra had open-shell electronic configurations. The powder pattern for $Bi_5(AlCl_4)_3$ accounted for the reported diffraction pattern of "$BiAlCl_4$" and the triangular units deduced earlier were consistent with the proposed geometry. All the faces of the regular trigonal bipyramid are triangular and the other distance between atoms in that polyhedron, between the apices, was probably too long to be resolved by the radial distribution function. The "$BiAlCl_4$" composition is close to the liquidus composition at the temperature used to initially prepare it.

The Bi^+ ion has also been observed spectrally (22) in the $NaBr-AlBr_3$ eutectic. The spectrum of Bi^+ in both the chloride and bromide media has been successfully rationalized (23) by a ligand field treatment of the perturbation of the $6p^2$ atomic states in an environment of lower than cubic symmetry. The relativistic treatment predicted a $^3P_0$ diamagnetic ground state would be well separated from the excited states.

The discovery of the Bi_5^{3+} and Bi_8^{2+} ions demonstrated that the original polynuclear cation of bismuth, Bi_9^{5+}, was not unique in specie, but part of a general class of heretofore unrealized cationic species. It was noticed that each of the two systems studied had uncovered different cations. The intent of the work reported herein was to be the investigation of factors affecting the stability of the polynuclear cations with respect to different anion environments. This was to be achieved by using different Lewis acids than aluminum chloride to prepare them. Changing the Lewis acid present in the melt changes the pCl^-, hence the polarization and coulombic interactions in the synthesis media, and, perhaps as importantly, changes the available anions for formation of an isolable solid containing these species.

To consider the possible variations of anions and their effects on the polynuclear cations, the electrostatic model was chosen as an appropriate framework; the bismuth cations were viewed as being discrete in the solids. The leading terms in this analysis are the coulombic and repulsive interactions represented by the "hard sphere" ionic model. Other terms, usually considered less important in cases involving mononuclear ions, represent dipole, induced dipole, and multipole interactions. The polarizability of the ions were viewed as being indicative of the magnitude of these last effects.

In a discussion of the stability of reduced metal halides to disproportionation, Johnson (24) has shown, in the hard sphere ionic limit and within the validity of the Kapustinskii equation, that the stability of a mononuclear lower oxidation state of a metal increases with increasing size of an anion of the same charge. For the common lattice types the Kapustinskii equation, through judicious reparameterization, eliminated the structural dependence of lattice energies from their calculation. In addition to noting the generalization reached by Johnson, the manner in which the particular geometry of the anion influences the ionic packing in the solid was considered another variable in this study.

The stabilization of lower oxidation states in solids using Lewis acid complexation was first demonstrated for $Cd_2(AlCl_4)_2$ (25). Further work has indicated that zinc dichloride and beryllium dichloride do not enhance the reduction of cadmium dichloride to the monovalent state (J. D. Corbett and W. J. Burkhard, 1968, personal communication). These results discouraged the use of these salts in the present investigation. The KCl-$ZnCl_2$ solvent used in the spectral identification of the Bi^+ and Bi_5^{3+} ions contained 72 mole % $ZnCl_2$, and therefore the $ZnCl_3^-$ and $Zn_2Cl_5^-$ ions were probably the predominant anions present in the melts.

Hafnium tetrachloride and tantalum pentachloride were chosen as the Lewis acids for initial study because of their availability, the stability to reduction of each metal in its highest oxidation state (26,27), and the presumed existence of only the hexachlorometallate ions in fused chloride media (28). The possible comparisons of the effects of charge, size, and geometry between the anions $HfCl_6^{2-}$, $TaCl_6^-$, $AlCl_4^-$, $BiCl_5^{2-}$, and $Bi_2Cl_8^{2-}$ were considered maximal. Other research was later conceived to clarify the results obtained in these systems.

EXPERIMENTAL PROCEDURES

Materials

The bismuth metal used was American Smelting and Refining 99.999% grade. Spectrographic analysis showed the presence of Cu and Ag at the trace level, and Pb, Fe, and Si at the faint trace level. The metal was vacuum fused to allow decomposition and physical removal of impurities, and then rebroken into small pieces for ease in handling and weighing. The metal was stored under vacuum; however, transfers and weighings were performed in the air.

Crystal bar hafnium was supplied by the Pittsburg Naval Reactors Office. Emission analysis revealed the metal to contain 1.4 weight per cent Zr, with Cu and Fe as trace impurities, and Mg and Si as faint trace impurities.

Two mil tantalum sheet was obtained from Fansteel with typical analyses showing the following impurity levels in p.p.m.: O, 15; N, 45; H, 5-; W, 25-; C, Nb, Zr, Mo, Ti, Fe, Ni, Si, Mn, Ca, Al, Cu, Sn, Cr, V, Co, Mg, 10-.

Commercial bismuth trichloride was purified by dehydration at 100°, distillation under a partial pressure of oxygen, and subsequently sublimation under dynamic vacuum. This procedure was employed to remove the carbon impurity present in the commercially available material. An attempt was made to omit the distillation under oxygen to avoid the excessive formation of bismuth oxychloride; however, even repeated sublimations through a course-grade sintered-glass disk were not as successful in removing the carbon impurity. Approximately a 33% yield of white crystalline bismuth trichloride was obtained through this process. In spite of the low yield, this procedure was considered practical in terms of effort and cost because the alternative method, direct reaction between the elements, was known to be extremely slow even under forcing conditions.

Dry box and vacuum line techniques were used throughout this investigation because of the sensitivity of the salts to oxygen and moisture. The drybox was continuously flushed with argon and its atmosphere recycled through Linde molecular sieves. To further insure a low partial pressure of water, an open tray of phosphorus pentoxide desiccant was kept inside the dry box. An evacuable port was used to facilitate entry. All manipulations and weighings of salts were performed in the dry box. The weighings were made using a triple beam, single pan balance which was accurate to five milligrams. Salts were stored in evacuable containers or sealed evacuated glass ampoules.

Commercial potassium chloride, dried under dynamic vacuum at 300°, was used without further purification. Other commercial salts, aluminum tribromide, bismuth tribromide, and ammonium chloride, were sublimed twice under dynamic vacuum before use. The pure salts were white, bright yellow, and white, respectively.

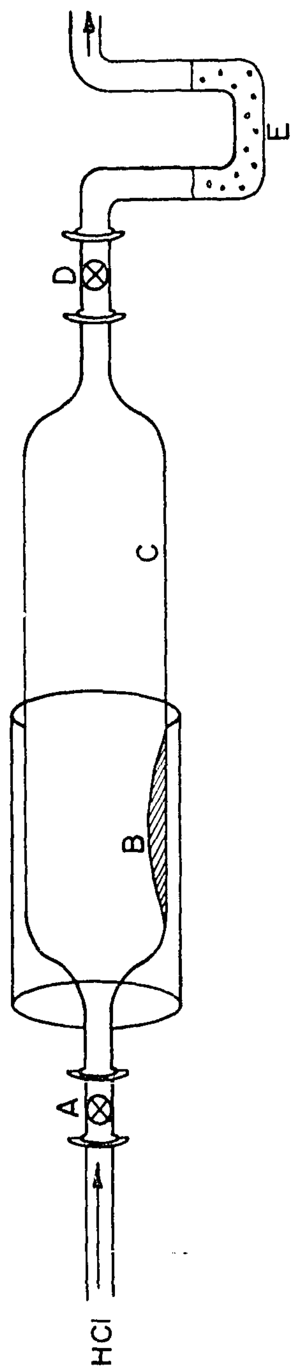
Chlorine gas was obtained in lecture bottles from Matheson Co. Electronic grade hydrogen chloride was supplied by Precision Gas Products.

Synthesis

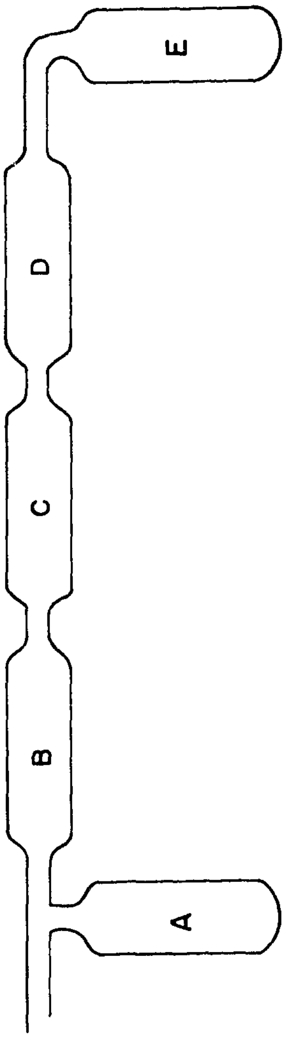
Hafnium tetrachloride was prepared from hafnium metal and hydrogen chloride gas in the apparatus pictured in Figure 1a. The main chamber of the apparatus was constructed with the hafnium metal contained inside it. The apparatus was flushed with a stream of HCl to purge it of air and moisture which would react with the product. The metal was slowly heated to 360° while the gas continued to pass over it. The hafnium tetrachloride formed by the reaction at point B collected in the cooler region of the compartment at site C. When the reaction was complete the stopcocks at A and D were closed and the tube was evacuated on a vacuum line. The container was taken into the dry box where it was cracked open and the salt was transferred to a sublimation vessel. The salt was sublimed under dynamic vacuum and then stored.

Tantalum pentachloride was prepared from the elements. Strips of tantalum were loaded into compartment C of the apparatus shown in Figure 1b. Chlorine was distilled into compartment A which was cooled using a Dry Ice-acetone slush bath. The apparatus was sealed off and placed in a furnace which encased the central chamber and parts of the neighboring chambers (B and D). Chlorine was moved back and forth between

Figure 1. Apparatus for the preparation of (a) hafnium tetrachloride and (b) tantalum pentachloride



(a)



(b)

the cold traps (A and E) passing over the metal heated first at 375° and later at 425°. The pentachloride which collected in the cooler regions of the tube had a yellow cast whereas the pure material is reported to be white. Sublimation of the product yielded crystals which retained a slight yellow tinge. This coloration may have been due to the presence of small amounts of yellow WCl_5 introduced by chlorination of the tungsten impurity present in the tantalum sheet metal.

Reduced bismuth phases were synthesized by the reduction by elemental bismuth of mixtures of bismuth trichloride and the appropriate metal chloride, $HfCl_4$ or $TaCl_5$. The composition of the unreduced mixture was determined by the requirement that all chloride be formally and stoichiometrically converted to the larger less basic MCl_6^{n-} anion present in the respective system. Previous investigations have shown, however, that there are no intermediate compounds formed in either the $BiCl_3$-$HfCl_4$ (29) or the $BiCl_3$-$TaCl_5$ (30) systems.

Reaction containers were constructed of fused silica to prevent side reaction between the melts and the container walls. Either 15 or 40 mm. dia. tubing was closed on one end and connected through 8 mm. tubing to a ball joint on the other end. The choice of the diameter of the reaction vessels was made according to the desire for either a low volume and less material in the vapor phase or a large interface between the metal and salt phases. When separation of crystals from the melt was necessary, a two compartment 20 mm. dia. tube was used. Separating the two chambers was a silica disk with 2 mm. slits cut along a 180 degree arc. These tubes were loaded in the dry box and then sealed off under vacuum; thus, the reactions occurred under the vapor composition and pressure determined by the reactants. In order to minimize the thermal gradients the reaction tubes were jacketed in a larger diameter glass tube and held in place using Fibrefrax (Carborundum Co.) insulation. The temperature was monitored by a thermocouple placed inside the glass jacket near the sample. Cylindrical resistance furnaces used to heat the samples were regulated by Minneapolis-Honeywell Brown Electronik Indicating Proportionating Controllers with a reported accuracy of ± 1°.

Samples of $Bi_{12}Cl_{14}$ were synthesized by bismuth reduction of potassium chlorobismuthate melts. The reactants were heated to 340° to facilitate reduction and then equilibrated below 323°, the compound's incongruent melting point, for at least eight hours. The reduced melt was cooled at a maximum rate of five degrees per hour to 285° and then the reaction vessel was inverted filtering off the mother liquor.

Attempts to prepare $Bi_5(AlBr_4)_3$ were conducted under the assumption that the phase relationships in the $Bi-BiBr_3 \cdot 3AlBr_3$ system were similar to those reported (19) for the analogous chloride system. To determine the appropriate temperatures for crystal growth, reactions and recrystallizations were carried out in a glass furnace. The furnace was made by winding 1 mm. Nichrome wire around a 30 mm. Vycor tube which was jacketed by a larger tube and held in place with asbestos tape. The advantage of being able to see the contents of the furnace was partly offset by the thermal gradients arising from the non-uniform spacing of the heating coil.

Analyses

Small glass vials were filled with samples and then capped while in the dry box. These sample containers were weighed in the air using an analytical balance accurate to 0.1 mg. Their contents were emptied into dilute nitric acid for dissolution and the empty vial weighed. The sample weights were determined by difference and were corrected for the buoyancy of argon. This correction was the difference in weights of a duplicate vial containing argon and then air.

Analysis for bismuth was carried out according to the method of Fritz (31) using EDTA with thiourea as the indicator. Aliquots were heated with concentrated perchloric acid until fuming to eliminate the chloride ions which prevent a sharp endpoint. The pH was monitored throughout the titration because of the sensitivity of the bismuth-thiourea complex to the level of acidity.

Chloride was determined gravimetrically as AgCl from a 50:50 water-acetone solution.

After several attempts it was decided that conventional gravimetric analysis for potassium as the tetraphenylborate salt could not meet the desired accuracy. Potassium was then determined by Mr. R. K. Hansen of the Ames Laboratory Analytical Services Group by atomic absorption spectroscopy using the 7664.9 Å resonance line.

Physical Measurements

The ultraviolet-visible spectra were recorded using a Cary 14 spectrophotometer. The samples were mulled with Nujol or petroleum jelly and placed between two thin optical grade quartz plates. A thin bead of Dow Corning high vacuum silicone grease was placed around the edges of the plates to provide a seal against oxygen and moisture.

The far-infrared spectra were measured on a Beckman Model IR-11 by Mr. C. Hill of the Ames Laboratory Spectroscopic Services Group. The samples were submitted as mulls placed between two sheets of polyethylene and secured in a cell equipped with an O-ring seal.

Magnetic susceptibility data were obtained over the temperature range 77°-300°K using the Faraday balance described in detail by Converse (32). The apparatus consisted of a Cahn model RG electrobalance housed in an evacuable chamber and a Varian electromagnet. Samples were loaded into a small Teflon bucket with a screw-in cap. Measurements were made at five field strengths and susceptibilities corrected for ferromagnetic impurities were obtained using the Hondo-Owens equation. The data were processed on an IBM 360/65 computer using a Fortran IV program written by Converse. The treatment of the data included a diamagnetic correction for the sample container.

X-ray powder patterns were obtained using a Phillips Debye-Scherrer camera with a diameter of 114.59 mm. and exposure to nickel-filtered copper K_α radiation. Powdered samples were loaded into 0.3 mm. Lindemann glass capillaries which were plugged with Apiezon Q wax in the dry box, and later sealed with a gas-oxygen hand torch. The d-spacings were read directly from the film with the aid of a calibrated template. Consideration was given to film shrinkage in the reported values. Intensities were estimated visually based on an arbitrary scale with a maximum value of 100.

Thermal Analysis

Sample containers for thermal analysis were constructed from 30 mm. lengths of 15 mm. o.d. fused silica tubing. The containers had a closed, 5 mm. length of 2 mm. tubing sealed inwardly through the bottom for a thermocouple well and a ball joint connected to the top through 8 mm. tubing. The containers were filled with three to eight grams of sample, sealed under vacuum, and jacketed in another tube with the thermocouple in its well. The junction potential of the thermocouple was plotted as a function of time on a Bristol Model 560 Dynamaster strip chart recorder and measured using a Rubicon potentiometer.

Crystallographic Procedures[1]

Crystal mounting

The crystals were taken into a glove box specifically designed (35) for working under an inert atmosphere while viewing the work area through a long focal-length microscope. A Bausch & Lomb "Stereozoom" microscope with 0.5X objective lens and 10X eyepieces containing a calibrated scale was used. A removable Plexiglass top to the box allowed entrance to the interior and which, when secured, allowed evacuation of the chamber.

The samples were broken into small pieces and crystals carefully separated from the matrix. Crystals were cut into desirable size, approximately 0.1 mm. cubed, using a surgical scalpel. Before being cut the crystals were lightly coated with petroleum jelly to prevent the cut pieces from scattering. Suitable crystals were picked up on the end of a thin glass stalk and carefully inserted into 0.3 mm. Lindemann capillaries. The latter were held in a piece of 2 mm. i.d. Pyrex tubing which enclosed all of the fragile capillary except for the funnel-shaped open end. The glass stalk was removed from

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[1] Contrary to usual practice no attempt has been made to discuss the theory or practical aspects of crystallography beyond the material directly relevant to the problem covered by this thesis. The reader desiring further exposition is referred to the excellent texts by Buerger (33) and Stout and Jensen (34).

the capillary leaving the crystal adhering to its walls. The open end of the capillary was then sealed using a resistance heated wire. When enough crystals had been mounted the capillaries were removed from the dry box, shortened using a gas-oxygen hand torch, and their ends coated with Apiezon W wax as an additional protection against leaks. The capillary was held in a short piece of metal tubing using Apiezon W. This tube was then mounted in a goniometer head for X-ray measurements.

$(Bi^{+})(Bi_9^{5+})(HfCl_6^{2})_3$

Preliminary Weissenberg and precession photographs taken with Ni-filtered Cu K_α radiation showed the crystal system to be hexagonal and to belong to the 6/m Laue class. Extinction conditions, $\ell = 2n+1$ for 00ℓ reflections, were consistent with space groups $P6_3/m$ (C_{6h}^2, No. 176) and $P6_3$ (C_6^6, No. 173).

Precise lattice parameters and their standard deviations, $a = 13.890 \pm 0.001$ and $c = 10.692 \pm 0.002$ Å, were determined by least-squares fitting[1] (36) to the two theta angles (Mo K_α radiation) of 21 independent reflections. The diffraction angles were measured as the difference in the readings of the ω arc of a previously aligned four-circle diffractometer for

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[1] The computer programs used in this investigation are listed and gratefully acknowledged in Table 1. They were run on an IBM 360 Model 65 computer.

Table 1. *Computer programs obtained from outside sources*

Program name	Language	Description	Authors	Reference
LCR-2	Fortran	Lattice constant refinement	D. E. Williams	(36)
ABCOR	Fortran	Absorption correction	D. J. Wehe, W. R. Busing, and H. A. Levy	(37)
ORFLS	Fortran	Oak Ridge Fortran Crystallographic Least-Squares Program	W. R. Busing, K. L. Martin, and H. A. Levy	(38)
OMEGA	Fortran	Adjustment of Least-Squares Weights	C. R. Hubbard[a]	
ALFF	PL/I	General Fourier synthesis	C. R. Hubbard and C. O. Quicksall[b]	

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[a] Hubbard, C. R., Department of Chemistry, Iowa State University, Ames, Iowa. Private communication. 1969.

[b] Hubbard, C. R., and Quicksall, C. O., Iowa State University, Ames, Iowa. Private communication. 1969.

Table 1. (Continued)

Program name	Language	Description	Authors	Reference
ORFFE	Fortran	Oak Ridge Fortran Crystallographic Function and Error Program	W. R. Busing, K. O. Martin, and H. A. Levy	(39)
ORTEP	Fortran	Oak Ridge Thermal Ellipsoid Plot Program	C. K. Johnson	(40)
TABLE	Fortran	Structure factor tabulation	M. L. Hackert[c]	

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[c] Hackert, M. L., Department of Chemistry, Iowa State University, Ames, Iowa. Private communication. 1969.

the peak positions of $hk\ell$ and $\overline{hk\ell}$ reflections. The center of each peak was determined by left-right, top-bottom beam splitting. By measuring the angle between the two positions of the crystal not only was the zero instrument error eliminated but also the errors due to absorption and incorrect centering of the crystal.

The density was measured micropycnometrically on a 1 g. sample by displacing chloroform previously dried over calcium hydride. The experimental value of 6.05 ± 0.2 g/cm^3 compares favorably with a value of 6.07 g/cm^3 calculated using $Z = 2$.

Three-dimensional peak height intensity data were collected on an automated Hilger-Watts four-circle diffractometer using Zr-filtered Mo K_α radiation and a take-off angle of 4.5°. The crystal was mounted with the c-axis colinear with the spindle axis. The diffractometer and experimental arrangement have been described in detail elsewhere (41). Stationary crystal-stationary counter background measurements were made on both sides of the peak along a theta-two theta path. Periodic measurement of three standard reflections confirmed the absence of crystal decomposition or motion. A total of 1122 reflections were measured in the unique sector of a sphere bounded by $\Theta = 25°$. Approximately 100 reflections with diffraction angles spanning the range from zero to twenty-five degrees were remeasured using a Θ-2Θ step scan technique. These integrated intensities were used to convert the remaining reflections from peak height to integrated intensities by the method of Alexander and Smith (42).

The net converted intensities were also corrected for Lorentz, polarization, and absorption effects. The crystal used to gather data was a 0.1 mm. length of a needle with a distorted hexagonal cross-section, approximately 0.1 x 0.15 mm. Examination of the crystal under 60X magnification gave approximate dimensions. The precise shape and orientation of the crystal used to calculate the absorption correction (43) were varied within reasonable limits to minimize the difference between symmetry equivalent $\{h0\ell\}$ and $\{0h\ell\}$ data. The transmission factors, computed using the program ABCOR (37) and a linear absorption coefficient of 571.0 ranged from 0.55% to 4.33%, almost an eight-fold range.

While treating the raw intensities the standard deviation in each measurement was estimated as

$$\sigma_I = [C_T + C_B + (K_T C_T)^2 + (K_B C_B)^2 + (K_A C_R)^2]^{1/2}/A$$

where C_T, C_B, C_R are the total, background, and net counts, respectively, and A is the transmission factor. K_T, K_B, and K_A are the fractional random errors in C_T, C_B, and A respectively, and were arbitrarily assigned values of 0.03, 0.03, and 0.06. The standard deviation in the structure factor can then be calculated by the method of finite differences (44) as

$$\sigma_F = \left(\frac{C_R}{LpA} + \frac{\sigma_I}{Lp}\right)^{1/2} - F_{obs}$$

where Lp is the Lorentz-polarization factor and the observed structure factor

$$F_{obs} = \left(\frac{C_R}{LpA}\right)^{1/2}.$$

Consideration of symmetry-extinct data determined that only those reflections with $F_{obs} \geq 3\sigma_F$ would be considered observed and used in the refinement. Of the 1122 measured reflections, 839 met this criterion. In the least-squares refinement the structure factors of the individual reflections were given weights equal to the square of the reciprocal of their respective standard deviations.

$(Bi_9^{5+})(BiCl_5^{2-})_2(Bi_2Cl_8^{2-})_{1/2}$

The structure of this compound was solved in 1961 (17) using film techniques. The least-squares refinement was carried to convergence using only isotropic thermal parameters. Because of the evidence in the final difference map of high anisotropy in the thermal motion of the bismuth atoms, and because of the desire to compare the nonabismuth cations in the two environments, the further refinement of the structure using anisotropic thermal parameters was attempted. Two independent sets of data were used in this process: the original film data and a new set of data collected by counter methods.

$Bi_{12}Cl_{14}$ was reported to belong to the orthorhombic crystal system with lattice parameters $\underline{a}$ = 23.057 ± 0.002, $\underline{b}$ = 15.040 ± 0.007, and $\underline{c}$ = 8.761 ± 0.003 Å. Extinction conditions limited the choice of space groups to Pnnm (D_{2h}^{12}, No. 58) or Pnn2 (C_{2v}^{10}, No. 34); successful refinement being achieved in the centric group. The intensities of 1957 observed reflections were earlier recorded with Cu K_α radiation using the equi-inclination Weissenberg technique supplemented by precession photographs. The data were treated for Lorentz, polarization, and absorption effects. The further refinement was begun using these reported data (45), unit weights, and a different scale factor for each of the six layers, hk0 through hk5, of data. 2881 peak height intensities were measured within one full octant of a two theta sphere of 50° using Mo K_α radiation and an automated Hilger-Watts four-circle diffractometer with a take-off angle of 4.5°. As described elsewhere (41), the diffractometer aligned the crystal after being given the location of three reflections whose indices collectively included non-zero terms for h, k, and ℓ. The center of each reflection was determined by left-right, top-bottom beam splitting. As part of the alignment procedure the lattice parameters computed from the orientation matrix were printed by teletype. The values of the unit cell constants determined by this procedure were substantially in agreement with those reported earlier: $\underline{a}$ = 23.067(6)[1], $\underline{b}$ = 14.992(19), and $\underline{c}$ = 8.772(8) Å.

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[1] Estimated errors in parentheses were based on the average deviations among several determinations; hence, they represent precision rather than accuracy.

As described above the new data were converted to integrated intensities and corrected for Lorentz, polarization, and absorption effects. The transmission factors, calculated for the cylindrical crystal (0.237 x 0.167 mm. in diameter) using a linear absorption coefficient of 678.2, ranged from 0.11% to 1.27%.

The standard deviations of the structure factors were estimated as before except the fractional random errors in the total count, background count, and absorption factor were assigned values of 0.10, 0.10, and 0.15, respectively. The square of the reciprocal of the standard deviation was used as the weight of each structure factor in the least-squares refinement. 1705 reflections exceeded the $3\sigma_F$ threshold established by consideration of symmetry-extinct data as the criterion for use in refinement.

RESULTS AND DISCUSSION

Synthesis and Preliminary Characterization

The isolation of new compounds prepared neat in the molten salt media was hampered by the tendency of the solidified solvent to adhere to the product. Even the determination of the composition of the phases was prevented by the very slow rate at which these systems reached equilibrium. This also made thermal analysis of limited value. Similarly the meticulous work of Corbett (3) failed to establish the true stoichiometry of the bismuth subchloride (17) so that the elucidation of the phase relationships in the Bi-$BiCl_3 \cdot 3AlCl_3$ system was only made possible by the multifarious spectral (20,21), synthetic (19), and crystallographic (46) investigations. Many of these approaches rely on the availability of a foreign solvent media, such as $NaAlCl_4$ and $KAlCl_4$, which allow synthesis and recrystallization by classical methods and provide a means to gauge the amount of solvent present in the isolated phase. Unfortunately the alkali metal hexachlorometallate systems appropriate for this investigation do not provide a suitable temperature range to serve as a solvent for the salts of interest. The attempts to prepare the pure phases are detailed below, but they were largely inconclusive. Resort to crystallography was necessary and possible in the hafnium system, but the lack of suitable crystals prevented this recourse in the other cases. The far-infrared spectra of reduced compounds and compositions were gathered to allow a comparison between the synthetic results as well as an evaluation of this technique as a means of identifying the polynuclear cations.

The Bi-$BiCl_3 \cdot 3/2HfCl_4$ System

The initial experiments performed with this system were exploratory equilibrations of bismuth metal and a 3:2 mixture of hafnium tetrachloride and bismuth trichloride. The unreacted bismuth was recovered, cleaned, and weighed. The amount of bismuth consumed was taken as the difference between the weights of the metal added and recovered. The results of these experiments are shown in Table 2. Powder patterns were taken of the product of each equilibration. Comparison between patterns from different equilibrations showed them to be identical. The disagreement in the extent of reduction appeared to be due to the difficulty encountered in cleaning the recovered metal pellet. No relationship was evident between the individual results and any of the other experimental conditions. A sample was prepared with 68 mole % bismuth in $BiCl_3 \cdot 3/2HfCl_4$. The powder pattern of this composition was a superposition of the diffraction patterns of the unknown phase and the starting salts. This suggested that only one reduced compound was formed.

Thermal analysis measurements were made on samples ranging from 50 to 95 mole % bismuth. The thermal halts were

Table 2. Data on the maximum reduction[a] in the $Bi-BiCl_3 \cdot 3/2HfCl_4$

Sample number	$HfCl_4/BiCl_3$ mole ratio	Weight of Bi reacted[b] (gm.)	Length of equilibration (day)	Temperature of equilibration (°C)	Extent of reduction[a]
1	1.44	3.265	1-1/2	450	82.8
2	1.64	1.662	7	425	77.1
3	1.51	2.491	7	440	78.5
4	1.46	2.846	7	375	81.4
5	1.48	3.092	7	400	83.4
6	1.50	2.771	7	460	81.5
7	1.49	6.108	3	490	81.8
8	1.51	6.278	3	490	83.0

[a] Extent of reduction is defined as:

$$\frac{\text{moles Bi (react)} \times 100}{\text{moles Bi (react)} + \text{moles } BiCl_3}.$$

[b] The weight of bismuth reacted is indicative of the size of the sample.

generally not reproducible and showed large degrees of supercooling. Although no additional information was deduced about the phase relationships in this system, a halt at 507° was visually confirmed to be the incongruent melting of the reduced phase. Fortuitously equilibration of excess bismuth and the stoichiometric mixture of $BiCl_3$ and $HfCl_4$ just below the peritectic temperature resulted in the growth of acicular crystals from the bulk product. A typical reaction tube with crystals is pictured in Figure 2. Further attempts at determining the stoichiometry of the reduced phase by classical techniques were abandoned. The precise composition of this compound, $Bi_{10}Hf_3Cl_{18}$, was determined by the X-ray structure determination described below.

The crystal structure revealed the ionic formulation $(Bi^+)(Bi_9^{5+})(HfCl_6^{2-})_3$ to be an appropriate description of the primary interactions in the solid. This raised the possibility of a paramagnetic contribution to the bulk magnetic susceptibility from the Bi^+ ion which has a $6s^2\ 6p^2$ electronic configuration. The magnetic susceptibility measured by the Faraday method eliminated this speculation. Table 3 summarizes the experimental data. The total molar susceptibility, χ_M, is $-964 \pm 34 \times 10^{-6}$ emu/mole and is independent of temperature in the range 77° to 298°K. Subtraction of the estimated diamagnetism for the Bi^{+3}, Hf^{+4}, and Cl^- cores (47) leaves a residual molecular diamagnetism of -198×10^{-6} emu/mole. This high value of the residual diamagnetism indicates that

Figure 2. Crystals of $Bi_{10}Hf_3Cl_{18}$ projecting from the bulk sample

Table 3. $(Bi^{+})(Bi_9^{5+})(HfCl_6^{2-})_3$[a] magnetic susceptibility by the Faraday method

Run	Temp. (°K)	χ_M[b] (emu/mole)
1	77	-0.976[c] ± 0.028[c]
2	77	-0.906 ± 0.028
3	77	-0.902 ± 0.028
4	77	-0.929 ± 0.025
5	143	-0.868 ± 0.052
6	143	-0.906 ± 0.025
7	143	-0.954 ± 0.029
8	143	-0.946 ± 0.025
9	143	-0.949 ± 0.021
10	296	-0.988 ± 0.024
11	297	-1.004 ± 0.027
12	297	-0.971 ± 0.049
13	298	-0.938 ± 0.024
14	298	-0.931 ± 0.027
15	298	-0.934 ± 0.030

[a] Molecular weight = 3263.42 grams/mole.

[b] Measurements were made at five field strengths and susceptibilities at infinite field were obtained from a least-squares fit to a Hondo-Owens plot.

[c] Values should be multiplied by 10^{-3}.

the twenty-two valence electrons of the Bi_9^{5+} ion make a sizable contribution to the diamagnetic susceptibility. This conclusion is compatible with the highly delocalized valence electron molecular orbital description proposed by Corbett and Rundle (18) for this cation.

The ligand field theory used to interpret the spectrum of the Bi^+ ion in molten salt media (23) predicts a $^3P_0$ diamagnetic ground state, in agreement with experiment. This theory can be used to assign the single peak observed at 500 mμ (20 kK) in the ultraviolet-visible spectrum of $Bi_{10}Hf_3Cl_{18}$ to a $^3P_0$ <-> $^3P_2$ transition. From Table 4 it is apparent that the 17.1 kK transition is the most intense in the Bi^+ spectrum in the $AlCl_3$-NaCl eutectic. Table 5 lists the observed band

Table 4. Band energies and oscillator strengths for Bi^+ in the $AlCl_3$-NaCl eutectic[a]

E (kK)	$10^4 f$
11.1	0.7
14.4	4.5
15.2	5
17.1	37
30.0	0.3
32.5	1.5

[a] Contents of this table are taken from (20)

Table 5. Band maxima for $^{3}P_{0}$ <-> $^{3}P_{2}$

Temp. (°C)	ε	$\bar{\nu}$ (kK)	Media	Ref.
25°	-	20	$Bi_{10}Hf_3Cl_{18}$	this work
380°	700	18.2	$ZnCl_2$- KCl eutectic (72:28)	(20)
243°	5800	17.9	Bi-$BiCl_3$ melt	(13)
310°	300	17.1	$AlCl_3$-NaCl eutectic (63:37)	(20)
130°	400			
250°	550	16.4	$AlBr_3$-NaBr eutectic (68:32)	(22)

maxima for this transition in several molten salts. The energy of this transition seems to shift to higher energy with increasing field strength. Bromide ligands provide weaker fields than chloride ligands as evidenced by their relative positions in the spectrochemical series. The relative basicities of the $AlCl_3$-NaCl and $ZnCl_2$-KCl eutectics implied by this correlation are consistent with the existence of the large low-field Bi_8^{2+} ion in the former but not the latter system (21). The assignment made for the spectrum recorded using the Bi-$BiCl_3$ system is questionable. The band was attributed to Bi^+ (13) and does have a reasonable position for the band maximum, but the molar absorptivity is high relative to the intensity of this band in other media. Finally the dinegative hexachlorohafnate(IV) ion provides a much stronger field than the mononegative anions probably present in the molten salts. The assignment is considered reasonable but not exclusive.

The Bi-$BiCl_3 \cdot 3TaCl_5$ system

Thermal analysis measurements on this system gave results which were not reproducible except for a halt at ~440°. This temperature was confirmed visually as being the melting point of the most reduced phase. Samples containing 63.1, 80.2, 83.4, 90.5, and 93.8 mole % bismuth in $BiCl_3 \cdot 3TaCl_5$ were prepared by equilibration for 2-1/2 weeks. Earlier thermal analysis had revealed a halt in the range from 310° to 330° for compositions greater than 75 mole % metal. Since this halt may be due to the melting of an intermediate phase, the first four samples were equilibrated at 300° and the last sample was heated at 410°. The powder patterns of the products are listed in Table 6. The $BiCl_3$-$TaCl_5$ system is a simple eutectic (30), therefore the powder pattern of the unreduced composition will be a superposition of the diffraction lines of the constituent salts.[1] There appear to be two new phases formed in the reduced system. The intermediate phase has a composition between 80 and 83 mole % bismuth and the most reduced phase has a composition between 90 and 94 mole % metal.

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[1] The principal diffraction lines for $BiCl_3$ (48) with the relative intensities in parentheses are: 4.75(100), 4.07(18), 3.68(18), 3.365(33), 2.86(33), 2.73(15), 2.58(24), 2.44(21), 2.38(17), 2.23(32), 2.15(14), 2.04(22).

The principal lines for $TaCl_5$ (J. Ebner, 1969, personal communication) are: 9.0(50), 5.8(100), 5.2(80), 5.05(80), 4.49(90), 4.29(80), 3.35(25), 3.10(30), 2.95(25), 2.74(100), 2.64(75), 2.53(75), 2.47(75), 2.44(30), 2.36(30), 2.13(100), 2.10(25), 2.03(25).

Table 6. Powder patterns of reduced compositions in the $Bi-BiCl_3 \cdot TaCl_5$ system

63.1[a]		80.2		83.4		90.5		93.8	
d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0
10.3	<5	10.3	80	10.3	80	10.3	40	10.3	30
-	-	9.0	30	9.0	30	9.0	10	9.0	5
-	-	8.7	40	8.6	20	8.7	5	8.7	5
-	-	8.0	30	-	-	-	-	-	-
-	-	-	-	7.7	10	7.6	5	-	-
-	-	-	-	-	-	7.3	10	7.3	15
5.7	35	5.8	30	5.8	20	-	-	-	-
-	-	5.42	40	5.41	50	5.4	40	5.45	8 d
5.3	30	5.3	100	5.3	100	-	-	-	-
-	-	5.2	40	5.18	50	5.15	65	5.22	40
4.8-4.9	20	4.8	30	4.80	25	-	-	-	-
4.4	20	4.4	20	4.42	5	4.4	5	-	-
-	-	4.05	5	4.05	10	-	-	-	-
-	-	3.80	60 b[b]	3.80	50	3.81	10	-	-
-	-	-	-	3.78	70	3.79	30	3.77	25
3.7	<5	3.70	50	3.69	60	3.66	40	3.65	30
-	-	3.60	20	3.60	20	-	-	3.60	8
-	-	3.50	20	3.51	5	3.50	5	-	-
-	-	3.45	35	3.43	35	3.43	65	3.42	75
3.30	50	3.30	40 d	3.30	30	3.30	30	3.30	30
2.90	10	-	-	2.92	10	2.93	85	2.92	100
-	-	-	-	-	-	2.80	35	2.80	5
-	-	-	-	-	-	2.77	15	-	-
2.73	80	2.73	60	2.72	40 d	2.70	100	2.70	100
-	-	2.65	30	2.64	25	2.65	5	2.64	15
2.51	15	-	-	-	-	2.50	20	2.50	40
2.45	20	2.46	40	2.45	50	2.45	40	2.45	60
-	-	2.38	70	2.37	40	-	-	-	-
-	-	2.33	35	2.33	35	2.34	45	2.33	75
-	-	-	-	-	-	2.32	30	2.31	30
2.28	35	-	-	-	-	2.28	20	-	-
-	-	2.20	10	2.20	15	-	-	-	-
2.13	100	2.14	40	2.14	30	2.15	60	2.41	80
2.10	20	2.12	20	2.11	10	-	-	-	-
2.06	10	-	-	2.07	10	2.07	10	2.08	10
-	-	2.03	5	2.02	10	2.02	15	2.01	20

[a] The composition given in mole % bismuth in $BiCl_3 \cdot 3/2HfCl_4$.

[b] b=broad, d=diffuse .

Microscopic examination of one of the thermal analysis samples had shown the presence of crystals with two different colors, dark red and black (D. A. Lokken, 1969, personal communication). The red color appeared similar to the intermediate phase found in the $Bi-BiCl_3 \cdot 3AlCl_3$ system. The two reduced compounds in the aluminum chloride pseudobinary system have compositions within the ranges determined for those compounds formed in the tantalum chloride system; $Bi_5(AlCl_4)_3$ with 80 mole % bismuth and Bi_4AlCl_4 with 91.7 mole % metal. Although the similarity is noted between the systems containing tantalum pentachloride and aluminum chloride, there is no unambiguous evidence to support the relationship.

Because difficulty was encountered in attempting to prepare the pure phases by direct synthesis, the most promising procedure for isolating the phases was considered to be recrystallization from a foreign solvent. Since the alkali metal chloride-tantalum pentachloride systems do not have suitable melting points, an attempt was made to use the ammonium analogue which is molten in the temperature range of interest. Unfortunately the work of Morozov and Toptygin (49) may be correct and the fused solvent was intensely colored. The other possibility is that the ammonium ion reduced the $TaCl_6^-$ to $TaCl_6^{2-}$ which is highly colored (50). This hindered the observation and isolation of the desired compounds. Further work in this system was discontinued. A source of the Bi_5^{3+} ion in the solid state was sought. It was hoped that the peculiarities of the interactions of this cation and anions in the solid might give some insight as to why its existence seems limited to media containing mononegative anions. The compound $Bi_{10}Hf_3Cl_{18}$ has the same average oxidation state for bismuth as the Bi_5^{3+} cation but the species present in the solid are Bi^+ and Bi_9^{5+} ions.

The Bi-$BiBr_3 \cdot AlBr_3$ system

The compound $Bi_5(AlCl_4)_3$ has been shown (46) to crystallize in a twinned pseudo-orthorhombic cell. The investigation of the Bi-$BiBr_3 \cdot AlBr_3$ system was conducted in the hope of obtaining suitable single crystals for an X-ray crystallographic study. The possibility existed that the change in anion might result in a different crystal habit. No good crystals were found. The powder patterns of the two compounds, shown in Table 7, suggest that the two phases may be isostructural. The tetrabromoaluminate obviously must have a larger unit cell. The relative intensities are dependent on the diffracting power of the constituent atoms; therefore the difference in relative intensities between the chloride and bromide salts are reasonable.

The Bi-$BiCl_3$-KCl system

The chemical composition of the bismuth subchloride has not been determined accurately by chemical analysis. The empirical formula Bi_6Cl_7 was determined by the elucidation of

Table 7. Interplanar spacings and relative intensities for diffraction lines of $Bi_5(AlCl_4)_3$ and $Bi_5(AlBr_4)_3$

$Bi_5(AlCl_4)_3$[a]		$Bi_5(AlBr_4)_3$	
d(Å)	I/I_0	d(Å)	I/I_0
9.45	0.1	9.8	3
8.60	100	8.8	100
7.45	10	7.5	5
6.8	10	6.25	50
6.58	0.1	5.1	85
5.97	70	3.95	8
4.96	30	3.57	8
4.84	50	3.25	5
3.83	50	3.12	20
3.29	10	2.9-3.0	100
3.25	30	2.78	35
3.103	0.5	2.66	30
3.051	10	2.44	8
3.025	10	2.14	8
2.966	40	2.08	20
2.914	10	2.03	15
2.692	50	1.88	10
2.657	50	1.85	10
2.569	30	1.80	15
2.547	60	1.76	5
2.369	0.5	1.73	10
2.345	0.5	1.70	15
2.302	10	1.64	15
2.266	10	1.535	10
2.241	10	1.51	5
2.210	0.1		
2.189	0.5		
2.164	15 diffuse		
2.102	15 diffuse		
1.998	10		
1.833	0.5		
1.710	50		
1.670	10		
1.647	20		
1.500	10		
1.465	30		
1.413	10		

[a] Diffraction lines for this phase are reported by Corbett (19) and Levy, et al. (16). The pattern reported here was taken from Grossaint (51) who placed the relative intensities on one scale.

the crystal structure. In an attempt to substantiate the results of the X-ray study, samples of the lower chloride were prepared from Bi-$BiCl_3$-KCl melts and the potassium content of the crystals used to correct their analysis for solvent retention. It is important to realize that correction for solvent retention can only be valid if the solvent retained by the crystals has the same composition as the solvent analyzed after having removed the crystals. This condition can only be approximated if the gross composition of the solvent does not change appreciably during crystallization. The correction will also be more accurate the greater the difference in composition of the solvent and the crystals. Table 8 shows the results of a typical analysis. The magnitude of the "solvent correction" suggests that the procedure is not capable of the necessary accuracy to differentiate between BiCl (85.85 weight % bismuth) and $Bi_{12}Cl_{14}$ (83.47 weight % bismuth).

Although the attempted analysis was not successful, experiments did reveal an improved synthetic procedure for the reduced compound. Contrary to the usual arguments about acid-base interactions, the addition of the base potassium chloride to the bismuth-bismuth trichloride binary increased the quantity of crystalline $Bi_{12}Cl_{14}$ recovered from the melt. Further experiments revealed that whereas small additions of the base to the binary increased the reduction, large concentrations of KCl prevented any reduction from occurring. These observations can be rationalized in terms of the structure of

Table 8. Typical analysis of $Bi_{12}Cl_{14}$ grown from $Bi\text{-}BiCl_3\text{-}KCl$ melts.

	Crystals	Solvent
Sample weight	1.132 g.	1.085 g.
Bi(EDTA titration)	0.891 g.	0.815 g.
Cl(AgCl ppt.)	0.236 g.	0.255 g.
K (At. Absorption)	0.014 g.	0.028 g.
Σ analyses	1.142 g.	1.098 g.
wt. check (%)	$100._9$%	$101._1$%
Bi correction[a]	0.418 g.	-
Cl correction[a]	0.131 g.	-
Bi corrected	0.474 g.	-
Cl corrected	0.106 g.	-
corrected wt. % Bi (=100Bi/(Bi+Cl))	$81._7$	-

BiCl wt % Bi=85.85%

$Bi_{12}Cl_{14}$ wt % Bi=83.47%

average wt % Bi(Corbett) = 84.93%[b]

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[a] Computed using the formula employed by Corbett (19).

[b] It is important to note that disproportionation and subsequent loss of Cl may have occurred in an attempt to remove excess $BiCl_3$ before analysis, giving high values for Bi content.

the KCl-$BiCl_3$ melts. Phase (52), cryoscopic (53), and spectral (54) studies suggest the presence of $BiCl_4^-$ and $BiCl_5^{2-}$ ions in the melt with very little $BiCl_6^{3-}$. Since these ions are present in the solid $Bi_{12}Cl_{14}$, it appears that a common ion effect increased the amount of the phase of interest. At higher chloride concentrations most of the bismuth in the melt is complexed thus increasing the stability of the Bi^{3+} state and decreasing the reduction to the Bi_9^{5+} ion. The best preparative conditions appeared to be reduction with excess bismuth of melts containing 20 to 30 mole % KCl in $BiCl_3$.

The far-infrared spectra

The far-infrared spectra were recorded for $Bi_{10}Hf_3Cl_{18}$, $Bi_{12}Cl_{14}$, and several reduced compositions in the Bi-$BiCl_3 \cdot 3TaCl_5$ system. Traces of the spectra are pictured in Figures 3, 4, and 5, respectively, and in Figure 6 for the compounds $Bi_5(AlCl_4)_3$ and $Bi_4(AlCl_4)$.[1] Possible bands have been marked with arrows. Representative bands for the stoichiometric compounds are listed in Table 9. Table 10 shows the bands for the reduced compositions. Table 11 contains the known vibrational frequencies of the anions present in the reported phases. The assignment of bands arising from anion vibrations are discussed below, but

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[1] The spectra of the tetrachloroaluminate salts were generously furnished by Dr. D. J. Prince (D. J. Prince, 1969, personal communication).

Figure 3. Far-infrared spectra of $Bi_{10}Hf_3Cl_{18}$

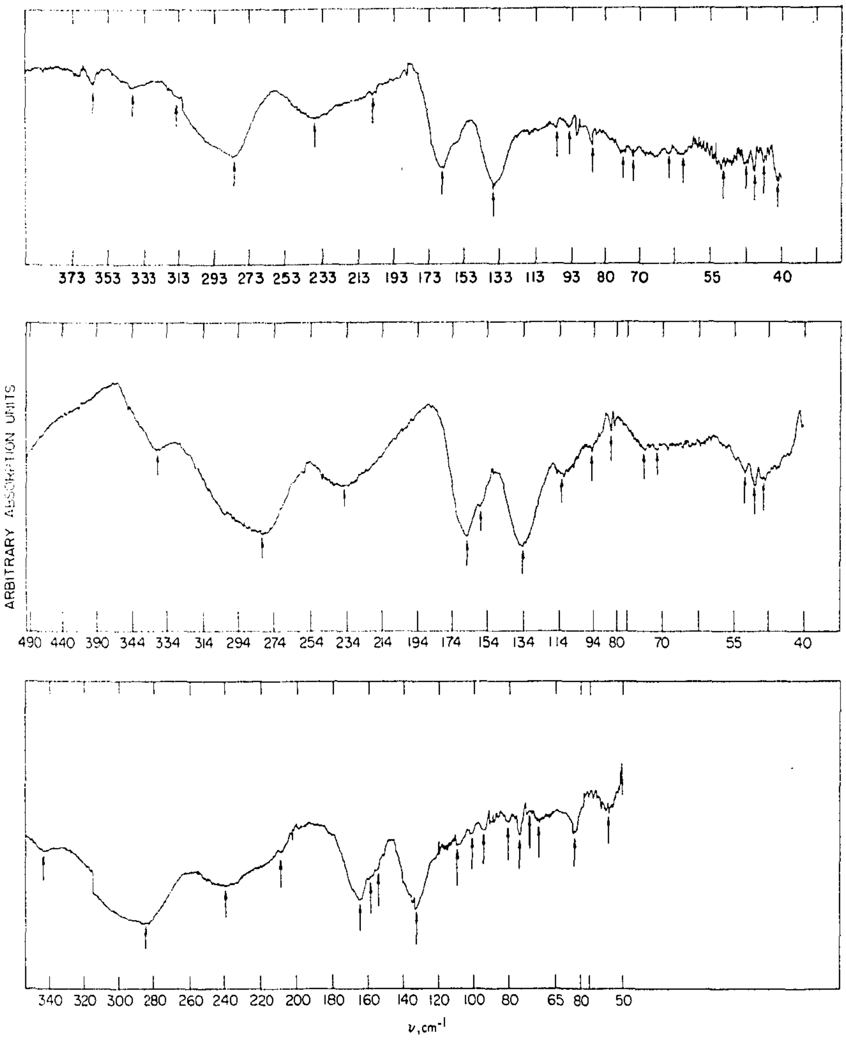
373 353 333 313 293 273 253 233 213 193 173 153 133 113 93 80 70 55 40
ARBITRARY ABSORPTION UNITS
490 440 390 344 334 314 294 274 254 234 214 194 174 154 134 114 94 80 70 55 40
340 320 300 280 260 240 220 200 180 160 140 120 100 80 65 80 50
ν, cm⁻¹

Figure 4. Far-infrared spectra of $Bi_{12}Cl_{14}$

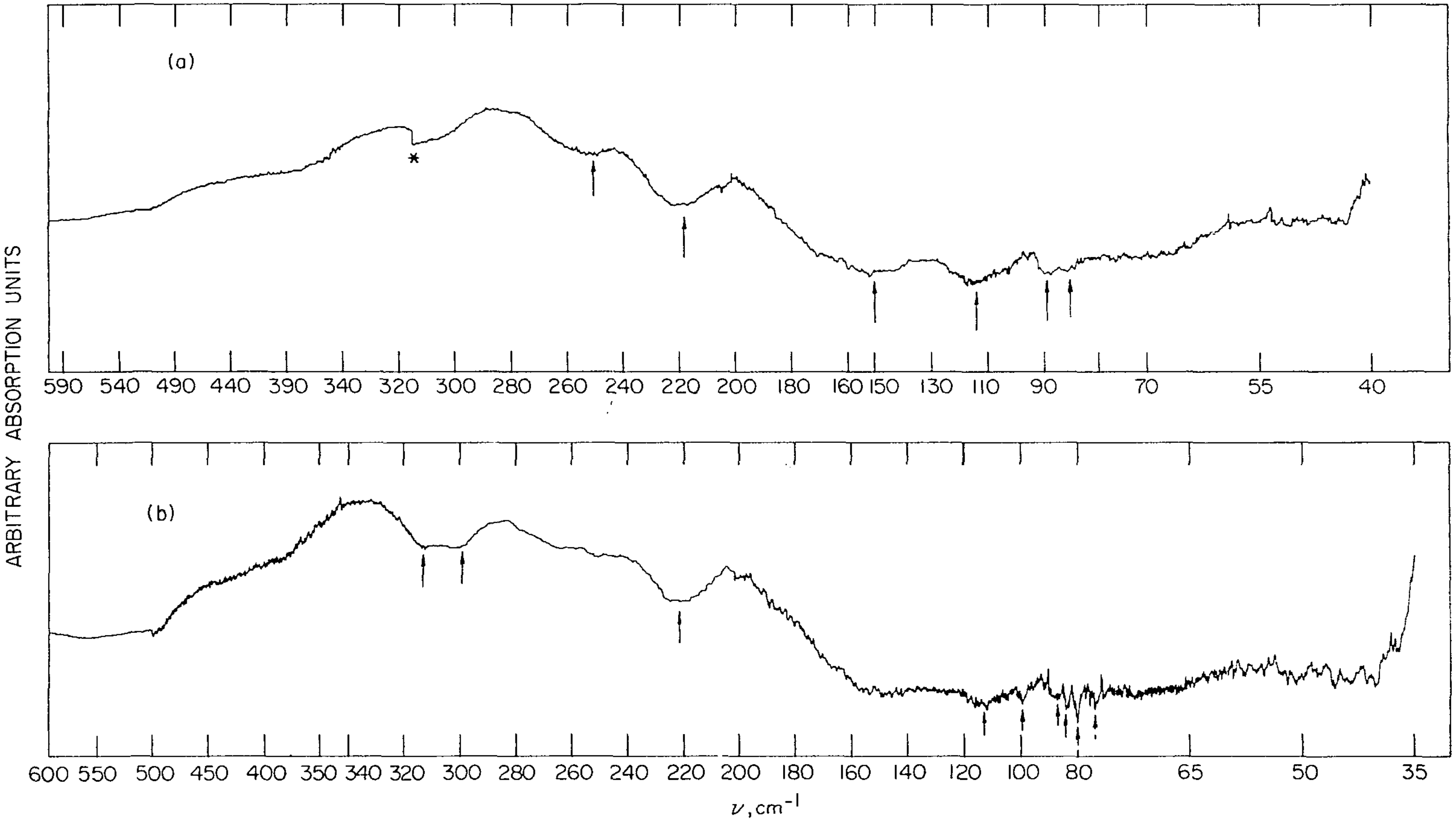
(a)
*
590 540 490 440 390 340 320 300 280 260 240 220 200 180 160 150 130 110 90 70 55 40
(b)
600 550 500 450 400 350 340 320 300 280 260 240 220 200 180 160 140 120 100 80 65 50 35
ARBITRARY ABSORPTION UNITS
ν, cm^{-1}

Figure 5. Far-infrared spectra of reduced compositions in the system $Bi-BiCl_3 \cdot 3TaCl_5$:

(a) 80.2 mole % bismuth;
(b) a different sample with the same composition as (a);
(c) sample (b) rerun 4 hr. later;
(d) 90.5 mole % bismuth; and
(e) 93.8 mole % bismuth

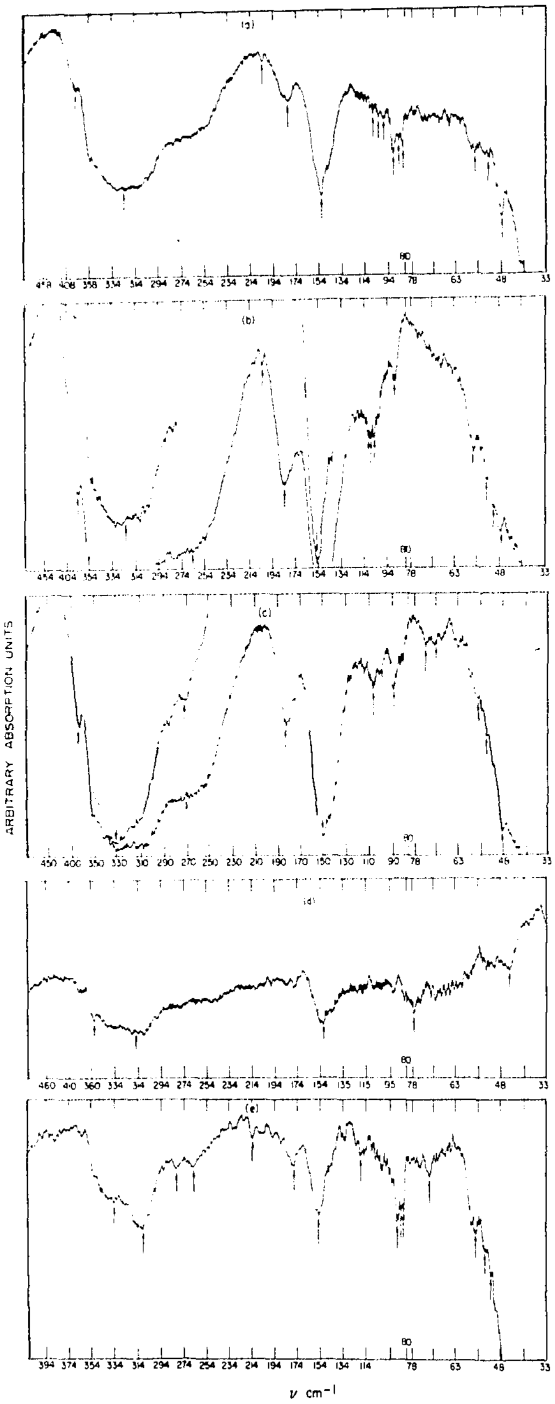
(a)
418 408 358 334 314 294 274 254 234 214 194 174 154 134 114 94 78 63 48 33
80
(b)
454 404 354 334 314 294 274 254 234 214 194 174 154 134 114 94 78 63 48 33
80
(c)
450 400 350 330 310 290 270 250 230 210 190 170 150 130 110 90 78 63 46 33
80
(d)
460 410 360 334 314 294 274 254 234 214 194 174 154 135 115 95 78 63 48 33
80
(e)
394 374 354 334 314 294 274 254 234 214 194 174 154 134 114 78 63 48 33
80
ARBITRARY ABSORPTION UNITS
ν cm⁻¹

Figure 6. Far-infrared spectra of (a) $Bi_5(AlCl_4)_3$ and (b) $Bi_8(AlCl_4)_2$ (D. J. Prince, 1969, personal communication)

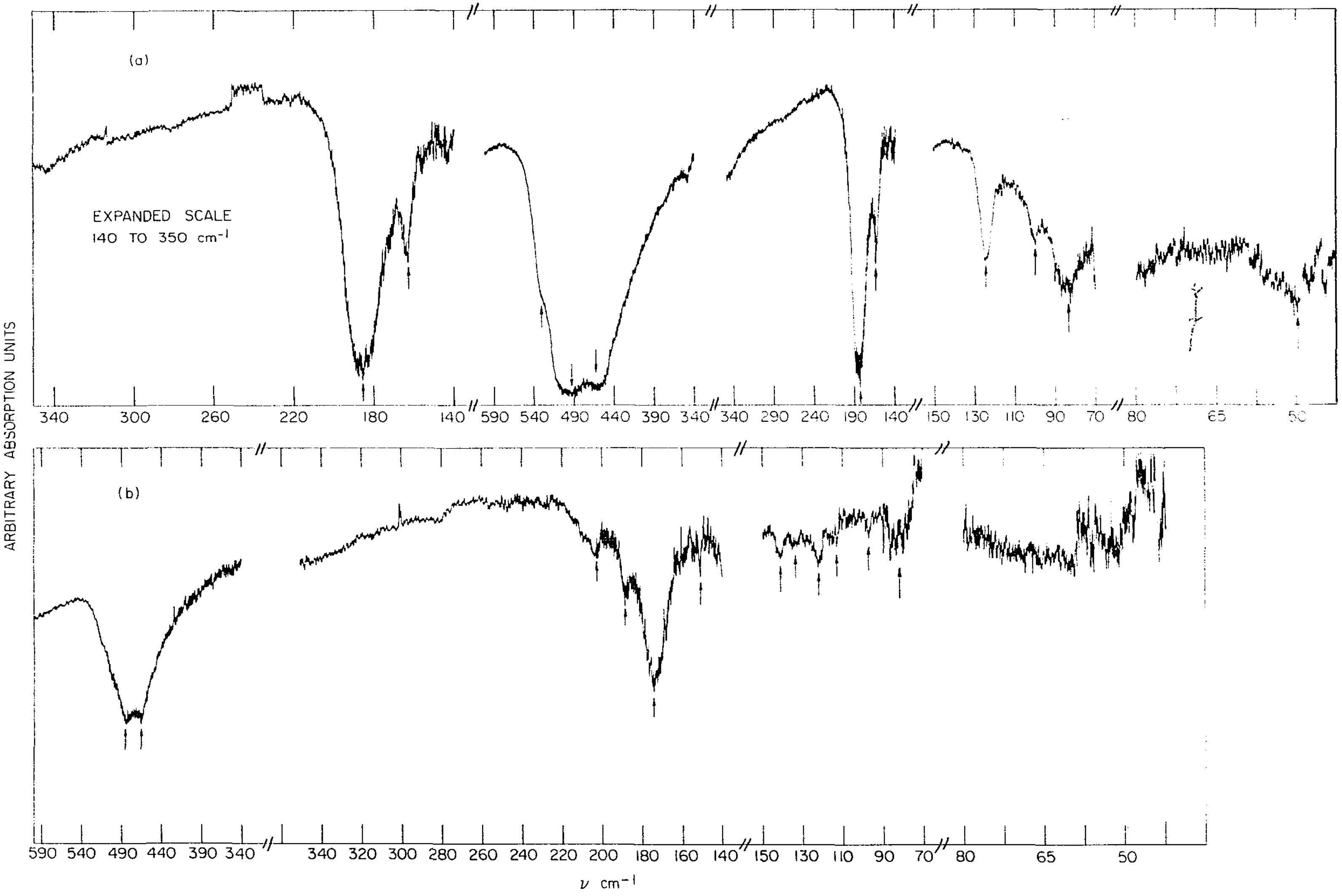
(a)
EXPANDED SCALE
140 TO 350 cm⁻¹
340 300 260 220 180 140 590 540 490 440 390 340 340 290 240 190 140 150 130 110 90 70 80 65 50
(b)
590 540 490 440 390 340 340 320 300 280 260 240 220 200 180 160 140 150 130 110 90 70 80 65 50
ARBITRARY ABSORPTION UNITS
ν cm⁻¹

Table 9. Far-infrared frequencies of $Bi_{10}Hf_3Cl_{18}$, $Bi_{12}Cl_{14}$, $Bi_5(AlCl_4)_3$, and $Bi_4(AlCl_4)$ in the solid state (in cm^{-1})

	$Bi_{10}Hf_3Cl_{18}$	$Bi_{12}Cl_{14}$		$Bi_5(AlCl_4)_3$		$Bi_4(AlCl_4)$
	53 w,br[a]	80 vw		50 mw,br		82 ?
	61 w	89 vw		83 m, br		90
	71 vw	115 w,br		100 w		97 ?
	74 vw	218 mw,br		124 m		102
	82 vw	250 mw,br	ν_3	163 sh		114
	95 vw			185 s		124 w
	102 vw		ν_4	460 vs,br	ν_2	?140
	110 vw			494 vs,br	ν_3	174 vs
ν_4[b]-	134 ms			530 sh,?		185 sh
ν_5	154 sh					?203 br
	165 ms,asym				ν_4	467 s
ν_2-	235 m					485 s
ν_3-	280 s,asym					
ν_1-	333 mw					

---

[a] s=strong, m=medium, w=weak, v=very, sh=shoulder, br=broad, asym=asymmetric.

[b] Assigned bands are for the anion

Table 10. Far-infrared frequencies of reduced compositions in the system Bi-$BiCl_3 \cdot TaCl_5$ (in cm^{-1})

63.1[a]	80.2	83.4	90.5	93.8
48 mw[b]	48 mw	48 vw	77 w	51 w
53 w	50.5 vw	53 vw	$\nu_4$150 m	53 w
58 w	52.5 vw	57 vw	$\nu_3$315 vbr	57 w
82 mw	57 mw	93 mw		73 w
85 w	90 mw	109 mw		82 w
90 m	105 w	$\nu_4$150 s		$\nu_4$152 ms
97 w	109 w	$\nu_5$185 m		$\nu_5$183 w
102 w	111 w	$\nu_2$270 m		?214 vw
106 w	$\nu_4$150 s	$\nu_3$341 vs,br		ν_2 268 w
ν_4-151 s	$\nu_5$184 m	$\nu_1$386 sh		282 vw
ν_5-181 m	?203 w			$\nu_3$311 s
?202 w	$\nu_2$262 ms			ν_1?337 w
ν_2-267 s	$\nu_3$322 vs, br			
ν_3-324 vs,br	$\nu_1$383 sh			
ν_1-383 sh				

[a] The composition is given in mole % bismuth in $BiCl_3 \cdot 3TaCl_5$.

[b] s=strong, m=medium, w=weak, v=very, br=broad, sh=shoulder.

consideration of the metal-metal vibrations is complicated by the poor spectra and the possible presence of lattice modes in the region below 100 cm^{-1}. The region anticipated for bismuth-bismuth vibrations is between 50 and 200 cm^{-1} based on the known frequency of the gaseous dimer (55) and the estimated frequencies of the gaseous trimer (linear) and tetramer (tetrahedral) (56).

The octahedral anions have six fundamental bands; $\nu_1(a_{1g})$, $\nu_2(e_g)$, and $\nu_5(t_{2g})$, are expected to be Raman active, while $\nu_3(t_{1u})$ and $\nu_4(t_{1u})$ are infrared active and ν_6 is vibrationally inactive. In both the $HfCl_6^{2-}$ and $TaCl_6^-$ systems the vibrationally active fundamental modes appear in the infrared spectra. The assignment of almost all bands at frequencies greater than 134 cm^{-1} to vibration of the anions seems reasonable on the basis of intensity and coincidences with the known frequencies. The appearance of the ν_1, ν_2, and ν_5 modes in the infrared indicate that the ions are distorted from O_h symmetry. The intensities suggest strong interactions between the cations and anions in the lattice. These effects are also noted with the tetrachloroaluminate salts where the triply degenerate ν_3 and ν_4 modes are each split into two bands.

The very low intensity of the other bands indicate that the infrared spectra are not very useful in fingerprinting the different phases. It is interesting to note change in spectra for the different compositions in the $Bi\text{-}BiCl_3 \cdot 3TaCl_5$ system.

Table 11. Fundamental vibrations of the anions present in polynuclear bismuth compounds (in cm^{-1})

Octahedral ions

$HfCl_6^{2-}$:

Compound	ν_1(r)	ν_2(r)	ν_3(i)	ν_4(i)	ν_5(r)	ν_6	Reference
$(Et_4N)_2(HfCl_6)$	333	237	288	145	157	(80)[a]	(57)
Aqueous solution saturated with HCl	331 s[b]	204 m	272 s 304 sh	-	152 m		(58)
$(Et_2NH_2)_2(HfCl_6)$	328 vs	264 w	286 s 273 s,sh	147 s 138 s,sh	153 163 ms		(59)
$(Et_4N)_2(HfCl_6)$	326 s	257 w,sh	275 s	145 s	156 s		(60)
Cs_2HfCl_6	333 s	(261)	284 s	150 s	167 s	(110)	(60)
	333 mw	235 m	280 s	134 ms	154 sh 165 ms		this work

---

[a] The frequencies listed in parentheses were not observed but were calculated from combination bands.

[b] s = strong, m = medium, w = weak, v = very, sh = shoulder.

Table 11 (Continued)

Octahedral ions

$TaCl_6^{2-}$:

Compound	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	Reference
$(Et_4N)(TaCl_6)$ in CH_3NO_2	380 vs	295 w			180 s		(58)
$(Et_4N)(TaCl_6)$	378 s	298 w	318 s	156 s	179 s		(60)
$CsTaCl_6$	382 s	299 w	320 s	158 s	{180 s 188 s	(101)	(60)
	383-6 sh	266±4	323±1 vs	151±1 s	183±2 m		this work

Tetrahedral ions

$AlCl_4^-$:

Compound	$\nu_1(a)$	$\nu_2(e)$	$\nu_3(f_2)$	$\nu_4(f_2)$	Reference
$AlCl_4^-$ in molten salt media	349	145	183	496	(61)
	-	140?	163-185	460-494	this work

The results appear to corroborate the tentative conclusions reached earlier on the basis of the powder pattern data; there may be two reduced compounds in the system. Unfortunately the poor quality of the spectra preclude more definitive conclusions.

The Crystal Structure of $(Bi^{+})(Bi_9^{5+})(HfCl_6^{2-})_3$

Solution and refinement

The structure was solved by conventional heavy atom techniques (34). An unsharpened Patterson map with approximately 0.25 Å resolution and sectioned along the W-axis was computed using the observed data. A notable feature of the Patterson function was the periodicity of vector maxima lying in UV planes for which values of W occurred in multiples of one-sixth. Maxima along the W-axis were found at (0,0,1/3) and (0,0,2/3) in addition to the origin peak. Analysis of the Patterson proceeded using Harker lines and planes calculated from the general positions of the centric space group. Centrosymmetry had been suggested by the Howells, Phillips, and Rogers statistical test (62).

Using the Harker peaks and the inter-set vectors two compatible sets of bismuth atoms, one twelve-fold degenerate and one six-fold degenerate, were found which described a Bi_9

unit. These positions were refined by least-squares[1] minimization of the function $R_\omega = [\sum\omega(|F_O| - |F_C|)^2/\sum\omega|F_O|^2]^{1/2}$ to yield a conventional residual ($R_1 = \sum(|F_O| - |F_C|)/|F_O|$) of 0.52. The structure factors phased by this model were used to construct a Fourier synthesis which revealed the hafnium ($R_1 = 0.30$) and subsequently the chlorine ($R_1 = 0.20$) positions in a $HfCl_6$ grouping. A Fourier difference map computed with the resultant model with the stoichiometry $Bi_{18}Hf_6Cl_{18}$ showed electron density along the Z axis at $z \simeq 0.1$ and at the symmetry related positions.

The symmetry of the centric space group requires atoms at 0,0,1/2-z, 0,0,1/2+z, and 0,0,-z when an atom is present at 0,0,z. Since the Z axis is only 10.692 Å, to prevent two atoms from being in too close proximity to each other either this site must be partially occupied or the acentric space group, with symmetry generating only positions 0,0,z and 0,0,1/2+z, must be correct.

Because of the nature of the least-squares equations one cannot take a centric model and refine it in an acentric space group (65,66). The results obtained are unreliable because of the correlation of parameters related by the pseudosymmetry.

---

[1] A full-matrix least-squares refinement was carried out using ORFLS (38) modified to correct for both real and imaginary parts of anamolous dispersion. The scattering factors used were taken from the tables of Hansen, *et al.* (63) and corrections for anomalous dispersion were taken from the International Tables (64).

An attempt, albeit questionable, was made to avoid this problem by fixing the parameters of the atoms in the model, and to refine only the Bi atom added to the structure in the alternative ways; i.e., in one of the two independent positions in the acentric space group or with partial occupancy of the position in the centric space group. The conventional R factor for refinement in the centric model, 0.163, was lower than that computed for refinement in the acentric model, 0.171. Further refinement of the trial structure in the centric space group with 50% statistical occupancy of the axial bismuth position converged to $R_1 = 0.157$ and $R_\omega = 0.167$.

At this stage three reflections, (100), (010), and (001), for which $\Theta \leq 2.25°$, were found to be unreliable because in each case the diffracted beam had passed through the metal casing of the scintillation counter. This gave rise to a non-linear background count and required discarding these data. The remaining data were used for refinement in which the temperature factors of all the atoms were allowed to vary anisotropically ($R_1 = 0.102$; $R_\omega = 0.116$). These data were then examined for reflections which may have been measured incorrectly. Thirteen additional pieces of data were discarded because they met the criterion $|F_O - F_C| \geq 9\sigma_F$. Further inspection of these data revealed a common factor; the transmission factors for all these data were less than 1%. Successive refinement with the 823 remaining reflections converged to a conventional residual of 0.093 and a weighted

R factor of 0.096. The standard deviation of unit weight $[(\sum w||F_O|-|F_C||^2/(NO-NV)^{1/2})$ where NO is the number of observations (823) and NV is the number of variables (55)] was 1.87 electrons. This indicated that the values of the constants chosen to describe the random errors which have subsequently been used in calculating the standard deviations of the individual reflections were too low. The weights were therefore changed by plotting $\omega\Delta^2$ versus F_O for 15 overlapping groups of 110 reflections per group and adjusting the weights such that $\omega\Delta^2$ for the groups were constant [$\omega = 1/\sigma^2$ and $\Delta^2 = (|F_O - F_C|)^2$]. Refinement using this weighting scheme did not change the conventional R factor, in fact R_ω increased from 0.096 to 0.107, but it did lower the standard deviations of the computed distances and angles. In the final least-squares cycle each variable shifted an average of 0.02 times the error associated with it. The largest residuals in the final difference map were ± 4 e/Å^3 in the region of the Bi_9^{5+} ion and ± 1 e/Å^3 in the region of the Bi^+ ion on a scale of 170 e/Å^3 for a bismuth atom. The final standard deviation of an observation of unit weight was 0.98 electrons. Based on the agreement of the large structure factors, no extinction correction was necessary.

The final positional and thermal parameters are listed in Table 12. The mean thermal amplitudes of displacement along the three principal axes were listed in Table 13 for the eight

Table 12. Final positional and anisotropic thermal parameters[a] (errors in least significant figures in parentheses)

Atom	X	Y	Z
Bi1	0.5205(2)	0.2141(2)	0.0753(2)
Bi2	0.4877(2)	0.3722(3)	0.25
Bi3[b]	0	0	0.1041(21)
Hf1	0.1193(2)	0.3400(2)	0.25
Cℓ1	0.3054(12)	0.5032(14)	0.25
Cℓ2	0.2601(16)	0.0702(14)	0.25
Cℓ3	0.0658(8)	0.4347(8)	0.0870(9)
Cℓ4	0.0830(9)	0.2239(10)	0.0876(11)

---

[a] Form of anisotropic temperature factor expression is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell)]$.

[b] Fractionally (0.5) occupied.

Table 12 (Continued)

Atom	β_{11}[c]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Bi1	57(2)	50(1)	98(2)	29(1)	-32(1)	-23(1)
Bi2	50(2)	78(2)	79(2)	44(2)	0	0
Bi3	33(3)	33[d]	505(34)	17[e]	0	0
Hf1	38(2)	47(2)	64(2)	23(2)	0	0
Cℓ1	21(9)	50(12)	129(20)	-6(9)	0	0
Cℓ2	93(16)	44(11)	75(14)	47(12)	0	0
Cℓ3	36(7)	40(7)	71(9)	23(6)	-12(6)	1(6)
Cℓ4	36(7)	56(8)	77(10)	9(6)	-25(7)	-3(7)

[c] β's are x 10^4.

[d] $\beta_{22} = \beta_{11}$ by symmetry.

[e] $\beta_{12} = 1/2\ \beta_{11}$ by symmetry.

Table 13. RMS components of thermal displacements along the principal axes (amplitude in Å)

Atom	Axis 1	Axis 2	Axis 3
Bi(1)	0.161(3)	0.188(3)	0.268(2)
Bi(2)	0.154(4)	0.214(3)	0.240(3)
Bi(3)	0.156(30)	0.156(39)	0.541(18)
Hf	0.161(4)	0.186(4)	0.193(3)
Cl(1)	0.106(30)	0.251(21)	0.274(20)
Cl(2)	0.141(24)	0.209(19)	0.262(21)
Cl(3)	0.134(15)	0.174(14)	0.212(12)
Cl(4)	0.128(17)	0.210(14)	0.256(14)

atoms in the asymmetric unit. The observed and calculated structure factors are shown in Figure 7.

Description and discussion

The crystal structure found for bismuth(I) nonabismuth hexachlorohafnate(IV) is shown in projection in Figure 8 and in a stereogram in Figure 9. The structure is comprised of the large Bi_9^{5+} cations and $HfCl_6^{2-}$ anions which appear to govern the packing arrangement and the small Bi^+ ions which restore charge neutrality to the compound and contribute to the lattice energy, and thus to the stability, of the phase. The bonding distances and angles are listed in Tables 14 and 15. The important interatomic non-bonding interactions are shown in Table 16.

The Bi_9^{5+} ion is a tricapped trigonal prism similar to that found in bismuth subchloride (see Figure 10). The polyatomic cation has crystallographic C_{3h} symmetry. There are four bismuth-bismuth bonding distances in the cation: 3.241(3) Å within the triangular face of the prism, 3.737(4) Å for the height of the prism, and 3.086(3) and 3.103(3) Å from the prism to the waist atoms. The difference between the two prism to waist distances is just significant at the level of four times the standard deviation and it is only by this difference that the cation deviates from full D_{3h} symmetry.

Figure 7. Observed and calculated structure factors for $Bi_{10}Hf_3Cl_{18}$ (* mark reflections not used in final refinement)

```
     L =  0
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  3  0  218 -222
  4  0  316  324
  5  0  257 -277
  6  0  325  348
  7  0  363 -374
  8  0  157  193
  9  0  260  285
 10  0  343  363
 11  0  124 -117
 12  0  130 -111
 14  0   96  113
 *2  1  269  193
  4  1  139 -115
  5  1  531  542
  6  1  262  277
  7  1  104  -90
  8  1   46   13
  9  1   62  -55
 10  1  191 -212
 11  1  353 -422
 12  1   54  -43
  1  2  366  397
  2  2  133  -81
 *3  2 1468 1197
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  5  2  145 -115
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  7  2  357  354
  8  2  108 -103
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 11  2   98  113
 12  2   62  -50
 13  2   63  109
  1  3  399  451
  2  3  220 -195
  3  3  365 -315
 *4  3  509  399
  5  3  128  143
  6  3  145  161
  8  3  191  221
  9  3   53   50
 10  3   62   81
  1  4  239  253
  2  4   53   27
  4  4   94  -51
  5  4  326 -265
  6  4  656  702
  7  4   91  124
  8  4  179 -192
 10  4  181  242
  1  5  260 -294
  2  5  663  659
  4  5  253  234
  5  5  165 -132
  7  5   66  113
  8  5  102  129
  9  5   77  -93
 10  5   65  -93
 11  5  175  199
  1  6  207 -196
  2  6  165  170
  3  6  317  294
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  6  6  192 -157
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  9  6  215  277
  1  7  615  578
  2  7  228 -187
  3  7  103  -76

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  5  7  572  553
  6  7  112  -97
  7  7  126  140
  8  7   63  -59
  9  7   70  -77
  2  8  329  295
  3  8  207  194
  5  8  127 -112
  6  8  146  159
  1  9  123  -94
  2  9   90  -67
  3  9   94  -79
  4  9  314  294
  7  9   56  -48
  4 10   96  -98
  5 10  156  172
  6 10   81  106
  1 11  372  351
  2 11  132  142
  5 11  101  104
  1 12  137  152
  3 12  166  175
  2 13  120  -85

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  8  0   86  -71
  1  1   96 -102
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  3  1  491  451
  4  1   93  -81
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  7  1  110   96
  8  1  123 -121
  9  1  216  227
 10  1  247 -264
 12  1   73   69
  1  2  113  115
  2  2  126   94
  3  2  167 -128
  4  2  332  289
  5  2  212 -200
  6  2  192 -210
  7  2  256 -287
  8  2  142  161
  9  2   51   78
 10  2  127  145
 11  2   44  -42
  1  3   68  -69
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  6  3  161  169
  7  3   45   35
  8  3   47   31
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 12  3   56  -77
  1  4  158  190
  2  4  319  321
  4  4  203  190
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  6  4  149 -154
  8  4  238 -254
  9  4  101 -109
 10  4  112  106
 11  4  113  126
  1  5  128 -110

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  4  5  257 -232
  6  5   68   81
  7  5   52   64
  8  5   83  102
 11  5   45  -62
  2  6  124 -119
  3  6  299  279
  4  6  204 -196
  5  6  184  163
  8  6   82  -91
  1  7  211 -223
  2  7  237  222
  4  7  195 -173
  6  7   97   91
  8  7  116  129
  9  7   73  -79
  2  8   52   32
  3  8  140  128
  4  8  156  147
  5  8  227 -206
  6  8   67  -57
  8  8   74   72
  1  9   61   59
  2  9  313 -272
  3  9   61  -55
  1 10   96   90
  2 10   75  -64
  3 10  164  142
  4 10  141  123
  1 11   94   96
  3 11  106  -98
  4 11   90  -76
  1 12   63  -53
  3 12  110 -100
  1 13   79   67
  2 13  127  117

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  4  0  383  402
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  7  0  127  141
  8  0  318 -311
  9  0   81  -89
 13  0  169  131
  1  1  436  359
 *2  1  551  624
  3  1  294 -242
  4  1  123  -96
  5  1  219 -224
  6  1  164 -150
  7  1  233  232
  9  1  111  112
 10  1   67   79
 11  1  136  154
 13  1   64  -58
  1  2  364 -351
  2  2  240 -213
 *3  2  616  471
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 11  2  147 -139
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 13  2   55   59
  2  3   82  -73
  3  3  113   99

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 10  3   47  -44
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  2  4  280  271
  3  4  159 -145
  4  4  153  135
  5  4   75   73
  6  4  220  210
  7  4  217 -232
  8  4   63   75
  9  4   65  -69
 10  4  117  124
  1  5  265  264
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  4  5   68  -66
  6  5   56  -38
  7  5   79  110
  8  5   80   96
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 10  5   39   35
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  4  6   57   67
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  6  6  112  111
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  8  6  178 -204
  9  6   99  129
 10  6   65  -77
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  3  7   65  -48
  4  7  125 -119
  5  7  136 -105
  7  7   88  -84
  1  8  103  -94
  2  8   99   79
  4  8  101  -94
  6  8  218  194
  7  8  104   92
  8  8   36  -18
  2  9  239  203
  3  9   67  -58
  4  9  276  256
  5  9  151 -134
  6  9  131 -113
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  1 10   89  -71
  3 10   59  -42
  4 10   69   60
  5 10   58   18
  1 11   63   67
  2 11   80  -73
  3 11   96   74
  4 11   49  -51
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  3 12   49   72
  1 13   74   67

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  7  0  266  259
  8  0  212 -194

  9  0   56  -60
 10  0  153  152
 11  0  328  327
 12  0  261 -271
  1  1  167 -144
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  8  1   99  103
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 12  1   77   86
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  2  2  770 -680
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  6  2  205 -196
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  8  2  102  107
  9  2  252 -259
 11  2   65  -73
 12  2   44  -45
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 11  3   38   53
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  2  4   98 -110
  3  4   48   52
  4  4   87   71
  5  4  419 -374
  6  4  151  150
  7  4  236  242
  8  4  197  224
  9  4  131 -133
 10  4  137 -164
 11  4   59   44
  1  5  261 -287
  2  5  259 -251
  3  5  501  455
  4  5   43  -19
  5  5  247  242
  6  5  313 -295
  7  5   79  -76
  9  5  177  216
 10  5  179 -208
  1  6  537  518
  2  6  477 -429
  3  6  176 -175
  4  6  131  138
  5  6   48  -31
  6  6   90  -91
  7  6  107   95
  8  6  110 -108
  9  6   58   50
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  2  7  212  197
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  3  8   80   76

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  5  9  182  171
  1 10  233  208
  2 10   96  -89
  4 10  277 -250
  5 10   45   37
  1 11   46  -38
  2 11   57   60
  3 11  169  143
  4 11   45  -10
  1 12   51  -71
  2 12  136 -120
  3 12   44   11

     L =  4
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  4  0  252 -265
  5  0  145 -156
  7  0  133 -153
  8  0  231  229
  9  0  143  148
 11  0   71  -80
 13  0   94 -106
  1  1  202 -220
  2  1  358 -312
  3  1  140  111
  5  1  297  286
  6  1   90   77
  7  1  174 -176
  8  1   72  -61
  9  1   77  -88
 10  1   92  -98
 11  1   74  -80
 12  1   60  -43
  1  2  254  272
  2  2  113  117
  3  2  302 -264
  4  2  104 -107
  5  2   42  -41
  6  2   94  -53
  7  2  131 -141
 10  2  122  105
 11  2   99   99
 12  2   75  -81
  1  3   81   99
  2  3  183 -175
  4  3  111   75
  5  3  259 -254
  6  3  205  202
  7  3   72   53
  8  3   87 -108
  9  3  130 -137
 10  3   54   50
 11  3   57  -67
  1  4  124  117
  2  4  156 -163
  3  4   66   44
  4  4  148 -139
  5  4  105  -98
  6  4   86 -100
  7  4  127  124
  8  4   90 -117
  9  4   64   74
 10  4   90  -94
  1  5  207 -233

  2  5   73   73
  3  5  127  129
  4  5   67   55
  5  5   97 -105
  9  5   56  -55
 10  5   44  -68
  2  6  194  191
  3  6  178 -188
  4  6  140 -137
  5  6   80  -69
  6  6  148 -158
  7  6   45   17
  8  6  163  164
  9  6   51  -71
  1  7  338 -348
  2  7  124 -122
  3  7   54  -19
  4  7  152  125
  5  7  121   99
  6  7   52  -55
  7  7   71   58
  3  8   54  -38
  4  8   72   51
  5  8   88  -81
  6  8  140 -124
  7  8  138 -138
  1  9   60  -55
  2  9  221 -214
  3  9   64   36
  4  9  181 -171
  5  9   67   64
  6  9   82   63
  1 10   71   56
  4 10   87 -102
  5 10   72   40
  1 11   43  -23
  1 12  182  143
  1 13   94  -82

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 *2  0  228 -285
  4  0   95  102
  5  0   77  -75
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  2  1  272 -260
  3  1  425  420
  4  1  165 -159
  5  1   84   77
  7  1   86   82
  8  1   78  -86
  9  1  161  159
 10  1  207 -224
 12  1   82  102
  1  2   55   72
  3  2  110  -94
  4  2  330  313
  5  2  203 -212
  6  2  146 -165
  7  2  209 -226
  8  2  158  179
 10  2  131  149
 11  2   57  -66
  1  3   42  -68
  2  3   79   66
  3  3  547 -517
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  8  3   35   28

  9  3   36  -23
 11  3   97  -99
  1  4  110  143
  2  4  229  242
  3  4   57   49
  4  4  113  121
  5  4   52  -46
  6  4  101 -118
  7  4   93  107
  8  4  247 -263
  9  4   62  -87
 10  4   90   82
  1  5   57  -63
  4  5  225 -206
  8  5   68   84
  9  5   65   74
  1  6   66   53
  2  6  162 -160
  3  6  217  219
  4  6  150 -136
  5  6  144  121
  8  6   78  -85
  1  7  139 -160
  2  7  255  261
  3  7   73  -67
  4  7  130 -123
  5  7   43  -32
  6  7  121  101
  8  7  116  131
  1  8  112  -90
  2  8   48   27
  3  8  128  115
  4  8  156  134
  5  8  223 -212
  1  9  105   96
  2  9  244 -236
  3  9   68  -71
  4  9   58   36
  5  9   61   76
  1 10  102   86
  2 10   49  -68
  3 10  167  149
  4 10   54   62
  1 11   94   80
  3 11   95  -92
  1 12   93  -90

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  3  0  174  196
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  5  0  212  230
  6  0  163 -161
  7  0  292  298
  8  0   93  -91
  9  0  127 -134
 10  0  193 -202
 11  0  126  110
 12  0   94  102
  1  1   47  -42
  2  1   40  -29
  3  1   56   58
  4  1  147  129
  5  1  459 -457
  6  1  136 -136
  7  1  119  121
  9  1   90   94
 10  1  166  192
 11  1  197 -227
  1  2  170 -189

  2  2   98   92
  3  2  644 -594
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  5  2  108  113
  6  2  142  141
  7  2  197 -192
  8  2  116  115
  9  2   84  -93
 10  2   36   31
 11  2   83  -56
  1  3  175 -212
  2  3  154  166
  3  3  248  247
  4  3  181 -166
  6  3   66  -72
  7  3   42   25
  8  3   55  -90
  1  4   84 -105
  4  4   92   93
  5  4  239  237
  6  4  395 -401
  7  4   64  -54
  8  4  152  155
 10  4  113 -130
  1  5  233  244
  2  5  346 -376
  4  5  111 -102
  5  5  142  134
  6  5   64   61
  8  5   52  -55
  9  5   87   90
  1  6  164  169
  2  6   81  -75
  3  6   97 -116
  5  6   92   86
  6  6  143  142
  7  6   68  -61
  1  7  294 -289
  2  7  181  164
  3  7   92   88
  5  7  349 -335
  6  7  127  109
  7  7   69  -69
  2  8  121 -122
  3  8  103  -92
  5  8  117  104
  6  8   44  -60
  1  9  105   94
  2  9   89   82
  3  9  113   99
  4  9  163 -153
  1 10   55   34
  4 10  110   93
  1 11  212 -198
  2 11   81  -73
  1 12   98  -81

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  3  0   63  -61
  4  0   93  -99
  5  0  147  157
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  2  1  236  229
  3  1  171 -185
  4  1   64  -54
  5  1   47  -49
  8  1   90   82
  9  1  146 -160
 10  1  144  149
  1  2   57  -70
  2  2  111 -115

  3  2   76 [illegible]
  4  2   72  -63
  5  2   45  -44
  6  2  116 [illegible]
  7  2  153  166
  8  2   72  -62
  9  2   76  -78
 10  2   63  -67
  2  3   92 [illegible]
  3  3  230  241
  4  3   42   22
  5  3  160 -174
  6  3   57  -61
  7  3   90  -94
  8  3   42  -17
  9  3   54   50
 10  3   42  -26
  1  4   86 -117
  2  4  161 -178
  3  4   45   33
  4  4  147 -142
  6  4   64   62
  7  4   77   42
  8  4   88   86
  9  4   46   71
  1  5   62   69
  3  5   73   76
  4  5  127  116
  5  5   73   73
  6  5  116 -125
  8  5   42  -46
  3  6  161 -157
  4  6  127  136
  5  6  113 -125
  1  7  131  122
  2  7   54  -51
  3  7   75  -70
  4  7  105  117
  1  8   72  -58
  4  8   62  -75
  5  8  103   88
  1  9   53 [illegible]
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  4  9   42  -38
  3 10   62  -54
  1 11   76  -59

     L =  8
  H  K   FO   FC
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  1  0   58   75
  2  0   46   42
  4  0  195 -213
  7  0   51  -57
  8  0  182  182
  9  0   55   38
  1  1  190 -197
  2  1  204 -224
  3  1  153  145
  4  1   63   92
  5  1  112 [illegible]
  6  1  117  111
  7  1  122 -132
  9  1   58  -61
 10  1   39  -25
  1  2  177  211
  2  2  135  144
  3  2  278 -258
  4  2   59   48
  5  2   65   53
  7  2  116 -116
  1  3   46   33
  2  3   66   54

  4  3   50  -36
  5  3  149 -148
  6  3  173  161
  7  3  122  115
  8  3  115 -126
  1  4  122  148
  2  4  134 -154
  3  4   97  110
  4  4   53  -59
  5  4  124 -129
  7  4  144  161
  2  5  117 -126
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  2  6  196  194
  3  6  175 -164
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  6  6   63  -35
  1  7  298 -289
  3  7   52   53
  4  7   71   71
  5  7   65   53
  1  8   75   57
  2  8   52  -63
  4  8   56   72
  1  9   43   26
  2  9  126 -100
  3  9   52   46
  1 10   51   51

     L =  9
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  3  0  190  204
  4  0  135  141
  5  0  156 -194
  6  0  129  111
  7  0   83  -85
  8  0   67   64
 10  0   53  -68
  1  1  270 -257
  3  1   83  -69
  4  1  193  200
  5  1   39   87
  7  1   61  -56
  8  1   35  -47
  1  2   99  -98
  2  2  251  250
  3  2   52  -53
  4  2   51  -67
  5  2   44  -40
  6  2   56   75
  7  2   65  -69
  1  3   61   56
  2  3  155 -176
  3  3   53  -86
  5  3   42   47
  6  3  140 -137
  7  3  164  180
  1  4  145  151
  2  4   49   53
  4  4   39  -32
  5  4  169  157
  6  4   59  -71
  7  4   34  -64
  1  5  135  126
  2  5   77  101
  3  5  195 -189
  5  5  110  -99
  6  5  103  117

  1  6  205 -215
  2  6  175  166
  3  6   79   80
  4  6   45  -61
  1  7   92  -88
  3  7   46   52
  4  7   42   44
  1  8  104   95
  1  9   67   55

     L = 10
  H  K   FO   FC
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  5  0   76   61
  7  0   52   57
  8  0  113 -100
  1  1   40   32
  2  1   72   83
  3  1   34  -29
  4  1   45   29
  5  1  193 -184
  7  1   50   43
  8  1   61   49
  1  2  119 -117
  2  2   53  -54
  4  2   70   59
  7  2   40   25
  1  3  101  -87
  3  3  100   84
  4  3   88  -85
  5  3   93   89
  6  3   79  -81
  1  4   48  -34
  4  4   55   44
  5  4   43   37
  1  5   81   76
  2  5   60  -65
  3  5   78  -69
  4  5   48  -41
  2  6   75  -70
  4  6   74   74
  1  7   87   98
  2  7   70   72

     L = 11
  H  K   FO   FC
  1  0  115 -109
  2  0  111  107
  4  0   47  -42
  7  0   68  -66
  2  1  102   96
  3  1  186 -166
  4  1   49   63
  4  2  120 -116
  5  2   62   80
  1  3   41   26
  3  3  201  199
  5  3  107  -95
  1  4   53  -59
  2  4  106  -90
  4  4   71  -48
  2  5   34  -11

     L = 12
  H  K   FO   FC
  0  0  368  356
  1  0   46  -44
  2  0   55  -36
  1  2   74   70
  3  2  150  140
  1  3   63   59
  2  3   46  -42
```

Figure 8. Projection of four adjacent unit cells between $z=0$ to $z=1/2$ of $Bi_{10}Hf_3Cl_{18}$ along the (001) direction (single atoms represented by one circle are at $z=1/4$, double atoms represented by two concentric circles are related by the mirror plane at $z=1/4$)

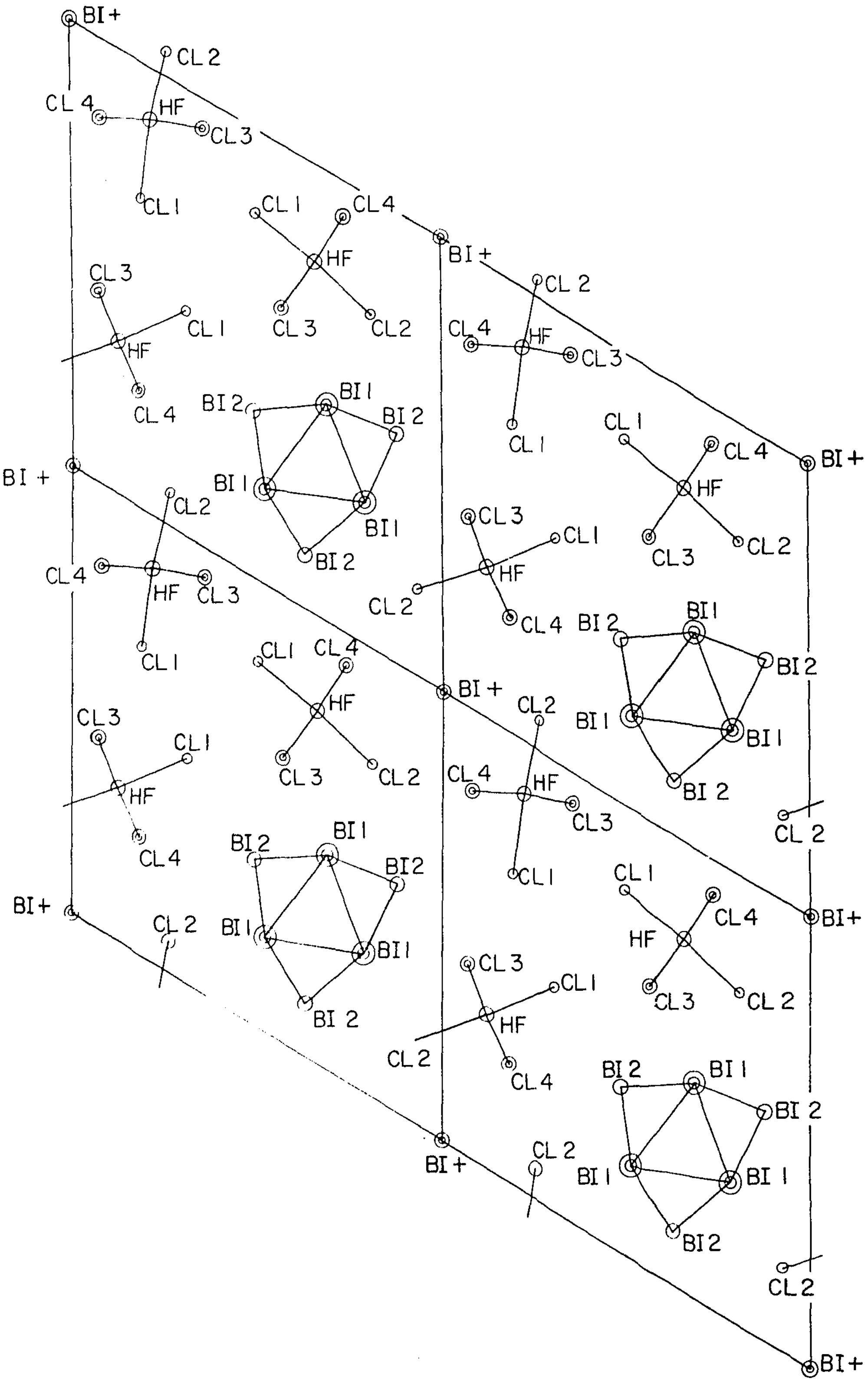
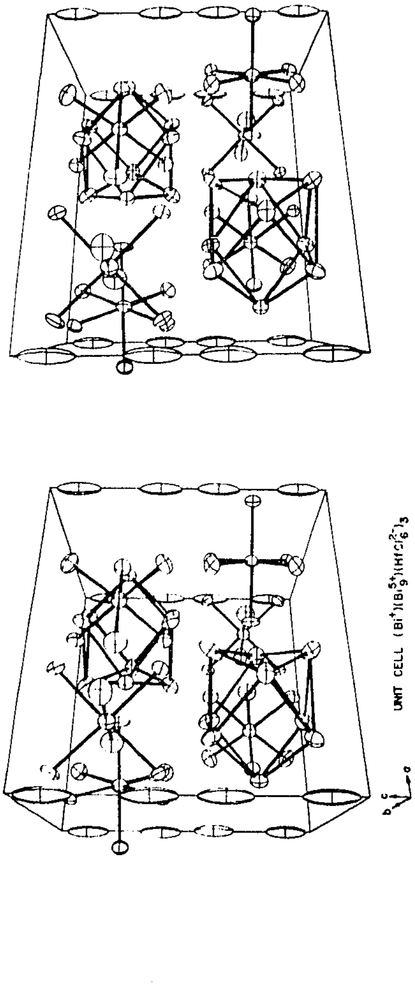

BI+
CL 2
CL 4
HF
CL 3
CL 1
CL 1
CL 4
BI +
HF
CL 3
CL 2
CL 2
CL 4
HF
CL 3
CL 3
CL 1
HF
CL 4
BI 2
BI 1
BI 2
CL 1
CL 1
CL 4
BI+
HF
BI 1
BI 1
BI 2
CL 3
CL 2
BI +
CL 2
CL 4
HF
CL 3
CL 1
CL 3
HF
CL 4
CL 2
BI 2
BI 1
BI 2
CL 1
CL 1
CL 4
HF
BI +
CL 2
BI 1
BI 1
BI 2
CL 3
CL 2
CL 3
CL 1
HF
CL 4
HF
CL 3
CL 1
CL 2
BI 2
BI 1
BI 2
CL 1
BI+
CL 2
BI 1
BI 1
BI 2
CL 3
CL 1
HF
CL 4
HF
CL 2
CL 3
CL 2
CL 4
BI 2
BI 1
BI 2
BI+
CL 2
BI 1
BI 1
BI 2
CL 2
BI+

Figure 9. Stereoscopic view of the contents of one unit cell of $Bi_{10}Hf_3Cl_{18}$



UNIT CELL $(Bi^{+})(Bi_9^{5+})(HfCl_6^{2-})_3$

Table 14. Bond distances and angles[a]

Distances	
Bi(1)-Bi(1)	3.241(3)Å 3.737(4)Å
Bi(1)-Bi(2)	3.086(3)Å 3.103(3)Å
Hf -Cl(1)	2.441(14)Å
Hf -Cl(2)	2.406(15)Å
Hf -Cl(3)	2.508(9)Å
Hf -Cl(4)	2.406(10)Å

Differences between two interatomic distances	
Bi(1)-Bi(2) Bi(1)-Bi(2)	0.017(4)Å
Hf-Cl(1) Hf-Cl(2)	0.036(20)Å
Hf-Cl(1) Hf-Cl(3)	0.067(17)Å
Hf-Cl(1) Hf-Cl(4)	0.036(17)Å
Hf-Cl(2) Hf-Cl(3)	0.103(18)Å
Hf-Cl(2) Hf-Cl(4)	0.000(18)Å
Hf-Cl(3) Hf-Cl(4)	0.103(13)Å

Angles	
Cl(1)-Hf-Cl(2)	175.15(67)°
Cl(1)-Hf-Cl(3)	88.12(39)°
Cl(1)-Hf-Cl(4)	89.51(44)°
Cl(2)-Hf-Cl(3)	88.39(40)°
Cl(2)-Hf-Cl(4)	93.85(43)°
Cl(3)-Hf-Cl(3)	87.99(44)°
Cl(3)-Hf-Cl(4)	89.99(44)° 176.78(42)°
Cl(4)-Hf-Cl(4)	92.39(57)°
Bi(2)-Bi(1)-Bi(2)	102.94(7)°
Bi(1)-Bi(2)-Bi(1)	63.17(6)°
Bi(2)-Bi(1)-Bi(1)	58.16(7)°

Symmetry requires

Bi(1)-Bi(1)-Bi(1) = 60.00°

Bi(2)-Bi(2)-Bi(2) = 60.00°

---

[a] Standard deviations are given in parentheses and correspond to the least-significant figure. They were calculated by ORFEE (39) using the full variance-covariance matrix produced by the least-squares refinement.

Table 15. Distances within ionic entities calculated with final positional and thermal parameters using the riding model[a] (in Å)

Bi(1)-Bi(1)	3.241 (3) 3.737 (4)
Bi(1)-Bi(2)	3.085 (3) 3.104 (3)
Bi(2)-Bi(2)	4.841 (4)
Hf -Cl(1)	2.456 (14)
Hf -Cl(2)	2.415 (15)
Hf -Cl(3)	2.509 (9)
Hf -Cl(4)	2.414 (10)

[a] Interatomic distances averaged over thermal motion. Second atom is assumed to ride on the first. The function is

$$\bar{R} = R_o + (\overline{r_2^2} - \overline{\xi_2^2} - \overline{r_1^2} + \overline{\xi_1^2})/2R_o$$

where R_o is the uncorrected interatomic distance, $\overline{r_i^2}$ is the mean square radial thermal displacement of atom i, and $\overline{\xi_i^2}$ is the mean square component of displacement of atom i in the direction defined by the interatomic vector.

Table 16. Non-bonding interactions[a] (in Å)

Bismuth-Chlorine distances:	
Bi(1)-Cl(1)	3.486(2)
Bi(1)-Cl(2)	3.653(16)
Bi(1)-Cl(3)	3.374(9) 3.408(9) 3.575(10)
Bi(1)-Cl(4)	3.595(13)
Bi(2)-Cl(1)	3.785(19)
Bi(2)-Cl(2)	3.785(17)
Bi(2)-Cl(3)	3.642(9) 3.674(10)
Bi(2)-Cl(4)	4.173(11)
Bi(3)-Bi(3)	2.227(44) 3.119(43)
Bi(3)-Cl(2)	3.593(19)
Bi(3)-Cl(4)	3.188(12) 3.786(16)

Chlorine-chlorine distances:	
Cl(1)-Cl(1)	3.644(32)[b]
Cl(1)-Cl(3)	3.442(16)[c] 3.579(16)[b]
Cl(1)-Cl(4)	3.413(18)[c]
Cl(2)-Cl(3)	3.427(16)[c]
Cl(2)-Cl(4)	3.514(18)[c] 3.615(11)[b] 3.784(18)[b]
Cl(3)-Cl(3)	3.485(19)[c] 3.664(17)[b]
Cl(3)-Cl(4)	3.468(14)[c] 3.638(14)[b]
Cl(4)-Cl(4)	3.473(22)[c] 3.693(14)[b]

Angle Cl(4)-Bi(3)-Cl(4) - 119.7°

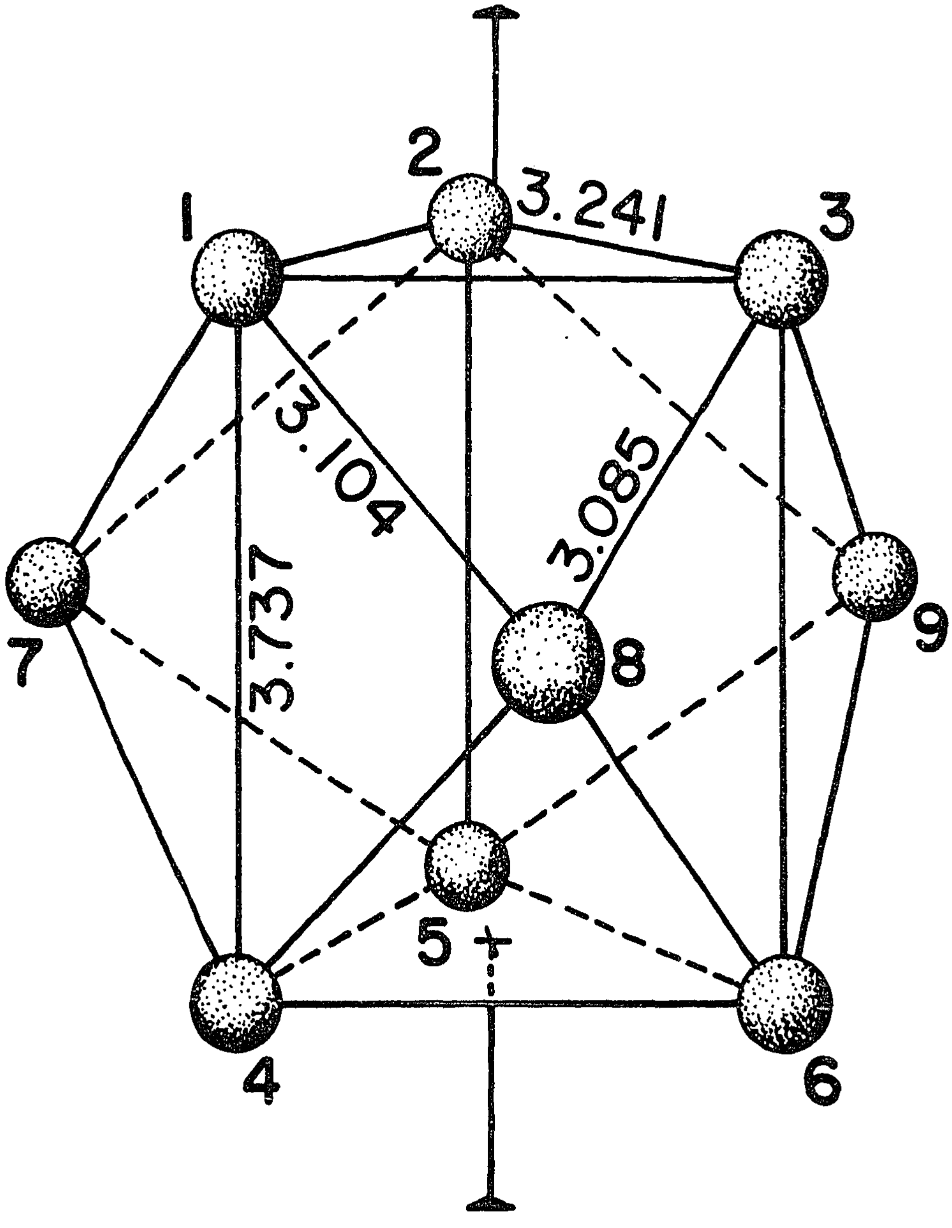
---

[a] Standard deviations are given in parentheses and correspond to the least-significant figure.

[b] Interionic interaction.

[c] Intraionic interaction.

Figure 10. The Bi_9^{5+} cation found in the structure of $Bi_{10}Hf_3Cl_{18}$


2
3.241
1
3
3.104
3.085
7
3.737
9
8
5
4
6

The high symmetry observed for the cation in the solid reflects the absence of any close chlorine-bismuth contacts, the shortest being 3.374(9) Å between Bi(1) and Cl(3).

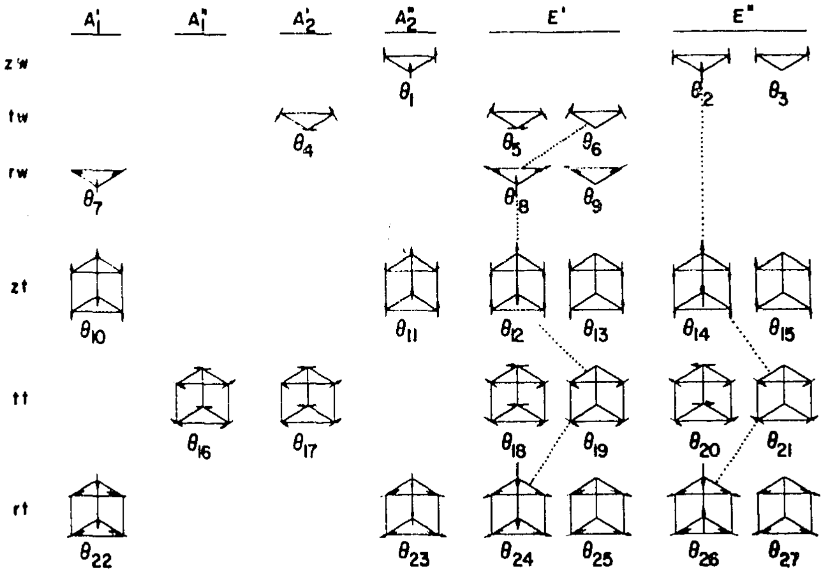
The cluster geometry is analogous to the ligand framework found in many discrete nine-coordinate metal complexes. The obvious difference lies in the absence of a central atom binding the cluster and in the substitution of bonding interactions for the non-bonding ligand interactions present in the complex. Additionally the prism of the cation is shortened by 6% from the idealized arrangement of nine atoms equidistant from a central atom. This is the direction of distortion predicted by Kepert (67) for coordination compounds from consideration of ligand-ligand repulsions. The explanation of the relative distances in the polyhedron must consider bonding forces. The molecular orbital diagram and the symmetry-adapted basis orbitals used by Corbett and Rundle (18) to rationalize the electronic structure of this cation are pictured in Figure 11. The height of the prism relative to the other distances in the polyhedron must be dictated by the maximization of the waist to terminal orbital overlap. The population analysis of the computed molecular orbitals has shown these interactions to contribute substantially to the overall bonding.

The Bi^+ ions form a broken column along the Z axis (see Figure 12). Three chlorine nearest neighbors form a plane normal to the Z axis with its center displaced 0.18 Å from the

Figure 11. Molecular orbitals for Bi_9^{5+}

(a) Symmetry orbitals for Bi_9^{5+} and

(b) Energy level diagram for Bi_9^{5+}
(taken from (18))


A'1
A''1
A'2
A''2
E'
E''
z'w
tw
rw
zt
tt
rt
θ1
θ2
θ3
θ4
θ5
θ6
θ7
θ8
θ9
θ10
θ11
θ12
θ13
θ14
θ15
θ16
θ17
θ18
θ19
θ20
θ21
θ22
θ23
θ24
θ25
θ26
θ27

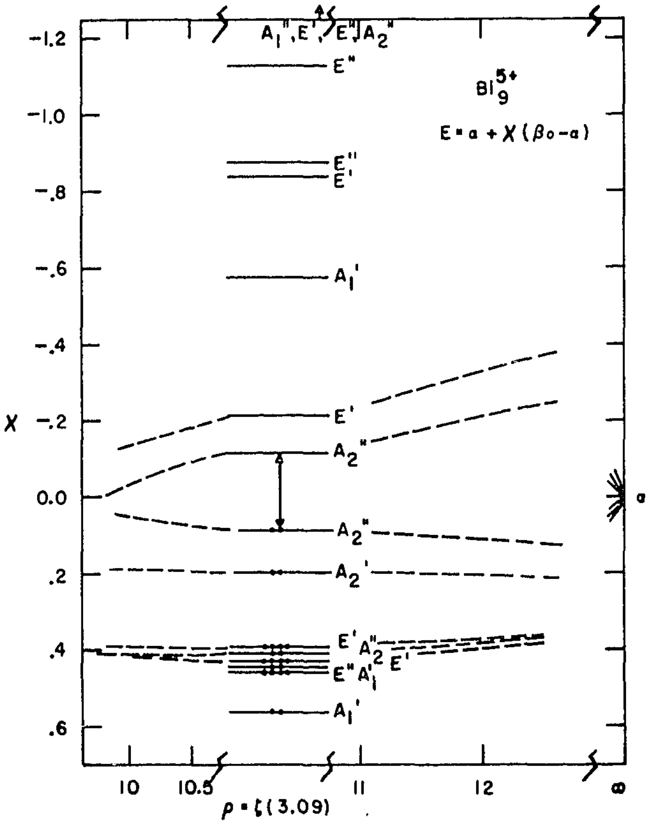
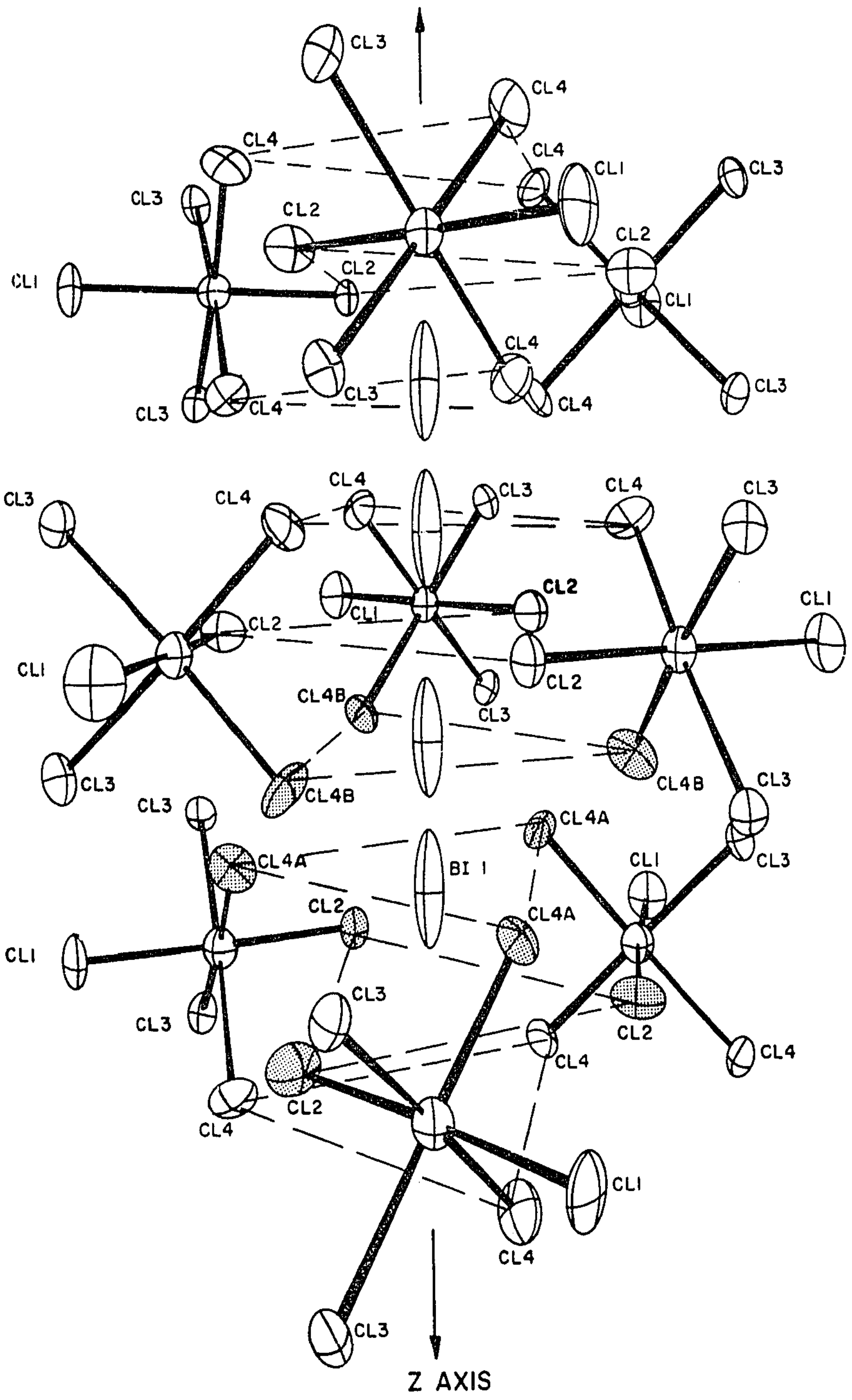

A1'', E', E'', A2''
E''
E''
E'
A1'
E'
A2''
A2''
A2'
E' A2'' E'
E'' A1'
A1'
Bi9 5+
E = α + χ(β0 − α)
χ
−1.2
−1.0
−.8
−.6
−.4
−.2
0.0
.2
.4
.6
α
10
10.5
11
12
∞
ρ = ζ(3.09)

Figure 12. The Bi^+ ions and their environment in $Bi_{10}Hf_3Cl_{18}$ (Dotted lines between shaded chlorine atoms delineate the triangular arrangements described in the text.)



BI+ AND ITS ENVIRONMENT IN (BI)(BI9)(HFCL6)3

Bi^+ ion (CL4A about BI1 in Figure 12). The distance from the bismuth ion to these chlorine atoms is 3.188(12) Å, close to the sum of the estimated van der Waals radii, 3.2 Å (17). There are six next nearest neighbors in triangular units above and below the bismuth ion (CL4B at 3.786(16) and CL2 at 3.593(19) Å from BI1 in Figure 12). The latter pair of triangles are nearly equidistant from the unit formed by CL4A. This results from the accidental equality of the x and y coordinates of CL2 and CL4B and the nearly equal spacing between successive triangles along the Z-axis: CL2 (0.260, 0.070,0.250), CL4A (0.083,0.824,0.088), CL4B (0.259,0.083, 0.912). These triangles of chlorine atoms leave an open column along the Z axis, therefore, uniaxial ionic conduction parallel to this axis might be expected.

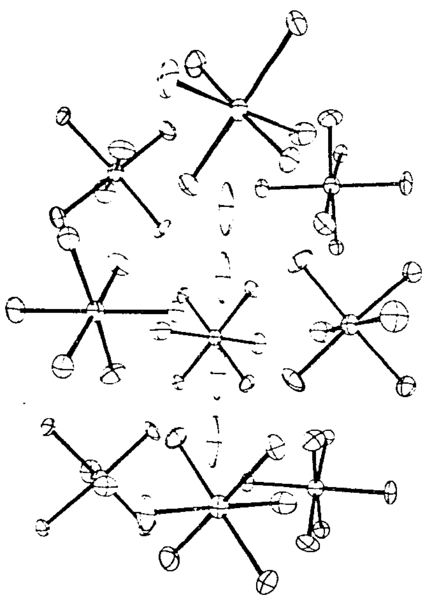
The symmetry about the bismuth(I) ion is exactly C_3 with only small deviations from D_{3h} as described; the coordination is best described as substantially trigonal since the CL4A-BI1-CL4A angles are 119.7°. The large anisotropic thermal motion of the bismuth ion can easily be understood in terms of the local environment about the ion. There is another factor which might contribute to the large root-mean-square thermal displacement along the Z axis for this ion, 0.541(18) Å. The statistical occupancy of the position is all that is sampled by the X-rays; there exists the possibility that the refined position represents a space-averaged rather than a time-averaged distribution. This would mean that the individual bismuth ions do not undergo the motion implied by the thermal parameter. The environment about the Bi^+ ion is clearly pictured in the stereogram in Figure 13.

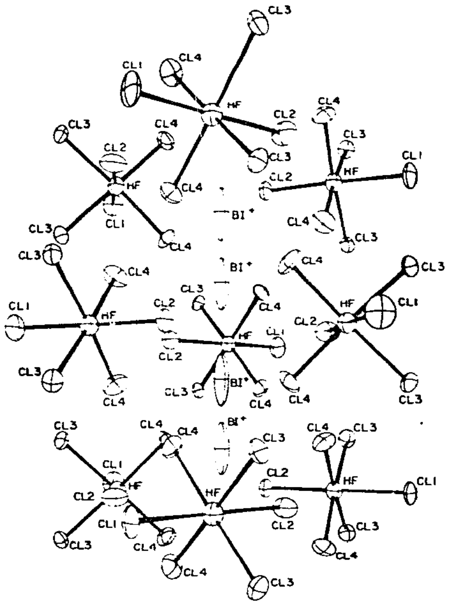
The hexachlorohafnate(IV) anions are distorted octahedra in agreement with the interpretation of the far-infrared spectra presented earlier. The hafnium-chlorine bond distances are slightly longer than the 2.33 Å found by electron diffraction as the mean metal-halide distance in the gaseous $HfCl_4$ (68). Surprisingly the two chlorine atoms nearest the relatively high field Bi^+ ion have the shortest, and identical, hafnium-chlorine bond lengths, 2.406 Å. The longest bond distance in the $HfCl_6^{2-}$ ion is between the metal and the chloride which is in closest proximity to the large Bi_9^{5+} ion. This cation is electrophilic, but the distance and the absence of any appreciable distortion of the cation suggest that there are no very strong forces on the ion. It is possible that the high field Bi^+ ion polarizes the anion and accumulates charge density in the region between the hafnium and the neighboring chlorides but for the moment the variations in the bond distances within the hexachlorohafnate(IV) ion remain attributed to packing.

The Refinement of $(Bi_9^{5+})(BiCl_5^{2-})_2(Bi_2Cl_8^{2-})_{1/2}$

Concomitant refinements were carried out on the structure of $Bi_{12}Cl_{14}$ using either the older film data or the new counter data. If a complete anisotropic refinement is attempted with

Figure 13. Stereoscopic view of the environment about the Bi^+ ions in $Bi_{10}Hf_3Cl_{18}$




CL3
CL1
CL4
HF
CL2
CL3
CL3
CL4
CL2
HF
CL3
CL4
CL2
HF
CL1
CL3
CL1
CL4
CL4
BI+
CL3
CL3
CL4
BI+
CL4
CL3
CL1
HF
CL2
CL3
CL4
HF
CL1
CL2
HF
CL1
CL2
CL3
CL4
CL3
BI+
CL4
CL4
CL3
CL3
CL3
CL4
CL4
BI+
CL3
CL4
CL3
CL1
HF
CL2
HF
CL2
HF
CL1
CL2
CL1
CL2
CL3
CL3
CL4
CL4
CL4
CL3
CL4

film data collected about only one axis and a different variable scale factor is allowed for each layer, the least-squares equations will generate a singular matrix. In order to determine a common scale factor for the layers hk0 to hk5, several cycles of least-squares were therefore performed using isotropic thermal parameters and unit weighting of each observed reflection. After the data had thus been converted to a single scale, the thermal parameters of the bismuth atoms were allowed to vary anisotropically. The weights of the reflections were subsequently adjusted using the program OMEGA (C. Hubbard, 1969, personal communication). Successive iterations of least-squares yielded a conventional residual of 0.148 and a weighted residual of 0.206. Attempts to vary the chlorine atoms anisotropically gave non-positive definite, i.e., physically unreal thermal parameters. Since the earlier isotropic refinement using these data with seven-tenths as many parameters had resulted in values of 0.151 and 0.186 for R_1 and R_ω respectively, it appears that the adjusted weighting scheme used was not as good as the weights chosen by the previous workers to reflect the experimental uncertainties in the data. A difference Fourier synthesis revealed peaks of ± 9 e/Å^3 in the neighborhood of the Bi_9^{5+} cation and ± 4 e/Å^3 in the region of the chlorine atoms on a scale of 186 and 35 e/Å^3 for the bismuth and chlorine atoms respectively.

Least-squares refinements using counter data yielded values of $R_1 = 0.208$ and $R_\omega = 0.232$ with isotropic thermal parameters and $R_1 = 0.169$ and $R_\omega = 0.192$ with anistropic thermal parameters for the bismuth atoms. It was found that the chlorine thermal parameters could not be varied anisotropically. The poor quality of these data were manifest in the observation that twenty-one symmetry-extinct data had structure factors greater than three times their individual standard deviations. To confirm that this did not indicate that the extinction conditions were in error, the symmetry-extinct data were carefully examined. It was found that the net intensity of these data and the subsets of these data represented by the $h0\ell$ and $0k\ell$ zones were arranged in a Gaussian distribution about zero counts. This suggested that the troublesome peaks were only part of large random fluctuations. The final difference map revealed peaks of ± 5 e/Å^3 near the bismuth positions and ± 6 e/Å^3 near the chlorine positions on a scale of 195 and 28 e/Å^3 for bismuth and chlorine respectively. The relatively large peaks near the chlorine atoms show the sensitivity of the lighter atoms to the quality of the data and an evidently poor absorption correction. Structure factors from symmetry-equivalent data differed from each other by an average of 16%.

The structure of $Bi_{12}Cl_{14}$ is shown in projection onto the (001) plane in Figure 14. The atom positions from the three different refinements are shown in Table 17. The bond distances within the Bi_9^{5+} cation computed from these parameters are shown in Table 18.

Figure 14. Projection along the (001) axis of one octant of the structure of $Bi_{12}Cl_{14}$ (taken from (17))

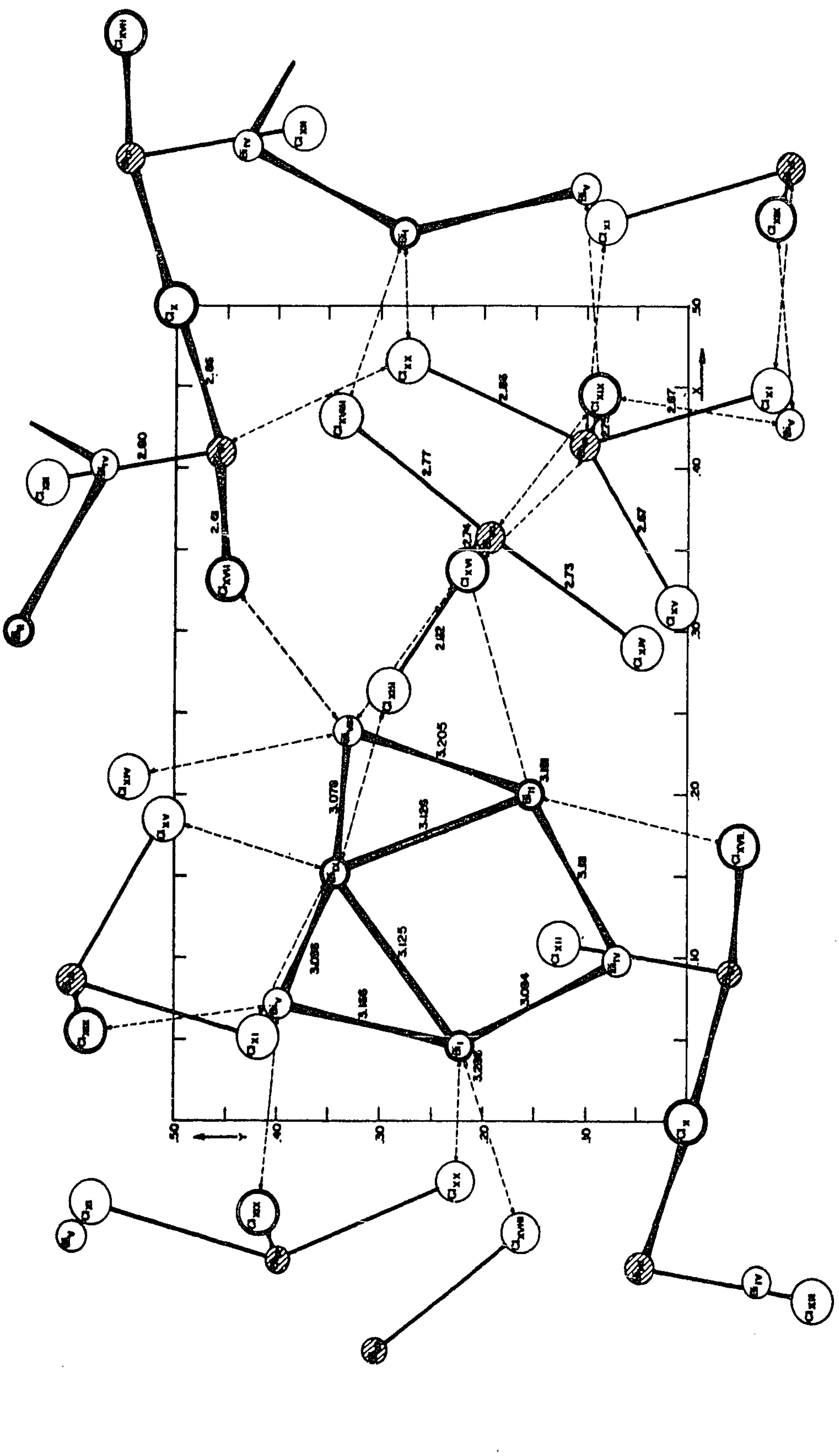

X
Y
.50
.40
.30
.20
.10
10
20
30
40
50
3.205
3.078
3.126
3.125
3.088
3.186
3.094
3.18
2.86
2.80
2.61
2.77
2.74
2.82
2.73
2.87
2.86
Cl X
Cl XVII
Cl XX
Cl XVI
Cl XV
Cl XI
Cl XII
Cl XIX

Table 17. Comparison of positional parameters from different refinements of $Bi_{12}Cl_{14}$

	X (a=23.057)	Y (b=15.240)	Z (c=8.761)
BI1	0.0459(2)	0.2229(3)	0.1876(7)[a]
	0.0460(2)	0.2230(3)	0.1871(7)[b]
	0.0461(3)	0.2230(3)	0.1870(6)[c]
BI2	0.2002(2)	0.1544(2)	0.1815(6)
	0.2003(2)	0.1541(2)	0.1828(7)
	0.2004(2)	0.1546(3)	0.1822(7)
BI3	0.4101(2)	0.4550(3)	0
	0.4101(2)	0.4542(2)	
	0.4103(3)	0.4545(4)	
BI4	0.0984(2)	0.0692(3)	0
	0.0985(2)	0.0689(3)	
	0.0984(3)	0.0694(4)	
BI5	0.0723(3)	0.3982(4)	0
	0.0725(3)	0.3977(3)	
	0.0733(4)	0.3981(5)	
BI6	0.4139(2)	0.1009(4)	0
	0.4137(3)	0.1014(4)	
	0.4132(4)	0.1014(5)	

---

[a] Initial refinement of film data isotropic thermal parameters (71 variables, 1957 data, 27.6 observations/parameters) [from (17)].

[b] Refinement of film data using anisotropic thermal parameters for bismuth atoms (99 parameters, 1957 data, 19.9 observations/parameters).

[c] Refinement of counter data using anisotropic thermal parameters for bismuth (99 parameters, 1705 data, 17.2 observations/parameter).

Table 17 (Continued)

	X	Y	Z
	(a=23.057)	(b=15.240)	(c=8.761)
BI7	0.3578(2) 0.3574(2) 0.3576(3)	0.1930(2) 0.1922(2) 0.1918(3)	1/2
BI8	0.2390(2) 0.2390(2) 0.2386(3)	0.3296(3) 0.3294(3) 0.3297(5)	0
BI9	0.1525(2) 0.1527(2) 0.1528(3)	0.3425(3) 0.3427(3) 0.3422(4)	0.2669(7) 0.2663(7) 0.2672(7)
CL10	0	0	0.288(5) 0.284(5) 0.278(6)
CL11	0.052(1) 0.048(1) 0.049(2)	0.418(2) 0.416(2) 0.417(3)	1/2
CL12	0.109(1) 0.110(1) 0.111(2)	0.126(2) 0.128(2) 0.125(3)	1/2
CL13	0.264(2) 0.265(1) 0.264(2)	0.291(3) 0.291(2) 0.293(3)	1/2
CL14	0.290(1) 0.287(1) 0.283(2)	0.044(2) 0.051(2) 0.056(3)	1/2
CL15	0.315(1) 0.314(1) 0.314(2)	0.010(2) 0.014(1) 0.020(3)	0

Table 17 (Continued)

	X (a=23.057)	Y (b=15.240)	Z (c=8.761)
CL16	0.338(1)	0.216(2)	0.194(4)
	0.337(1)	0.213(1)	0.189(4)
	0.339(1)	0.214(2)	0.193(4)
CL17	0.332(1)	0.449(2)	0.216(4)
	0.333(1)	0.445(1)	0.222(4)
	0.333(1)	0.444(2)	0.212(4)
CL18	0.433(1)	0.337(1)	1/2
	0.431(1)	0.337(2)	
	0.436(2)	0.338(3)	
CL19	0.445(1)	0.086(2)	0.302(5)
	0.443(1)	0.083(1)	0.305(4)
	0.441(1)	0.084(2)	0.302(5)
CL20	0.466(1)	0.274(1)	0
	0.463(1)	0.280(2)	
	0.465(2)	0.274(3)	

Table 18. Bond distances within the Bi_9^{5+} cation. Comparison of refinements of the structure of $Bi_{12}Cl_{14}$ (in Å)

	Film Isotropic	Film Anisotropic	Counter Data
I-I	3.286(12)	3.279(11)	3.276(11)
I-II	3.704(5)	3.707(5)	3.705(8)
I-IV	3.084(6)	3.085(6)	3.078(8)
I-V	3.166(7)	3.158(6)	3.164(9)
I-IX	3.125(6)	3.127(5)	3.126(8)
II-II	3.181(11)	3.203(11)	3.192(11)
II-IV	3.111(6)	3.119(5)	3.117(8)
II-VIII	3.205(5)	3.210(5)	3.204(8)
II-IX	3.126(6)	3.128(5)	3.118(7)
V-VIII	3.979(7)	3.973(7)	3.947(12)
V-IX	3.096(7)	3.089(6)	3.090(8)
VIII-IX	3.078(6)	3.073(6)	3.070(8)

The nonabismuth cations found in the compounds $Bi_{12}Cl_{14}$ and $Bi_{10}Hf_3Cl_{18}$ are compared in Table 19 and Figure 15. The appreciable distortion of the ion found in the former compound was attributed to the effects of close neighboring chlorine interactions (17). There are nine chlorine-bismuth contacts at distances between 3.22 and 3.37 Å in $Bi_{12}Cl_{14}$ whereas the shortest contact found for the less distorted cation in the hafnium salt was 3.374 Å. In addition, the high symmetry of the space group in which $Bi_{10}Hf_3Cl_{18}$ crystallizes requires that even these longer interactions are symmetrically arranged about the cation. The average value for each of the two ions of symmetry independent distances in the idealized structure are very similar (see Table 19).

The attempted refinements have not improved the agreement between the model and the data. Comparison of the computed errors in the positional parameters and the standard deviations of the calculated distances indicate that the original refinement gave the best agreement between the data and the model. The use of an independent set of data to refine the model and the agreement between the results of the refinements corroborate the structure. The largest difference between the bond distances computed by the different refinements have the largest standard deviations and are associated with the light atoms; i.e., the distance between BI7 and CL14 computed from the film data decreases from 2.73(3) to 2.66(5) computed from the counter data. The absence of any apparent similarity

Table 19. Comparison of the Bi_9^{5+} cations in $Bi_{12}Cl_{14}$ and $Bi_{10}Hf_3Cl_{18}$ (in Å)

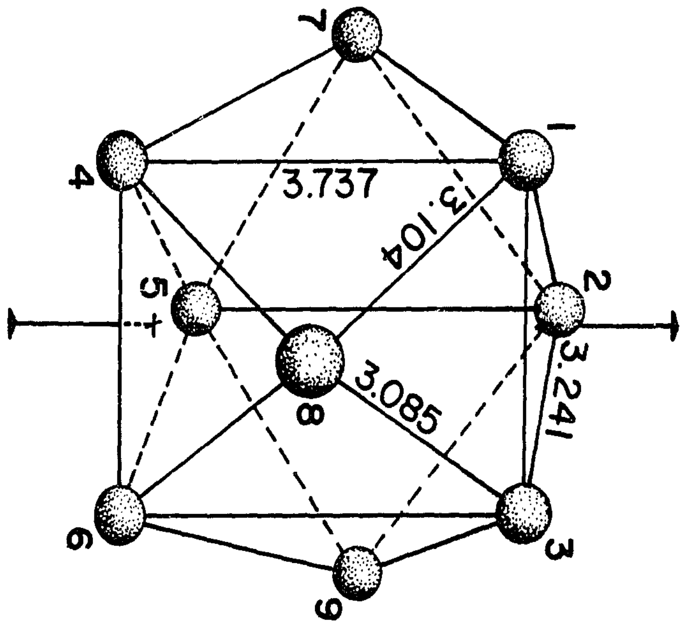
	$Bi_{12}Cl_{14}$[a]	$Bi_{10}Hf_3Cl_{18}$
Height of prism	3.704(5)[b] x 2[c] 3.979(7)	
	avg. 3.796(7)	3.737(4) x 3
Prism to waist	3.084(6) x 2 3.125(6) x 2 3.096(7) x 2 3.126(6) x 2 3.111(6) x 2 3.078(6) x 2	3.104(3) x 6 3.085(3) x 6
	avg. 3.103(6)	avg. 3.094(3)
Triangular face of prism	3.286(12) 3.166(7) x 2 3.181(11) 3.205(5) x 2	
	avg. 3.202(11)	3.241(3) x 6

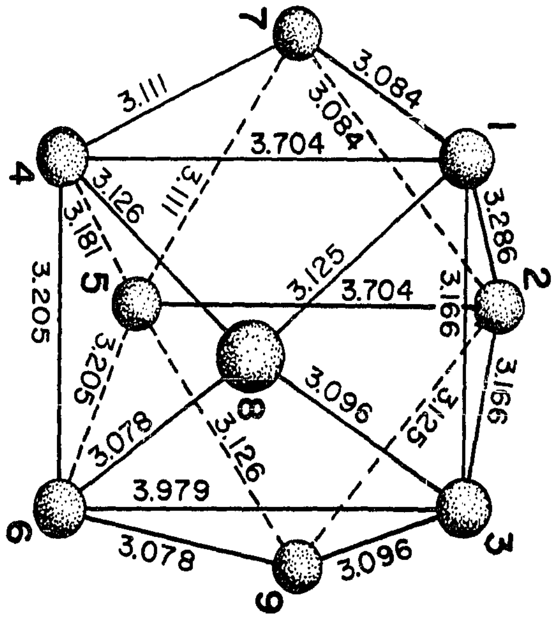
[a] Distances reported in (17) based on isotropic refinement.

[b] Standard deviation in parentheses refer to the least significant figure.

[c] The number of times the distance repeats within the cation.

Figure 15. Comparison of the Bi_9^{5+} cations found in $Bi_{12}Cl_{14}$ (on the right) and $Bi_{10}Hf_3Cl_{18}$ (on the left). Polyhedra shape have been idealized. (Data for $Bi_{12}Cl_{14}$ taken from (17)).


7
1
4
3.737
3.104
5
2
8
3.085
3.241
6
3
9


7
3.111
3.084
3.084
1
4
3.704
3.126
3.111
3.181
3.286
2
3.205
5
3.125
3.704
3.166
3.205
3.078
8
3.096
3.125
3.166
3.126
3.979
6
3.078
9
3.096
3

between the final Fourier difference functions calculated with the two sets of data suggests that the peaks remaining in the maps reflect errors associated with the data and not a systematic error in the structure.

THE LEWIS ACID STABILIZATION EFFECT

Lewis acid complexation has been used to vary the nature of the anion present in the solid compounds and to probe the effect that this change has on the stability of the polynuclear bismuth cations which are formed. The general increase in the stability of the lower oxidation states of metals to disproportionation with increasing anion size has been attributed to the decrease in the difference between the lattice energies of the oxidized and reduced compounds (69). This rationalization is not valid in cases where the two states of the metal have different anions. When mononegative complex anions are formed, the additional stability is determined by the competition between the loss in lattice energy and the heat of association released on formation of the complex anion. It is evident from Table 20 that the addition of the first halide to a Lewis acid is energetically favorable but that successive additions are less favorable. In cases where a multicharged anion is formed, the complexation energy is considerably reduced but the higher ionic charge contributes to the lattice energy of the product. It is the interplay of these factors which aid in the formation of the unusual compounds discussed in this thesis.

The average oxidation state of bismuth in the compound $(Bi^+)(Bi_9^{5+})(HfCl_6^{2-})$ is the same as in the Bi_5^{3+} ion found in the tetrachloroaluminate(III) system. An explanation is possible as to why the Bi_5^{3+} ions are not present without

Table 20. Association energies for the reaction $MX_n(g) + mX^-(g) \rightarrow MX_{n+m}^{m-}(g)$

MCl_n	m	MCl_{n+m}^{m-}	$-\Delta H$(anion) (Kcal/mole)	$\frac{-\Delta H\text{(anion)}}{m}$	Reference
$AlCl_3$	1	$AlCl_4^-$	83±7	83	70,71
$GaCl_3$	1	$GaCl_4^-$	80±3	80	71
$FeCl_3$	1	$FeCl_4^-$	120	120	72
$CoCl_2$	2	$CoCl_4^{2-}$	53	26.5	72
$CuCl_2$	2	$CuCl_4^{2-}$	69	34.5	72
$ZnCl_2$	2	$ZnCl_4^{2-}$	37	18.5	72
BF_3	1	BF_4^-	76	76	73
TiF_4	2	TiF_6^{2-}	65	32.5	72
AlF_3	3	AlF_6^{3-}	-14	-4.6	72
$HgBr_2$	2	$HgBr_4^{2-}$	9	4.5	72
HgI_2	2	HgI_4^{2-}	-9	-4.5	72

consideration of the relative stabilization energies of the Lewis acids. Salts of dinegative anions will have half as many anions per unit charge of the cation as will salts containing mononegative anions. The ionic packing in $(Bi_9^{5+})_2(BiCl_5^{2-})_4(Bi_2Cl_8^{2-})$ and $(Bi^+)(Bi_9^{5+})(HfCl_6^{2-})_3$ reveal a single sheath of anions about the cations which prevents cation-cation contacts. Many ionic structures have anion-anion contacts, however, only those compounds which have extensive covalent interactions between the cations are known to have cation-cation contacts. In the hexachlorohafnate(IV) salt the large Bi_9^{5+} cations and the $HfCl_6^{2-}$ anions appear to control the packing. The Bi^+ ions fill the small holes in the lattice and, by their presence, require more anions to achieve charge neutrality of the compound. These small ions pack more efficiently than would a second polynuclear cation and therefore do not contribute to the problem of cationic interactions. In contrast bismuth subchloride has large $Bi_2Cl_8^{2-}$ anions which occupy more space per unit charge than the $HfCl_6^{2-}$ ions; thus, sufficient anions are available to prevent cation-cation contacts without the presence of the bismuth(I) ion. In the hypothetical compound $(Bi_5^{3+})_2(HfCl_6^{2-})_3$ the ratio of polynuclear cations to anions is 2:3, probably too low to prevent the cations from having extensive interactions.

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