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Synthesis and Structural Characterization of Bismuth(1+) Nonabismuth(5+) Hexachlorohafnate(IV), $Bi^+Bi_9{}^{5+}(HfCl_6{}^{2-})_3$[1]

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The compound $Bi^+Bi_9{}^{5+}(HfCl_6{}^{2-})_3$ was prepared by reduction with elemental bismuth of a 3:2 mixture of hafnium tetrachloride and bismuth trichloride. The compound crystallizes in hexagonal space group $P6_3/m$ ($C_{6h}{}^2$) with $a = 13.890$ (1) Å, $c = 10.692$ (2) Å, $Z = 2$ molecules/unit cell, $d_{calcd} = 6.07$ g cm^{-3}, and $d_{obsd} = 6.05$ (14) g cm^{-3}. A total of 823 peak height intensities above background were measured by counter methods using Mo Kα radiation ($\mu = 571$ cm^{-1}) and were refined by full-matrix, least-squares methods with anisotropic thermal parameters to a conventional $R = 0.093$ and $R_w = 0.107$. The tricapped trigonal prism of the $Bi_9{}^{5+}$ has crystallographically required C_{3h} symmetry with bonding distances of 3.086 (3) and 3.103 (3) Å from prism to waist atoms and 3.241 (3) Å within the triangular face. The hexachlorohafnate octahedra are found to be distorted in agreement with far-infrared data. This compound contains the first known example of a Bi^+ ion in the solid state in a trigonal array of chlorine atoms from the $HfCl_6{}^{2-}$ anions.

Introduction

The first indication of the prolific chemistry of bismuth in oxidation states less than 3 came from studies of solutions of the metal in the molten bismuth trihalides. Although major problems of interpreting data from nonideal solutions evidently obscured the value of some early measurements, careful emf[2] and spectroscopic[3,4] studies on dilute solutions in $BiCl_3$ (≤6 mol % Bi) have since determined that Bi^+ and $Bi_3{}^+ \cdot nBi^{3+}$ are the probable products on reduction of the tripositive state in this range. The ion Bi^+ has also been identified spectroscopically in dilute solution in the more acidic solvent systems $NaCl-AlCl_3$ and $KCl-ZnCl_2$,[5,6] and its spectrum has been unambiguously assigned by a theoretical treatment.[7]

The most spectacular feature of this chemistry involves the variety of polyatomic cations which may be formed at higher concentrations or in different solvents. The ions $Bi_5{}^{3+}$ and $Bi_8{}^{2+}$ form at higher concentrations in the foregoing mixed-salt solvents,[5,6] and the same two species can be isolated from concentrated melts as the solid salts $Bi_5(AlCl_4)_3$ and $Bi_8(AlCl_4)_2$.[8] Yet another example was provided by the so-called "bismuth monochloride" which had been isolated earlier from concentrated solutions of the metal in $BiCl_3$.[9] This phase was shown by a crystallographic study to have the stoichiometry $BiCl_{1.167}$ and to be constituted $(Bi_9{}^{5+})_2(BiCl_5{}^{2-})_4(Bi_2Cl_8{}^{2-})$.[10] The MO treatments of these polybismuth cations were also examined and found to be particularly amenable to simple interpretation.[8,11]

The dependence of cation stability on anion identity in these solids is so great as to be mutually exclusive. The cations $Bi_5{}^{3+}$ and $Bi_8{}^{2+}$ but certainly not $Bi_9{}^{5+}$ occur as the solid $AlCl_4{}^-$ salts, while reduction of solvent $BiCl_3$ ultimately yields $Bi_9{}^{5+}$ with the larger chlorobismuthate(III) anions. The ideas of acid stabilization first established with $Cd_2{}^{2+}$ recognized the paramount importance of large anions of low basicity in stabilizing large cations.[12] Obviously subtle variations in pCl, charge, and size among more or less acidic anions may have substantial effects on stability in systems where a variety of cations is possible. The present investigation explored these effects with bismuth and a large anion which exhibits a necessarily low oxidizing power and a high thermal stability and hence a probably high pCl. An estimate of anion stability to dissociation can be gained from inspection of phase diagrams between candidate Lewis acids and the ionic, *e.g.* alkali metal, chlorides. The $HfCl_6{}^{2-}$ ion was selected from such considerations.

These synthetic efforts in the $Bi-BiCl_3-HfCl_4$ system yielded a single reduced phase which contained a much more symmetric example of the now familiar $Bi_9{}^{5+}$ plus the first known isolation of the Bi^+ ion in the solid state. A preliminary communication of these results has previously appeared.[13]

Experimental Procedures

Materials. The bismuth metal was indicated to be 99.999% pure (American Smelting and Refining). 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 fused under vacuum to facilitate decomposition and physical removal of nonmetallic impurities, principally oxide and carbon.

Commercial bismuth trichloride was purified by dehydration under vacuum at 100°, distillation under a partial pressure of oxygen, and subsequent repeated sublimation under dynamic vacuum, the middle step being added to remove the carbon impurity present in the commercially available material. Omission of the distillation under oxygen so as to reduce the formation of bismuth oxychloride always produced the dark "peppery color" in the fused product characteristic of a carbonaceous impurity, even after repeated vacuum sublimations through a coarse-grade sintered-glass frit. (The amount of oxychloride not removed by a sublimation is readily discerned on melting the product.) This procedure was considered practical in terms of effort and cost in spite of a yield of only about 35% because the alternative method, direct reaction between the elements, is known to be extremely slow even under forcing conditions. Powder patterns of $BiCl_3$ prepared in the two ways were identical.

The crystal bar hafnium (Pittsburgh Naval Reactors Office) contained 1.4 wt % Zr and, spectroscopically, Cu and Fe as "trace" and Mg and Si as "faint trace" impurities. Hafnium tetrachloride was prepared by passing electronic grade HCl (Precision Gas Products) over

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the metal at 360°. The product was twice sublimed under dynamic vacuum before use.

Standard drybox and vacuum-line techniques were used throughout the synthesis and structural studies because of the sensitivity of the salts to oxygen and moisture.

Synthesis. Reaction containers were constructed of fused silica to avoid slight side reactions between the melts and Pyrex containers. Either 15- or 40-mm diameter tubing was used 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 diameter tube was used in which the two chambers were separated by a silica disk in which 2-mm slits had been cut along a 180° arc.

All reaction tubes were loaded in the drybox and sealed off under high vacuum so that the reactions occurred under autogenous vapor composition and pressure. In order to minimize the thermal gradients, the reaction tubes were jacketed in a larger diameter glass tube and held in place using Fiberfrax (Carborundum Co.) insulation, with the temperatures monitored by a thermocouple placed inside the glass jacket near the sample. Equilibration times varied from 1.5 to 7 days.

Physical Measurements. The ultraviolet-visible spectra were recorded using a Cary 14 spectrophotometer with the samples 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. Mulled samples were 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 a Faraday balance. The apparatus consisted of a Varian electromagnet and a Cahn Model RG electrobalance housed in an evacuable chamber. Selected single crystals 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 from a Honda-Owens extrapolation. The treatment of the data included a diamagnetic correction for the sample container.

X-Ray powder patterns were obtained using a Philips Debye-Scherrer camera with a diameter of 114.59 mm and Ni-filtered Cu Kα radiation. Powdered samples were loaded into 0.3-mm Lindemann glass capillaries in the drybox.

The density was measured micropycnometrically on three different 1-g samples using chloroform which had been previously dried over CaH_2.

Crystallographic Procedures. Suitable single crystals were mounted in thin-walled Lindemann capillaries in a drybox and sealed under argon. Preliminary Weissenberg and precession photographs taken with Ni-filtered Cu Kα radiation showed the crystal system to be hexagonal and to belong to the $6/m$ Laue class. Extinction conditions (l odd for $00l$) determined from these photographic measurements were confirmed by scanning the hexagonal c axis with the diffractometer using Mo Kα radiation.

Three-dimensional intensity data were collected on an automated Hilger-Watts four-circle diffractometer using Zr-filtered Mo Kα radiation and a takeoff angle of 4.5°. The crystal was mounted with the c axis collinear with the spindle axis. The diffractometer and experimental arrangement have been described in detail elsewhere.[14] Stationary-crystal, stationary-counter background measurements were made for 5 sec on each side of the peak along a θ–2θ path. Periodic measurement of three standard reflections confirmed the absence of crystal decomposition or motion. The peak heights for a total of 1122 reflections were measured (10-sec count) in the unique sector of a sphere $0° < \theta < 25°$. Approximately 100 reflections which spanned the measurement range were measured 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.[15]

The net converted intensities were also corrected for Lorentz, polarization, and absorption effects. The crystal for data collection was a 0.1 mm long segment of a needle with a distorted hexagonal cross section, approximately 0.1 × 0.15 mm as determined from an examination under 60X magnification. The precise shape and orientation of the crystal used to calculate the absorption correction were varied from the initial values within reasonable limits to minimize the difference between symmetry-equivalent $\{h0l\}$ and $\{0hl\}$ data.[16] The transmission factors calculated with $\mu = 571.0$ cm^{-1} ranged from 0.0055 to 0.0433, almost an eightfold range.

The standard deviation of each net intensity measurement was estimated as

$$\sigma_I = [C_\mathrm{T} + C_\mathrm{B} + (K_\mathrm{T}C_\mathrm{T})^2 + (K_\mathrm{B}C_\mathrm{B})^2 + (K_\mathrm{A}C_\mathrm{R})^2]^{1/2}/A$$

where C_T, C_B, and C_R are the total, background, and net counts, respectively, and A is the transmission factor. K_T, K_B, and K_A, the fractional random errors in C_T, C_B, and A, respectively, were assigned values of 0.03, 0.03, and 0.06. σ_F was thereafter calculated by the method of finite differences as $[(C_\mathrm{R}/LpA + \sigma_I/Lp)^{1/2} - |F_\mathrm{o}|]$ where Lp is the Lorentz and polarization corrections.[17] In the least-squares refinement the structure factors of the individual reflections were weighted according to the respective values of σ_F^{-2}.

Only those reflections with $F_\mathrm{o} \geqslant 3\sigma_F$ were considered observed and used in the refinement; 837 of the 1122 measured reflections met this criterion. The (100) reflection was eliminated from the data set because a scan along the 2θ axis revealed a very nonlinear background count which suggested the diffracted beam had passed through the metal casing of the scintillation counter.

Precise lattice parameters and their standard deviations were determined by least-squares fitting[18] to the 2θ angles (Mo Kα radiation) of 21 independent reflections. The diffraction angles were measured as the difference in the readings of the ω arc of the previously aligned four-circle diffractometer for the peak positions of hkl and $\bar{h}\bar{k}\bar{l}$ 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 any instrument zero error but also the errors due to absorption and incorrect centering of the crystal were eliminated.

Atomic scattering factors used for the structural refinement were taken from Hanson, *et al.*,[19] with corrections applied for the real and imaginary parts of anomalous dispersion by all atoms.[20] All calculations were carried out on the IBM 360/65 computer at the Iowa State University Computer Center with the following programs: ABCOR[21] for absorption correction, ALFF[22] for Fourier summation, ORFLS[23] for least-squares parameter refinement, OMEGA[24] for adjustment of least-squares weights, ORFFE[25] for structure parameters and estimations of errors, and ORTEP[26] for figure illustrations.

Results

The intent to prepare reduced bismuth phases containing the $HfCl_6^{2-}$ anion is readily realized by utilizing bismuth metal to reduce the mixture ($2BiCl_3 + 3HfCl_4$). This is analogous to the approach used in reductions of $MCl_n + nAlCl_3$ mixtures by element M to form $AlCl_4^-$ salts,[8,12] the present stoichiometry being chosen to allow all the chloride to be

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Table I. Final Positional and Anisotropic Thermal Parameters for $Bi^+Bi_9{}^{5+}(HfCl_6{}^{2-})_3$[a]

Atom	x/a	y/b	z/c	β_{11}[c]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Bi(1)	0.5205 (2)	0.2141 (2)	0.0753 (2)	57 (2)	50 (1)	98 (2)	29 (1)	−32 (1)	−23 (1)
Bi(2)	0.4877 (2)	0.3722 (3)	0.25	50 (2)	78 (2)	79 (2)	44 (2)	0	0
Bi(3)[b]	0	0	0.1041 (21)	33 (3)	33[b]	505 (34)	17[b]	0	0
Hf	0.1193 (2)	0.3400 (2)	0.25	38 (2)	47 (2)	64 (2)	23 (2)	0	0
Cl(1)	0.3054 (12)	0.5032 (14)	0.25	21 (9)	50 (12)	129 (20)	−6 (9)	0	0
Cl(2)	0.2601 (16)	0.0702 (14)	0.25	93 (16)	44 (11)	75 (14)	47 (12)	0	0
Cl(3)	0.0658 (8)	0.4347 (8)	0.0870 (9)	36 (7)	40 (7)	71 (9)	23 (6)	−12 (6)	1 (6)
Cl(4)	0.0830 (9)	0.2239 (10)	0.0876 (11)	36 (7)	56 (8)	77 (10)	9 (6)	−25 (7)	−3 (7)

[a] Form of anisotropic temperature factor expression is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Bi(3) positions 50% occupied, with $\beta_{11} = \beta_{22} = 2\beta_{12}$ by symmetry. [c] β's have been multiplied by 10^4.

formally and stoichiometrically converted to the less basic $HfCl_6{}^{2-}$ when less acidic cations are formed on reduction. The unreduced $BiCl_3$-$HfCl_4$ binary is a simple eutectic system containing no other phases.[27]

Attempts at thermal analysis determination of the product phases and relationships for the section Bi-($2BiCl_3 + 3HfCl_4$) were hampered by the slow thermal response of the system, but sufficient evidence was accumulated to indicate only a single reduced phase is probably formed and this melts incongruently at about 507°. Limits on its composition were set from measurements of the weight loss of metal equilibrated with a known amount of salt. The results of eight equilibrations in the range of 375-490°, with 3 times the standard deviation of the average used to set the boundaries, gave an average oxidation state of +0.56 ± 0.05 for bismuth in the new phase. Loss of metal on manual separation of phases was probably a larger source of error than incomplete equilibration. The allowed range includes the known $Bi_5{}^{3+}$ (0.60) and $Bi_9{}^{5+}$ (0.55) cations as well as a multitude of other possibilities. High yields (>95%) characterized all preparations of the new material, and products from different reactions always had the same powder pattern attributable to a single new phase.

The far-infrared spectra gave a useful characterization in terms of the presence of a distorted hexachlorohafnate anion. Peaks were located at 134 (ms), 154 (sh) and 165 (ms, asym), 235 (m), 280 (s, asym), and 333 (mw) cm^{-1}. All other absorptions were very weak to the point of being questionable; eight such "hints" between 53 and 110 cm^{-1} could not be reliably identified with any found for the known polybismuth phases $Bi_{12}Cl_{14}$, $Bi_5(AlCl_4)_3$, and $Bi_8(AlCl_4)_2$. The present results are in close agreement with literature data for solid $HfCl_6{}^{2-}$ salts, namely (infrared and Raman), 138-150, 153-167, 237-264, 273-304, and 326-333 cm^{-1} (t_{1u}, t_{2g}, e_g, t_{1u}, and a_{1g}, respectively, in O_h symmetry).[28-30] The observation of all vibrationally active transitions in the infrared spectrum suggests that the indicated $HfCl_6{}^{2-}$ ion effectively lacks a center of symmetry in the solid compound. The black material did not yield meaningful electronic (mull) spectra, only a small peak at 500 nm being resolved.

The intransigence of the system toward further characterization by other methods and the presence of needlelike crystals of good quality from many equilibrations led to a detailed X-ray structure determination of the precise composition and cation identity.

Crystal Data. $Bi_{10}Hf_3Cl_{18}$, mol wt 3263.4, has hexagonal crystals of Laue class $6/m$, with $a = 13.890$ (1) Å, $c = 10.692$ (2) Å, $d_{obsd} = 6.05$ (14) g cm^{-3}, $d_{calcd} = 6.07$ g cm^{-3} for $Z = 2$, and $\mu = 571.0$ cm^{-1} for Mo Kα radiation (λ 0.71069 Å). Space groups $P6_3/m$ ($C_{6h}{}^2$, No. 176) and $P6_3$ ($C_6{}^6$, No. 173) are consistent with the systematic absences of $l = 2n + 1$ in $00l$ data.

Structure Solution and Refinement. The structure was solved by conventional heavy-atom methods. An unsharpened Patterson map was analyzed using Harker lines and planes calculated for the centric space group since centrosymmetry had been suggested by the statistical test of Howells, *et al.*[31] Two compatible sets of bismuth positions, one twelvefold general and one sixfold special, were found which immediately defined two Bi_9 units. These positions were refined by least-squares minimization of the function $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ to yield a conventional residual R_1 $[\Sigma(||F_o| - |F_c||)/|F_o|]$ 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 $HfCl_6$ groupings. A Fourier difference map computed with the resultant model with the stoichiometry $Bi_{18}Hf_6Cl_{36}$ showed electron density along the Z axis at $z \approx 0.1$ and at the symmetry-related positions $-z$ and $^1/_2 \pm z$. A preliminary refinement with variable chlorine occupancy of these positions (fixed B) indicated a total population equivalent to *ca.* 9Cl (≃2Bi), so the presence of the two metal atoms was thereafter assumed (and confirmed by the final difference map).

With a Z axis of only 10.692 Å either this site must be partially occupied or the acentric space group, with symmetry relating only positions 0, 0, z and 0, 0, $^1/_2 + z$, must be correct in order to prevent two bismuth atoms from being in too close proximity (~2.14 Å) to each other. Because of the nature of the least-squares equations one cannot take a centric model and refine it in an acentric space group;[32,33] the results obtained are unreliable because of the correlation of parameters related by the pseudosymmetry. An attempt, albeit questionable, was made to avoid this problem by fixing the parameters of the other atoms in the model and refining only a bismuth 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 50% occupancy of the positions in the centric space group. Refinement in the centric model gave a lower R_1 index, 0.163, than computed after refinement in the acentric mode, 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 $R_w = 0.167$ and with anisotropic temperature factors for all atoms, $R_1 = 0.102$, $R_w = 0.116$.

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Table II. Rms Components of Thermal Displacements along the Principal Axes (in Å)

Atom	*a* axis	*b* axis	*c* axis
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 (30)	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)

Inspection of the data at this stage for reflections which may have been measured or treated incorrectly led to the discard of 13 additional pieces of data according to the criterion $|F_o - F_c| \geqslant 9\sigma_F$. Further inspection of these data revealed a common factor; the transmission factors for all were calculated to be less than 0.01. Successive refinement with the 823 remaining reflections converged to a conventional residual of 0.093 and a weighted residual of 0.096.

At this point the standard deviation of an observation of unit weight $[(\Sigma w(|F_o|-|F_c|)^2/(N_o - N_v)^{1/2})$, where N_o is the number of observations (823) and N_v is the number of variables (55)], was 1.87. This indicated that the values of the constants chosen to describe the random errors subsequently used in calculating σ_F values were too low. The weights were therefore changed by plotting $w\Delta^2 = [(|F_o| - |F_c|)/\sigma_F]^2$ *vs.* F_o for 15 overlapping groups of 110 reflections per group and adjusting the weights such that $w\Delta^2$ values for the groups were constant.[24] Refinement using this weighting scheme did not change R_1, and R_w increased from 0.096 to 0.107, but the standard deviations of the computed distances and angles did decrease by up to 20%. The final standard deviation of an observation of unit weight was 0.98. 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. Based on the agreement of the large structure factors, no extinction correction was applied.

The final positional and thermal parameters are listed in Table I.[34] The mean thermal amplitudes of displacement along the three principal axes are listed in Table II for the eight atoms in the asymmetric unit.

Description of Structure. The phase is clearly comprised of the large $Bi_9{}^{5+}$ cations and $HfCl_6{}^{2-}$ anions. These appear to govern the packing arrangement, while the small Bi^+ ions in a broken column along the *c* axis restore charge neutrality. The structure is shown in projection in Figure 1 and in a stereogram in Figure 2. The bonding distances and angles are listed in Table III and important nonbonding interactions, in Table IV.

The $Bi_9{}^{5+}$ ion is a tricapped trigonal prism similar to but much more symmetric than that reported[10] and recently confirmed[35] for bismuth subchloride, $(Bi_9{}^{5+})_2(BiCl_5{}^{2-})_4(Bi_2Cl_8{}^{2-})$. As shown in Figure 3 there are four independent bismuth-bismuth bonding distances for the cation with crystallographic C_{3h} symmetry, 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 prismatic to the waist atoms. The 0.017-Å difference between the two prism-to-waist distances is 4 times the standard deviation and thus probably just significant. It is only by this difference that the cation deviates from full D_{3h} symmetry.

Table III. Bond Distances (Å) and Angles (deg)[a]

		Distances		
Bi(1)-Bi(1)	3.241 (3) 3.737 (4)	Hf-Cl(1)	2.441 (14)	+15[b]
		Hf-Cl(2)	2.406 (15)	+9
Bi(1)-Bi(2)	3.086 (3) 3.103 (3)	Hf-Cl(3)	2.508 (9)	−1
		Hf-Cl(4)	2.406 (10)	+8
Bi(2)-Bi(2)	4.841 (4)			
		Differences between Distances		
Bi(1)-Bi(2) Bi(1)-Bi(2)	0.017 (4)	Hf-Cl(2) Hf-Cl(3)	0.103 (18)	
Hf-Cl(1) Hf-Cl(2)	0.036 (20)	Hf-Cl(2) Hf-Cl(4)	0.000 (18)	
Hf-Cl(1) Hf-Cl(3)	0.067 (17)	Hf-Cl(3) Hf-Cl(4)	0.103 (13)	
Hf-Cl(1) Hf-Cl(4)	0.036 (17)			
		Angles		
Cl(1)-Hf-Cl(2)	175.15 (67)	Cl(3)-Hf-Cl(4)	89.99 (44) 176.78 (42)	
Cl(1)-Hf-Cl(3)	88.12 (39)	Cl(4)-Hf-Cl(4)	92.39 (57)	
Cl(1)-Hf-Cl(4)	89.51 (44)	Bi(2)-Bi(1)-Bi(2)	102.94 (7)	
Cl(2)-Hf-Cl(3)	88.39 (40)	Bi(1)-Bi(2)-Bi(1)	63.17 (6)	
Cl(2)-Hf-Cl(4)	93.85 (43)	Bi(2)-Bi(1)-Bi(1)	58.16 (7)	
Cl(3)-Hf-Cl(3)	87.99 (44)	Bi(1)-Bi(1)-Bi(1)	60.00	

[a] Standard deviations in the least-significant figure are given in parentheses. They were calculated by ORFFE[25] using the full variance-covariance matrix produced by the least-squares refinement. [b] Difference in the least significant figure obtained for the model in which the second listed is assumed to ride on first (ORFFE[25]).

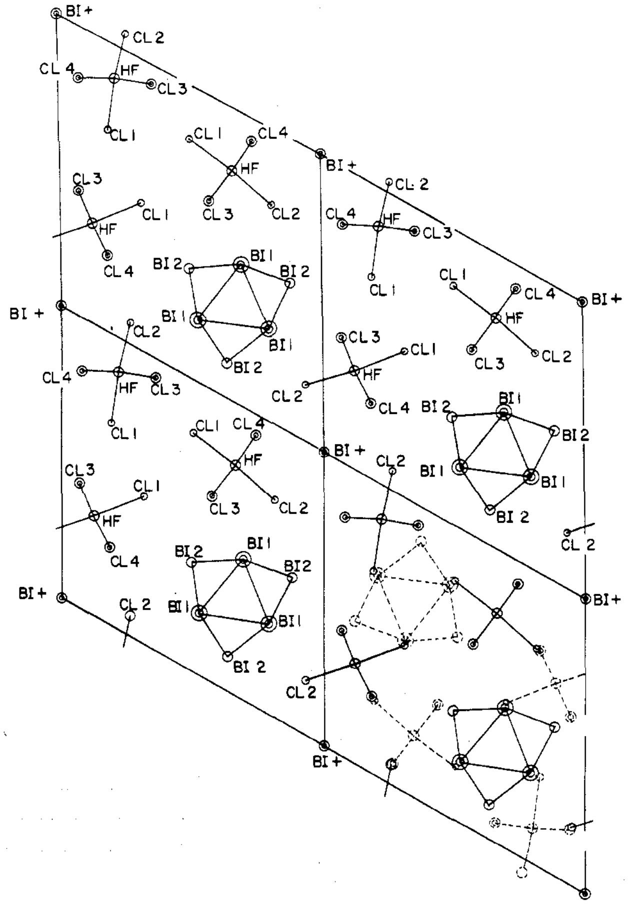

Figure 1. Projection of half of the unit cell of $Bi_{10}Hf_3Cl_{18}$ along the (001) direction with the packing in the other half of one cell shown by dashed lines. Single circles represent atoms on the mirror plane at *z* = 0.25; double circles, atoms related by the mirror plane.

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(34) A listing of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-1134.

(35) R. M. Friedman and J. D. Corbett, *Inorg. Chim. Acta*, in press.

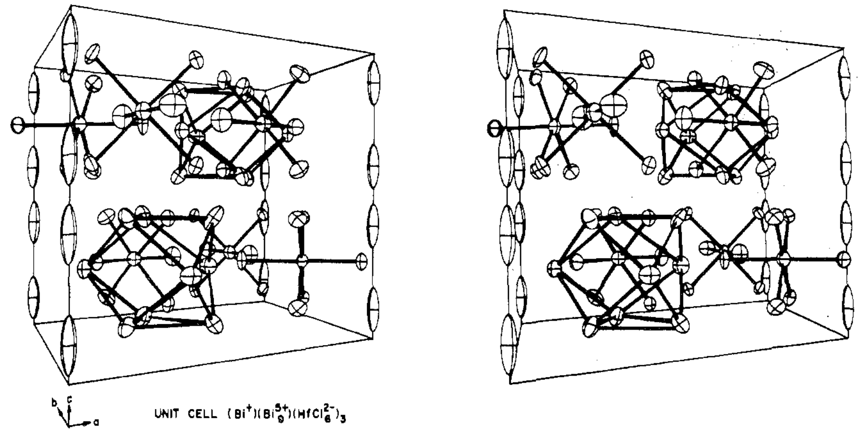

Figure 2. Stereoscopic view of the contents of one unit cell of $Bi^+Bi_9{}^{5+}(HfCl_6{}^{2-})_3$.

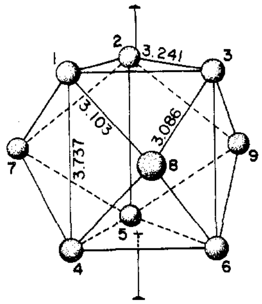

Figure 3. The $Bi_9{}^{5+}$ cation found in $Bi_{10}Hf_3Cl_{18}$.

Table IV. Nonbonding Distances (Å)

Bi(1)–Cl(1)	3.486 (2)	Cl(1)–Cl(1)	3.644 (32)[a]
Bi(1)–Cl(2)	3.653 (16)	Cl(1)–Cl(3)	3.442 (16) 3.579 (16)[a]
Bi(1)–Cl(3)	3.374 (9) 3.408 (9) 3.575 (10)	Cl(1)–Cl(4)	3.413 (18)
Bi(1)–Cl(4)	3.595 (13)	Cl(2)–Cl(3)	3.427 (16)
Bi(2)–Cl(1)	3.785 (19)	Cl(2)–Cl(4)	3.514 (18) 3.615 (11)[a] 3.784 (18)[a]
Bi(2)–Cl(2)	3.785 (17)	Cl(3)–Cl(3)	3.485 (19) 3.664 (17)[a]
Bi(2)–Cl(3)	3.642 (9) 3.674 (10)	Cl(3)–Cl(4)	3.468 (14) 3.638 (14)[a]
Bi(2)–Cl(4)	4.173 (11)	Cl(4)–Cl(4)	3.473 (22) 3.693 (14)[a]
Bi(3)–Bi(3)	3.119 (43)[b]		
Bi(3)–Cl(2)	3.593 (19)		
Bi(3)–Cl(4)	3.188 (12) 3.786 (16)		

[a] An interionic interaction. The remaining Cl–Cl distances are intraionic values. [b] The closest positions 2.227 (44) Å apart are presumed not to be simultaneously occupied.

The high symmetry observed for the $Bi_9{}^{5+}$ cation in this phase appears to result from both the absence of any close (strong) chlorine-bismuth contacts and the high (C_{3h}) site symmetry which dictates the disposition of the chlorine atoms about the cation, Figure 1. The shortest Bi–Cl contact for $Bi_9{}^{5+}$ found here is 3.37 (1) Å, which occurs six times per cation. In contrast, in $Bi_{12}Cl_{14}$ there are 19 chlorine-bismuth contacts per $Bi_9{}^{5+}$ at distances between 3.22 and 3.37 Å in an environment with only C_s symmetry. The elongation of one edge describing the height of the prism by 7% to 3.98 Å and of one edge of the triangular face of the idealized prism by 0.1 Å to 3.29 Å can be attributed to the effects of close and evidently attractive chlorine interactions. Notwithstanding, the averages of each of the three independent types of metal-metal distances in the two $Bi_9{}^{5+}$ structures are quite close: in $Bi_{12}Cl_{14}$ and in the present phase, respectively, height of prism (3), 3.796 (7) and 3.747 (4) Å; triangular face of prism (6), 3.202 (11) and 3.241 (3) Å; prism to waist atom (12), 3.103 (6) and 3.094 (3) Å.

The disposition of the Bi^+ ions along the *c* axis is best seen in the stereoview, Figure 4, noting that only one position in each close pair of sites about a center of symmetry at $z = 0$ and 0.5 is presumably occupied on an atomic scale. The coordination of the Bi^+ is essentially trigonal with respect to the only close neighbors, three Cl(4) atoms at 3.19 (1) Å, remarkably equal to the estimated van der Waals sum.[10] The Bi^+ ion is actually displaced 0.18 Å from this Cl(4) triangle, but this reduces the angle Cl(4)–Bi(3)–Cl(4) only slightly to 119.7°. The next nearest neighbors occur in two other triangles of chlorine atoms, Cl(2) at 3.59 (2) and Cl(4) at 3.79 (2) Å from Bi^+. These nearly equally spaced triangles of chlorine atoms leave an open column along the *c* axis, and uniaxial ionic conduction along this axis might be expected. That the refined positional distribution represents a space-averaged effect seems a more reasonable interpretation of the results than an actual time-averaged "thermal" motion. This alternative must qualify any arguments based on distances calculated using the center of the bismuth distribution. The magnitude can be estimated by the rms *c*-axis component of 0.5 Å, twice that for the other bismuth atoms in the structure (Table II). In either case the distribution of Bi(3) is entirely reasonable in view of the relative absence of near chlorine atoms in the *z* direction.

The unusual shape of the distribution of the Bi^+ raises another possibility, that the site is occupied (still 50%) by BiO^+ rather than the stated Bi^+.[36] Although such an alternative certainly could not be eliminated by the limited presentation of the preliminary communication,[13] it is definitely inconsistent when all of the facts are considered. The synthesis was achieved with high yield, and the crystal used represented the major product, not a trace impurity. The high yield of this BiO^+ salt would have required 17 mol % BiOCl in the total salt mixture, or 37 mol % in the $BiCl_3$ alone, clearly impossible with the care used. In addition an average oxidation state of 0.70 would have been calculated when the metal weight loss needed to form this alternative was attributed to reduction of the 2:3 $BiCl_3$-$HfCl_4$ mixture, substantially different from the 0.56 ± 0.05 observed and 0.60 for the compound reported here. The isolated BiO^+ ion has not been reported in any structure either.

Another interpretation of the Bi^+ distribution is also worth considering, namely, that these, in pairs, represent $Bi_2{}^{2+}$ ions. Though that species was suggested following some of the earlier studies of Bi-$BiCl_3$ melts, later more informative and sensitive methods have given it no support; in contrast, Bi^+ has been well established in dilute tetrachloraluminate and $BiCl_3$

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(36) L. Pauling, private communication, 1971.

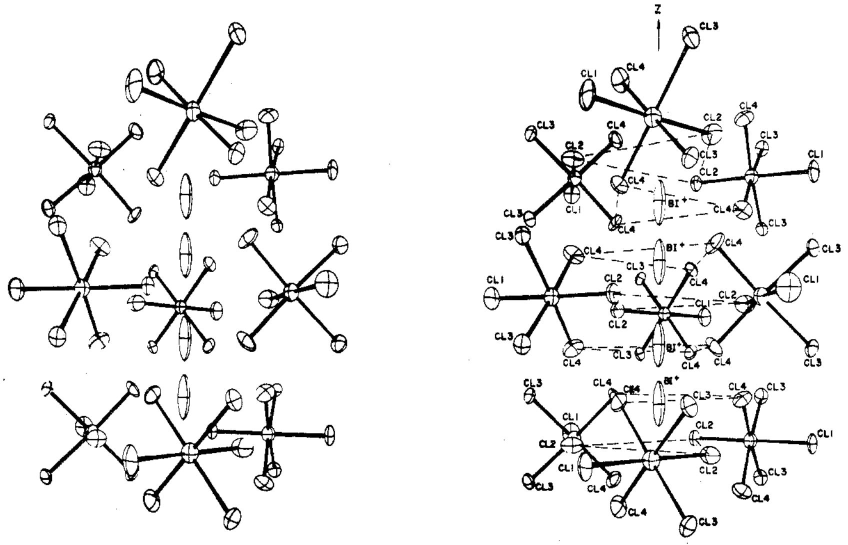

Figure 4. Stereoscopic view of the environment about the Bi^+ ions in $Bi^+Bi_9^{5+}(HfCl_6^{2-})_3$, with triangular arrays of nearest neighbor chlorine atoms located by dashed lines.

melts.[2-5] Nonetheless, dimeric Bi_2^{2+} units might be considered arranged in pairs in sites separated by about 2.23 or 3.18 Å. The former distance seems unreasonably small considering bonding distances in Bi_9^{5+}. The latter is more reasonable but such dimers can still not be randomly distributed in these sites without simultaneously placing two in adjacent positions only 2.23 Å apart, inconsistent with a van der Waals radius of 1.3 Å found to chloride.

This first isolation of the Bi^+ ion in the solid state offers a unique opportunity to test its predicted[7] diamagnetic ground state $^3P_0$. The measured magnetic susceptibility completely supports this expectation. The total molar quantity, χ_M, is $(-964 \pm 34) \times 10^{-6}$ emu/mol and independent of temperature in the range 77-298°K. Subtraction of the estimated diamagnetism for the Bi^{3+}, Hf^{4+}, and Cl^- cores[37] leaves a residual molecular diamagnetism of -198×10^{-6} emu/mol for the added contribution of the 22 delocalized electrons in Bi_9^{5+} (and the extra two in Bi^+).

The hexachlorohafnate(IV) anions have the shape of distorted octahedra, in agreement with the interpretation of the far-infrared spectra mentioned earlier. The hafnium-chlorine bond distances are appropriately slightly longer than the 2.33-Å mean distance found in the gaseous $HfCl_4$ by electron diffraction.[38] The two chlorine atoms nearest the relatively high-field Bi^+ ion are bound to hafnium with the shortest and identical bonds, 2.406 Å, suggesting that the Bi^+-Cl^- interaction is not particularly strong. The longest Hf-Cl bond (by about 6σ) is associated with the chlorine in closest proximity to the large Bi_9^{5+} ion, which suggests the cation is appreciably electrophilic. Similar but larger effects have been noted between $AlCl_4^-$ ions and Se_8^{2+} [39] and Te_4^{2+} [40] ions, but the distance and the absence of any greater distortion of the cation here indicate that the forces are probably not very large.

Although quantitative data are lacking, published phase results[41] suggest that $HfCl_6^{2-}$ represents a relatively stable anion with respect to chloride dissociation. On the other hand, phase data for MCl-$BiCl_3$ systems[42] suggest that $BiCl_5^{2-}$ exhibits substantially less stability. Accordingly, the occurrence of Bi_9^{5+} with two such evidently contrasting anions raises substantial questions as to the relative importance of acid-base interactions in determining stability of different polybismuth cations. Indeed, it appears instead that the number of anions per polyatomic cation may be considerably more important in the sense that anion size and number must be sufficient to sheath the cations and thereby avoid cation-cation contacts. There are two or more anions per cation in *all known solid salts* of homopolyatomic cations of metals which are less stable than Hg_2^{2+}, namely, Cd_2^{2+}, Hg_3^{2+}, Bi_5^{3+}, Bi_8^{2+}, Bi_9^{5+}, Se_8^{2+}, and Te_4^{2+}. Admittedly, the great number of studies to date have utilized uninegative anions, particularly the relatively small $AlCl_4^-$ and SO_3F^-, and sufficiently large anions may still allow the formation of stable 1:1 and 2:3 examples.

In addition to the foregoing positive evidence, the inability to isolate solid $ZnCl_4^{2-}$ [43] or $HfCl_6^{2-}$ salts of Bi_5^{3+} and $ZnCl_4^{2-}$ or $BeCl_4^{2-}$ salts of Cd_2^{2+} [44] may be significant and supportive, although in the latter case it is not clear that these MCl_2 acids are sufficiently strong to stabilize Cd_2^{2+} in any case. Interestingly, the hypothetical $(Bi_5^{3+})_2(HfCl_6^{2-})_3$ has the same stoichiometry as the phase reported here, but the Bi_5^{3+} must, in effect, disproportionate into the cations Bi^+ and Bi_9^{5+}. The instability of the salt $Bi_9^{5+}(AlCl_4^-)_5$ may, on the other extreme, result from an excessive number of anion-anion contacts which a higher charged anion would avoid. The occurrence of the relatively small Bi^+ in the present phase may well represent just a simple way to achieve neutrality of a particularly good packing arrangement. Until further examples can be studied and correlated with other measurements, our understanding obviously must remain qualitative and probably simplistic.

Registry No. $Bi_{10}Hf_3Cl_{18}$, 12591-16-1.

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(43) J. D. Corbett, D. A. Lokken, and R. M. Friedman, unpublished research.

(44) J. D. Corbett, W. J. Burkhard, and N. C. Swanson, unpublished research.