Bismuth(I) in the Solid State. The Crystal Structure of $(Bi^+)(Bi_9^{5+})(HfCl_6^{2-})_3$

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Summary The Bi^+ ion has been stabilized in the solid state in the compound $(Bi^+)(Bi_9^{5+})(HfCl_6^{2-})_3$.

RECENT studies[1,2] have shown earlier reports of monovalent bismuth compounds to be fallacious in that known compounds all contain homonuclear polyatomic cations of bismuth. The Bi^+ ion has been characterized only in dilute solutions of bismuth in its molten halides[3,4] or in dilute solution in $NaCl-AlCl_3$, $KCl-ZnCl_2$, and $NaBr-AlBr_3$

FIGURE. *The Bi^+ ion and its environment in $(Bi^+)(Bi_9^{5+})(HfCl_6^{2-})_3$ (Dotted lines between shaded chlorine atoms delineate the triangular arrangements described in the text.)*

solvents.[5] We have prepared a compound with the stoicheiometry $Bi_{10}Hf_3Cl_{18}$ for which the X-ray crystallographic structure determination reveals the ionic formulation $(Bi^+)(Bi_9^{5+})(HfCl_6^{2-})_3$. This is the first unambiguous identification of Bi^+ ions in the solid state.

Black needles of $Bi_{10}Hf_3Cl_{18}$ were prepared by the reduction *in situ* of a 3 : 2 mixture of hafnium tetrachloride and bismuth trichloride with elemental bismuth. Crystals

were mounted under argon. Weissenberg and precession photographs showed the crystals to be hexagonal, $a = 13\cdot890(1)$ $c = 10\cdot692(2)$ Å, Laue class $6/m$. Extinction conditions were consistent with space groups $P6_3/m$ (C_{6h}^2; No. 176) and $P6_3$ (C_6^6; No. 173); $D_m = 6\cdot05 \pm 0\cdot2$ g cm^{-3}; $D_c = 6\cdot07$ g cm^{-3} for $Z = 2$. Three-dimensional peak height intensity data were collected on an automated Hilger–Watts diffractometer using Zr-filtered Mo-K_α radiation ($\theta < 25°$). The net peak height intensities for 1122 reflections were converted into integrated intensities[6] and then corrected for absorption, Lorentz, and polarization effects.

Analysis of the three–dimensional Patterson function yielded trial positions for two sets of bismuth atoms which accounted for *ca.* 56% of the electron density in the unit cell. These positions were used to phase a difference Fourier synthesis which revealed the hafnium and chlorine positions. Full-matrix least-squares refinement with isotropic thermal parameters for 839 observed reflections ($>3\sigma_F$) converged to a conventional R value of $0\cdot20$. A Fourier difference map showed electron density along the Z-axis at z *ca.* $0\cdot1$ and at the symmetry-related positions z *ca.* $0\cdot4$, $0\cdot6$ and $0\cdot9$. These positions are too close to each other to allow full occupancy, and two Bi^+ cations have been shown to occupy this set of positions statistically.

The successful refinement of the trial structure in the centrosymmetric space group with 50% statistical occupancy of the axial bismuth position converged to $R_1 = 0\cdot157$ and confirmed the model and the choice of space group. Refinement using anisotropic thermal parameters yielded values of $0\cdot093$ for R_1 and $0\cdot107$ for F_w. 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 structure consists of $HfCl_6^{2-}$, Bi_9^{5+}, and Bi^+ ions. The anions are slightly distorted octahedra with an average Hf–Cl bond distance of $2\cdot446(11)$ Å. The Bi_9^{5+} ion is a tricapped trigonal prism similar to that found in 'BiCl'[1] but far less distorted. The polyatomic cation has crystallographic C_{3h} symmetry. There are four Bi–Bi distances in the cation: $3\cdot241(3)$ Å within the triangular face of the prism, $3\cdot737(4)$ Å for the height of the prism, and $3\cdot086(3)$ and $3\cdot103(3)$ Å from the prism to the waist atoms, the difference in the latter being a measure of the deviation from full D_{3h} symmetry.

The Bi^+ ions form a broken column along the z axis (Figure). Three chlorine nearest neighbours form a plane normal to the z-axis with its centre displaced $0\cdot18$ Å from the Bi^+ ion [Cl(4A) about Bi(1) in the Figure]. The distance from the bismuth ion to these chlorine atoms is $3\cdot188(12)$ Å, close to the sum of the estimated van der Waals radii, $3\cdot2$ Å.[1] There are six next nearest neighbours forming triangular units above and below the bismuth ion [Cl(4B) at $3\cdot786(16)$ and Cl(2) at $3\cdot593(19)$ Å from Bi(1)]. The latter pair of triangles are nearly equidistant from the unit formed by Cl(4A). The symmetry about the bismuth ion is exactly C_3 with only small deviations from D_{3h} as described; the co-ordination is best described as substantially trigonal since the Cl(4A)–Bi–Cl(4A) angles are
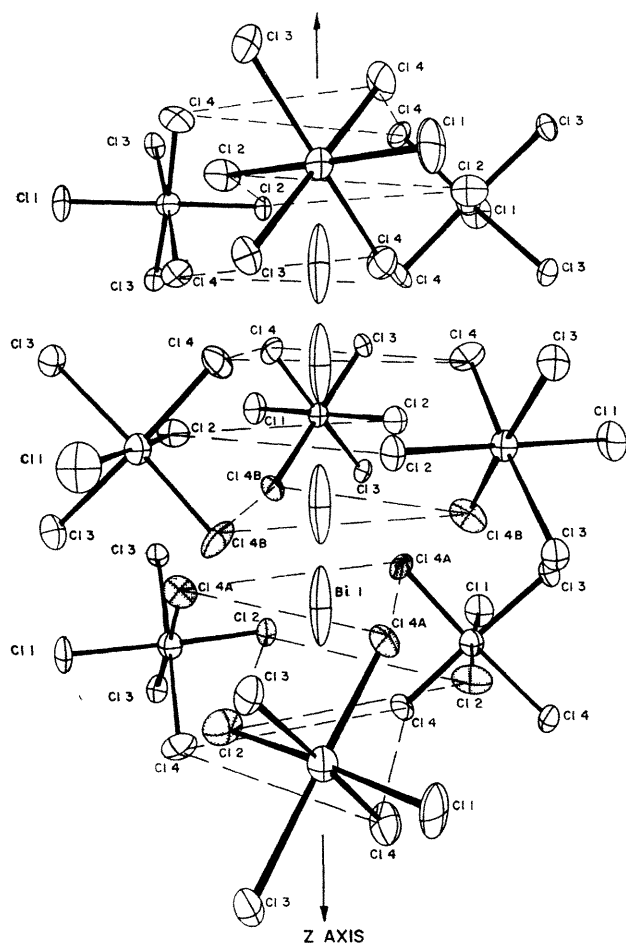
119·7°. The phase is properly diamagnetic and an insulator in bulk although uniaxial ionic conduction parallel to the z-axis might be expected.

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