Supplementary Material Available: Tables of observed and calculated structure factor amplitudes and of the parameters used in calculating the hydrogen atom contributions to the F_c (20 pages). Ordering information is given on any current masthead page.

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Polybismuth Anions. Synthesis and Crystal Structure of a Salt of the Tetrabismuthide(2−) Ion, Bi_4^{2-}. A Basis for the Interpretation of the Structure of Some Complex Intermetallic Phases[1]

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Received March 18, 1977 AIC70209A

The intermetallic compounds K_5Bi_4 and K_3Bi_2 have been found to react with solutions of 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (2,2,2-crypt) in ethylenediamine to form deep green–red dichroic solutions. These spontaneously deposit black crystals of the compound 2,2,2-crypt–potassium tetrabismuthide(2−), $(C_{18}H_{36}N_2O_6K^+)_2Bi_4^{2-}$, with more reduced compounds remaining in solution. This compound crystallizes in the triclinic space group $P\bar{1}$ with lattice constants $a = 11.604$ (4) Å, $b = 11.796$ (4) Å, $c = 11.096$ (3) Å, $\alpha = 98.12$ (3)°, $\beta = 98.02$ (3)°, and $\gamma = 61.37$ (3)° with one formula unit per cell. Three-dimensional x-ray data were collected from two crystals on an automated diffractometer using monochromatic Mo Kα radiation, and the structure was deduced by conventional heavy atom techniques. Positional and anisotropic thermal parameters of the 29 independent nonhydrogen atoms refined by full matrix least squares using 2704 unique observed ($I > 3\sigma_I$) reflections to $R = 0.121$, $R_w = 0.147$. Four of the carbon atoms in the ligand exhibit extremely anisotropic thermal parameters, which effect was resolved and refined in terms of pairs of disordered atoms at 0.50 occupancy. The Bi_4^{2-} anion effectively exhibits D_{4h} symmetry with observed bond lengths of 2.936 (2) and 2.941 (2) Å and bond angles of 89.85 (6) and 90.15 (6)°. The bonding is considered to be the same as in the isoelectronic Te_4^{2+}. The Bi_4^{2-} ion provides a useful starting point for the interpretation of the square metal groups found in the isostructural $Ca_{11}Bi_{10}$, $Ca_{11}Sb_{10}$, and $Ho_{11}Ge_{10}$.

Introduction

Cationic polybismuth clusters have been known for some time, the species Bi_5^{3+}, Bi_8^{2+}, and Bi_9^{5+} having been identified and characterized in the compound $Bi_{12}Cl_{14}$ or as solid and solution products of the reduction of $BiCl_3$ with bismuth in various acidic molten salt media.[2] Considerably less is known about anionic clusters of bismuth. Zintl et al.[3,4] found evidence for the existence of three polybismuthides, violet Bi_3^{3-} and brown Bi_5^{3-} by potentiometric titration in liquid ammonia of a solution of sodium with BiI_3 and yellow-brown Bi_7^{3-} through exhaustive extraction of bismuth-rich (Na:Bi = 1:3) alloys for a period of months. All solids recovered consisted of mixtures of NaBi and Bi.

As was recently noted,[5] the identification of the last species as Bi_7^{3-} appears questionable. The conclusion was based on the analytical result $Na_3Bi_{5.85}$ (or approximately Na_3Bi_6) which was presumed to indicate the existence of Na_3Bi_7 in solution on the grounds that no other group 5 anion had been observed with an even number of atoms and that all appeared to be trinegative. However if the analysis is taken to be correct, the resulting formulation could represent 1.5 Na_2Bi_4 and indicate that the solution species was Bi_4^{2-}, isoelectronic with the known Te_4^{2+}.[6] The compound investigated in this work indicates that this postulate does indeed appear likely and that the Bi_4^{2-} ion has the predicted[5] square-planar structure.

As in several other recent reports of the isolation of other "Zintl ions" in the solid state,[5,7–12] the key to the formation of a stable and tractable product has been the use of 2,2,2-crypt[13,14] to complex the alkali metal counterion, which both increases the solubility of the alloy and prevents formation of the otherwise more stable intermetallic compounds in the solid state.

Experimental Section

Synthesis. All manipulations were carried out either on a vacuum line using standard high-vacuum techniques or in a nitrogen-filled drybox, the atmosphere of which was dried with Molecular Sieve and phosphorus pentoxide to 4–10 ppm of H_2O. The 2,2,2-crypt (Merck) was used as received from E. M. Laboratories and was handled only in the drybox.

There are two relatively low melting intermetallic compounds in the K–Bi system with compositions intermediate between the high melting K_3Bi and KBi_2, namely, K_5Bi_4 and K_3Bi_2.[15] Both of these and their mixtures were synthesized by melting together potassium (J. T. Baker, "purified") and bismuth in a sealed tantalum tube in turn enclosed in an evacuated Vycor jacket. The compound K_3Bi_2 is barely congruently melting, so a single heating to 700 °C with slow cooling was sufficient. For the incongruently melting K_5Bi_4, the melt was quenched from 440 °C to near room temperature and the sample then reheated to 375 °C (6 °C below the melting point) where it was annealed for 10 days. The two friable bluish silver compounds were shown to be free of other compounds in the system by their powder patterns (Debye–Scherrer). Both compounds are extremely air sensitive and slowly form a thin golden coating even in the drybox.

The synthesis of the tetrabismuthide anion is accomplished by reacting stoichiometric quantities of crypt and the intermetallic compound in one arm of a two-armed apparatus in the presence of 40–50 mL of dry ethylenediamine (en, distilled from CaH_2 and stored over Molecular Sieve). A deep clear green solution rapidly forms and after standing overnight at room temperature the solution is intensely colored and exhibits a dichroic character, green in thin layers and red in thick. The solution does not appear to change with additional standing, but after 7–10 days tiny black crystals appear on the walls just above the alloy. These crystals exhibit no color under microscopic examination but leave a very dark green smear when ground to a very fine powder in a mullite mortar. After an additional week these crystals were about 0.2 mm in diameter, so the solvent was decanted and the crystals removed for structural study. When the reaction was allowed to continue past this point for several more weeks the starting material was completely consumed, and the product crystals were either larger or more numerous.

When the crypt was placed in the opposite arm and only en allowed to react with the intermetallic compound, a blue solution resulted after several hours, and this turned purple after several days, a color which corresponds to that reported for Zintl's Bi_3^{3-}.[3] When the solution was decanted from the intermetallic compound into the arm containing the crypt the solution turned from purple to green as soon as the first of the crypt was in solution. When the solution was returned to the intermetallic compound it darkened and became dichroic green and red within a day, whereafter the reaction proceeded as before.

Zintl[4] and Diehl,[16] working with liquid ammonia and en, respectively, both report the slow formation of a brown solute on solution of a sodium alloy with a composition of 75 mol % bismuth. We have observed that when a mixture of KBi_2 and Bi is used in the reaction with crypt a brown solution ultimately results after about a week at room temperature. No crystals grow spontaneously, even on extended standing, and removal of the solvent produces only a brown paste.

The reaction vessel was opened under a nitrogen atmosphere in a specially designed drybox,[17] and crystals with well-developed faces and maximum dimensions in the range of 0.2–0.3 mm were selected and sealed into 0.3-mm diameter Lindemann glass capillaries. It was found that crystals mounted with silicone grease rapidly decomposed, while those mounted with Vaseline were stable (outside of the x-ray beam). Oscillation photographs were taken, and the best specimens selected and mounted for data collection on an automated four-circle diffractometer designed and built in the Ames Laboratory and described in detail elsewhere.[18] The two crystals on which the final data set was taken exhibited no gross symmetry, aside from angles near what would be expected for a hexagonal crystal. One approximated a triangular prism 0.14 mm thick and 0.21 mm long and the other a hexagonal plate 0.22 mm across and 0.095 mm thick.

Data Collection and Structure Determination. Monoclinic symmetry and approximate lattice parameters of $a = 20.13$ Å, $b = 11.95$ Å, $c = 11.10$ Å, and $\beta = 99.5°$ with C centering was indicated by the initial orientation.[19] This turned out to be only an approximation to the true triclinic cell because of an accidental near-equality of a and b in the crude reduced cell combined with the actual near-equality of α and β. Four octants of intensity data were collected for the monoclinic cell at ~25 °C for $2\theta \leq 50°$ using Mo Kα radiation monochromatized with pyrolytic graphite (λ 0.709 54 Å) at a takeoff angle of 4.5°. During data collection the intensities of three standard reflections were monitored every 75 reflections to check for instrument and crystal stability. Whenever a significant drop in the intensity of one or more reflections was observed, all three of the reflections were relocated and their integrated intensities redetermined. A 40% decay in standard intensities was found by the end of the second octant and 75% by the end of the fourth. A total of 5345 reflections were examined, including 521 not allowed for C centering which were all unobserved. All intensities were corrected for isotropic decay through a least-squares fitting of a third-order polynomial to the measured standard intensity sum as a function of reflection count. After decay correction 2978 reflections with $I > 3\sigma_I$ were considered observed.

The observed intensities were corrected for Lorentz, polarization, and absorption effects ($\mu = 128.8$ cm^{-1} [20]) and the data averaged for monoclinic symmetry to yield two different data sets, one with reflections using only the first two octants (sufficient for monoclinic) and the other for all four octants averaged to the unique two. Patterson maps calculated from both data sets could not be interpreted in any chemically reasonable way given the limitation of four cryptated cations per unit cell imposed by the volume. A careful examination of the data averaging indicated that the data indeed possess only triclinic symmetry. Although many reflections were observed only once, only a statistical number of those observed twice matched well and almost all of the reflections observed four times showed a two-and-two pairing, all typical of averaging for too high a Laue group.

At this point, all of the reflections were reindexed using the primitive triclinic reduced cell which has half the volume of the monoclinic cell and for which all reflections correspond to those allowed with C-centered monoclinic. This cell had only enough volume for two cryptated cations, and the calculated Patterson map clearly revealed the positions of the two bismuth atoms comprising a square-planar Bi_4^{2-} anion with C_i point symmetry, indicating $P\bar{1}$ as the correct choice of space group. A Fourier synthesis indicated the position of the potassium atom and a second synthesis with the three heavier atoms revealed all 26 light-atom positions. Full-matrix least-squares refinement of the structure using anisotropic temperature factors for heavy atoms and isotropic temperature factors for light atoms converged at $R = 0.17$. A careful examination of the data indicated that the greatest variation between observed and calculated structure factors occurred for the reflections with the largest decay correction, so no further refinement was attempted using these data.

Data were retaken at room temperature using two crystals. The initial orientation for both indicated triclinic symmetry with approximate parameters of $a = 11.63$ Å, $b = 11.83$ Å, $c = 11.13$ Å, $\alpha = 98.3°$, $\beta = 98.0°$, and $\gamma = 61.4°$, the same as had been obtained before. One hemisphere of integrated intensity data was collected using four standard reflections in an effort to obtain a better measurement of crystal decay. Data collection with the first crystal was terminated at the point when the standard intensities had decayed to 40%, at the end of the first and largest octant, and the remaining reflections were measured on the second crystal with a 36% standard decay during data collection. All corrections were carried out as above, with the transmission coefficients for the first crystal ranging from 0.090 to 0.207 and the second from 0.135 to 0.328.

Final unit cell parameters of $a = 11.604$ (4) Å, $b = 11.796$ (4) Å, $c = 11.096$ (3) Å, $\alpha = 98.12$ (3)°, $\beta = 98.02$ (3)°, and $\gamma = 61.37$ (3)° were obtained from the second of these crystals by a least-squares fit to the 2θ values of 29 reflections ($24 < 2\theta < 32°$), each of which was tuned on both Friedel-related peaks to eliminate instrument and

Table I. Final Positional and Thermal Parameters for the Nondisordered Atoms of $(\text{CryptK}^+)_2\text{Bi}_4{}^{2-}$

	Fractional coordinates			Atomic temperature factors[a]					
Atom	x	y	z	$\beta_{1,1}$	$\beta_{2,2}$	$\beta_{3,3}$	$\beta_{1,2}$	$\beta_{1,3}$	$\beta_{2,3}$
B11	0.1952 (1)	0.8575 (1)	0.0011 (1)	14.6 (1)	17.5 (2)	14.3 (1)	−4.6 (1)	0.9 (1)	3.5 (1)
B12	0.0216 (1)	0.0671 (1)	0.8454 (1)	17.1 (2)	17.0 (1)	12.5 (1)	−6.6 (1)	1.0 (1)	3.6 (1)
K	0.3215 (6)	0.3243 (6)	0.4100 (6)	14.6 (8)	11.9 (6)	9.2 (5)	−5.7 (5)	1.8 (5)	0.1 (5)
N1	0.302 (3)	0.305 (3)	0.145 (2)	22 (4)	18 (3)	12 (3)	−11 (3)	5 (3)	−3 (2)
O4	0.328 (3)	0.518 (2)	0.291 (1)	36 (5)	14 (2)	7 (1)	−13 (3)	2 (2)	2 (1)
C5	0.245 (5)	0.639 (4)	0.342 (4)	33 (8)	18 (5)	17 (5)	−12 (5)	8 (5)	−2 (4)
C6	0.284 (3)	0.644 (3)	0.472 (3)	24 (5)	11 (3)	12 (3)	−9 (3)	−0 (3)	4 (2)
O7	0.269 (2)	0.563 (1)	0.535 (1)	18 (2)	10 (1)	10 (2)	−2 (1)	4 (1)	−0 (1)
C8	0.313 (4)	0.573 (3)	0.663 (3)	27 (6)	10 (3)	10 (3)	−8 (3)	3 (3)	−1 (2)
C9	0.275 (3)	0.486 (2)	0.726 (2)	15 (3)	12 (3)	9 (3)	−4 (2)	0 (2)	−3 (2)
N10	0.337 (2)	0.347 (2)	0.683 (2)	15 (3)	14 (3)	10 (2)	−6 (2)	−0 (2)	0 (2)
C11	0.282 (4)	0.278 (3)	0.722 (3)	23 (5)	15 (4)	12 (3)	−11 (3)	5 (3)	0 (3)
C12	0.146 (3)	0.310 (3)	0.657 (3)	13 (3)	17 (4)	11 (3)	−1 (3)	−2 (2)	2 (3)
O13	0.167 (2)	0.259 (2)	0.526 (1)	15 (2)	16 (2)	9 (1)	−11 (2)	−1 (1)	3 (1)
C14	0.055 (3)	0.264 (4)	0.457 (4)	9 (3)	28 (6)	24 (6)	−12 (3)	−5 (3)	13 (5)
C15	0.083 (3)	0.225 (4)	0.320 (4)	12 (4)	19 (5)	16 (5)	−4 (3)	−4 (3)	−5 (4)
O16	0.100 (2)	0.321 (3)	0.283 (2)	22 (4)	28 (4)	11 (2)	−17 (3)	−3 (2)	0 (2)
C18	0.176 (7)	0.298 (8)	0.099 (4)	4 (1)	5 (1)	13 (5)	−3 (1)	−4 (6)	7 (7)
C19	0.411 (6)	0.176 (5)	0.099 (4)	32 (9)	27 (7)	14 (5)	−13 (7)	4 (5)	−7 (5)
O21	0.517 (2)	0.106 (2)	0.289 (2)	17 (3)	18 (3)	15 (3)	−3 (2)	4 (2)	−1 (2)
C22	0.640 (6)	0.083 (3)	0.343 (4)	33 (9)	14 (4)	17 (5)	12 (5)	9 (6)	−4 (4)
C23	0.654 (3)	0.065 (3)	0.470 (4)	13 (4)	11 (3)	20 (5)	−7 (2)	2 (3)	−2 (3)
O24	0.561 (2)	0.177 (1)	0.538 (2)	14 (2)	6 (1)	17 (2)	−0 (1)	0 (2)	−0 (1)
C25	0.568 (3)	0.162 (3)	0.665 (2)	17 (4)	16 (3)	8 (2)	−7 (3)	0 (2)	2 (2)
C26	0.484 (3)	0.291 (2)	0.727 (2)	14 (3)	9 (2)	11 (3)	−3 (2)	2 (2)	−2 (2)

[a] $\beta_{i,j} \times 10^3$.

centering errors. These dimensions give a volume of 1315.2 (7) Å^3 and a density of 2.11 g/cm^3 for $Z = 1$ and a formula weight of 1667.12. Programs utilized were as referenced before[5,17] unless otherwise noted. Scattering factors used were those of Hanson et al.[21] and included corrections for the anomalous dispersion of bismuth and potassium.

Of the 4955 reflections examined in four unique octants (HKL, $HK\bar{L}$, $H\bar{K}L$, and $H\bar{K}\bar{L}$), 2880 reflections were considered observed with $I > 3\sigma_I$. Redundant reflections were averaged when both observations had been made on the same crystal, but when one observation had been made on each crystal that member of the pair was eliminated which required the larger decay correction, leaving 2704 unique reflections. The data from each crystal were scaled separately.

Structure Refinement. The final atomic parameters deduced with the first data set produced an R value of 0.14 with the new data set with no refinement, and after refinement $R = 0.128$ and $R_w = 0.157$ $= [(\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = \sigma_F{}^{-2}$. Introduction of anisotropic temperature parameters (of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$) for the light atoms produced a slight improvement in the unweighted residual, 0.122, and a significant[22] improvement in the weighted R, 0.149. Examination of both the isotropic and anisotropic temperature factors at this point revealed that the carbon atoms at the end of the crypt closer to the anion had much larger and much more anisotropic temperature factors than those at the other end. Drawings of the structure made at this point, Figure 1, indicated that the more anisotropic atoms were elongated in the direction in which the ethylene bridge was least constrained, with root mean square displacements in the longest dimension about twice those of the atoms at the other end of the ion (Figure 1b).

A difference map calculated with these six atoms (C2, C3, C17, C18, C19, and C20) removed clearly showed doubled peaks for four of the six, C2, C3, C17, and C20, serving to confirm directly the disorder which has been suspected in previous structures.[5,9,11] These four atoms were replaced by eight atoms at the locations indicated by the difference map, each with an occupancy of 0.50 and an isotropic temperature factor. Another map was calculated with C5 omitted since its temperature factor was similar to C2 and C3, but separate atoms at this location were unresolved. Refinement of all parameters converged at $R = 0.122$ ($R_w = 0.148$). Variation of the occupancies of the fractional atoms demonstrated that the occupancies and temperature factors were strongly coupled, even when they were varied in alternate cycles of refinement, and that the occupancies did not refine more than 1σ from 0.50, so these were fixed at that value. It did not seem appropriate to attempt anisotropic refinement of fractional carbon atoms in close proximity to each other and the bismuth atoms.

Table II. Final Positional and Thermal Parameters for the Disordered Carbon Atoms[a]

Atom	x	y	z	B, Å^2
C2a	0.371 (6)	0.378 (6)	0.113 (6)	5 (1)
C2b	0.282 (5)	0.430 (5)	0.096 (5)	4 (1)
C3a	0.294 (8)	0.505 (6)	0.158 (7)	6 (1)
C3b	0.37 (1)	0.491 (9)	0.149 (9)	9 (2)
C17a	0.112 (7)	0.248 (7)	0.162 (7)	6 (1)
C17b	0.070 (8)	0.333 (8)	0.143 (7)	6 (1)
C20a	0.559 (9)	0.117 (8)	0.171 (8)	8 (1)
C20b	0.496 (7)	0.077 (7)	0.163 (7)	6 (1)

[a] All atoms at 0.5 occupancy; see text.

Because there was a small dependence of $||F_o| - |F_c||$ on F_o and because the standard deviation for an observation of unit weight was 4.01, the data were reweighted in 20 overlapping groups sorted on F_o, after which the refinement converged at $R = 0.121$ ($R_w = 0.147$) for 260 independent variables. The largest change as a result of this reweighting was a small (≤8%) drop in positional standard deviations. The largest shifts during the last cycle of refinement were 0.12σ for light atom and 0.009σ for bismuth atom parameters. A difference Fourier map indicated a residual of 2.4 e/Å^3 (at 0.240, 0.995, 0.693) which could not be connected with any feature of the structure, while the rest of the map was flat to $<\pm 1$ e/Å^3 except near the bismuth atoms where variations were as great as ±2 e/Å^3. The final standard deviations in individual positional parameters ranged from 0.0014 to 0.0017 Å for bismuth, 0.02 to 0.03 Å for oxygen and nitrogen, and 0.03 to 0.06 Å for the carbon atoms, with the upper limit in the last being reached only for the disordered carbon atoms.

Although a final R value of 12.1% may seem somewhat large, it is not in this case indicative of a defective structure when the more pertinent positional errors are considered. Standard deviations of the atom positions are all acceptable, those for the light atoms in fact being equal to or better than determined for other low-symmetry structures involving crypt cations with lighter anion components (Ge, Sn, Sb, Te), all of which refined to comparable residuals.[5,9,11,12] The larger but relatively random errors in the data set are believed to arise from the need to collect data from two crystals with the consequential need for two major independent decay and absorption corrections.

Results and Discussion

The final atomic positional and thermal parameters appear in Tables I and II, while important distances and angles in the $\text{Bi}_4{}^{2-}$ anion and in the crypt–K$^+$ cation are given in Table

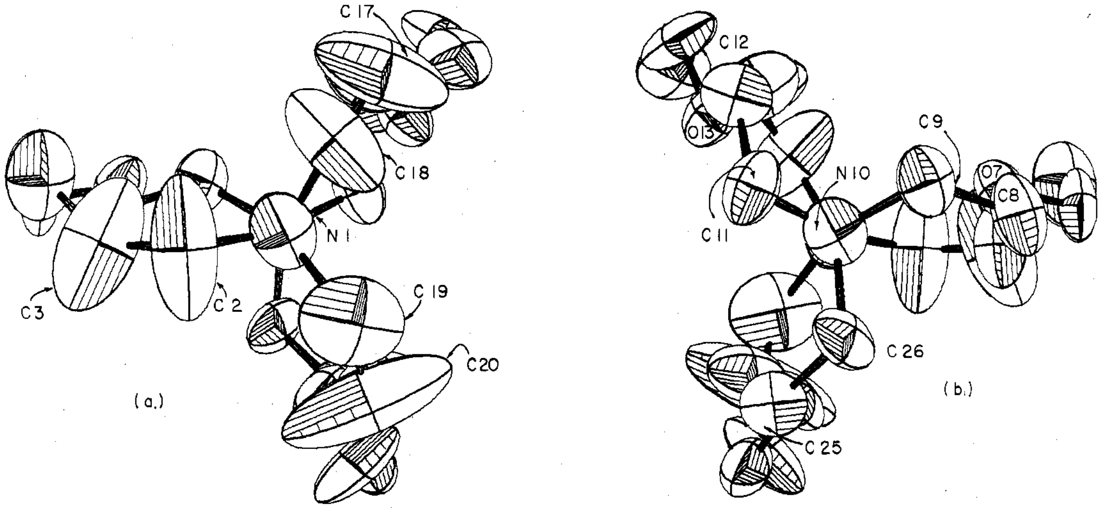


Figure 1. The crypt–potassium cation in $(\text{cryptK}^+)_2\text{Bi}_4^{2-}$ illustrating the difference between the anisotropic thermal ellipsoids (50% probability) of the (a) disordered and (b) ordered ends of the ion. All atoms are at unit occupancy.

III. Additional data for the cation (Table IV) as well as observed and calculated values of the structure factors are included in the supplementary material.

Aside from a slight shift of the potassium ion toward the end of the crypt closer to the anion (by 0.09 Å—3σ) and the disorder discussed above, the cryptated potassium ion in this structure is essentially the same as that presented in detail elsewhere.[23] Although no point symmetry is required for the cation, the potassium, nitrogen, and oxygen atoms have nearly threefold symmetry, the two oxygen planes are parallel, and the N1–K–N10 angle is within 1σ of 180° (see Table III).

Although there is no difference in the final residual, the cation model involving the disordered carbons has more reasonable distances and thermal parameters (Tables II and IV) and is preferred to the one with greatly anisotropic atoms (Figure 1). The ordered but anisotropic model requires a carbon–carbon bond length of 1.29 Å (between C2 and C3) while corresponding distances in the disordered model are 1.39 (9) and 1.56 (13) Å. In the disordered model the two fractional carbon chains (C2a–C3a and C2b–C3b) appear in an X configuration, perhaps to avoid what would be a short distance between these carbon atoms and the anion if the atoms adopted the normal arrangement. All of the disordered atoms except one (C2) are β to the nitrogen, a position where larger isotropic thermal parameters have been found previously and suspected to originate from disorder[5,9,11] but only now have been resolved by their occurrence in a small cell of low symmetry which thereby yielded a larger ratio of observables per parameter. The disordered atoms are in the end of the ion which is significantly (0.2 Å on the average) closer to the anion and has the closest contacts to the anion, 3.79 (10) Å for C20a–Bi1 and 3.99 (5) Å for C5–Bi2.

All three previously studied compounds with dinegative cluster anions, Sn_5^{2-}, Pb_5^{2-}, and Te_3^{2-}, adopt a hexagonal Bravais lattice.[9,10] Even in the present structure the trigonal habit of the crypt in the presence of a fairly small anion so dominates the packing that the triclinic unit cell, Figure 2, still comes out with nearly hexagonal proportions and packing (a differing from b by 1.6%, $\alpha \simeq \beta \simeq 98°$, and γ being only 1.4° from 60°). Likewise, the x and y coordinates of both nitrogen atoms and the potassium atom are all approximately $^1/_3$, closely corresponding to a location on the threefold axis of the proper hexagonal cell. The gross packing of the cell, Figure 2, is quite similar to that illustrated earlier[10] for $(\text{crypt-Na}^+)_2\text{Pb}_5^{2-}$ save for the obvious addition of a threefold axis to the anion (D_{3h}) and a doubling of the c axis, a second pair of cations arising by a translation of $c/2$ and a 60° rotation.

Table III. Distances and Angles in Bi_4^{2-} and Crypt-K$^+$

Anion

Distances			Angles			
Atom 1	Atom 2	Value, Å	Atom 1	Atom 2	Atom 3	Value, deg
Bi1	Bi2	2.936 (2)	Bi1	Bi2	Bi1′	89.85 (6)
Bi1	Bi2′	2.941 (2)	Bi2	Bi1	Bi2′	90.15 (6)
Bi1	Bi1′	4.150 (3)				
Bi2	Bi2′	4.161 (3)				

Difference between distances			Difference between angles		
Distance 1	Distance 2	Value, Å	Angle 1	Angle 2	Value, Å
Bi1-Bi2	Bi1-Bi2′	0.005 (3)	Bi1-Bi2-Bi1′	Bi2-Bi1-Bi2′	0.29 (12)
Bi1-Bi1′	Bi2-Bi2′	0.011 (4)			

Cation

Distances			Angles			
Atom 1	Atom 2	Value, Å	Atom 1	Atom 2	Atom 3	Value, deg
K	N1	2.90 (3)	N1	K	N10	179.3 (8)
K	O4	2.83 (2)	O4	O21	O16	60.0 (7)
K	O7	2.78 (2)	O4	O16	O21	60.2 (7)
K	N10	2.99 (3)	O16	O4	O21	59.7 (7)
K	O13	2.78 (2)	O7	O13	O24	59.1 (5)
K	O16	2.76 (3)	O13	O24	O7	61.5 (5)
K	O21	2.80 (3)	O24	O7	O13	59.4 (5)
K	O24	2.78 (2)				

Angle between Planes

Plane 1	Plane 2	Value, Å
O4–O16–O21	O7-O13-O24	0.7 (7)

The most significant feature of this structure is the Bi_4^{2-} ion, the distances and angles for which appear in Table III. This is the first discrete anionic cluster of bismuth isolated, although cationic clusters Bi_9^{5+}, Bi_8^{2+}, and Bi_5^{3+} are known.[2] As previously noted,[5] Zintl's original assignment of Bi_7^{3-} for this ion in NH_3 solution was based on analogies with other group 5 elements together with a substantial rounding of analytical results which in fact indicated the correct stoichiometry for K_2Bi_4. Although the only point symmetry required for the ion is C_i, which with two unique atoms produces a rigorously planar configuration, the anion does not vary significantly from D_{4h} symmetry. This is not unusual considering the isoelectronic (in valence electrons) ions Te_4^{2+} and Se_4^{2+}, both of which are also only required to have C_i

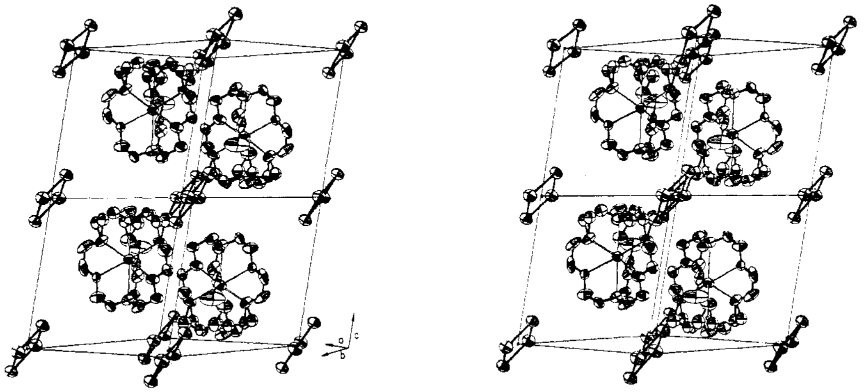


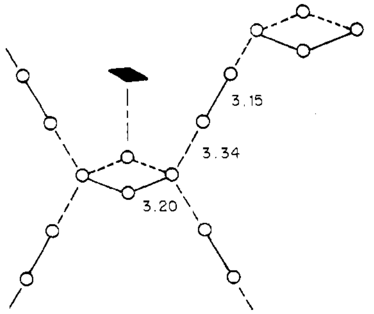
Figure 2. Stereoscopic [1$\bar{1}$0] view of two unit cells of (cryptK$^+$)$_2$Bi$_4^{2-}$. The Bi$_4^{2-}$ anions at all corners of both cells are included. The packing is essentially the same as in (cryptNa$^+$)$_2$Pb$_5^{2-}$ and (cryptNa$^+$)$_2$Sn$_5^{2-}$.[10]

symmetry in their structures but come within experimental error of possessing D_{4h} symmetry.[6,24]

The remarkable red–green dichroic effect observed for the solutions from which these crystals grow and earlier noted by Zintl[3] for other NH_3 solutions may arise from an uneven response of the human eye to colors at opposite ends of the visible spectrum. The characteristic intense green of thin layers presumably arises from transmission in both the red and the blue end of the visible spectrum, whereas thicker layers probably appear red because of the lower sensitivity of the human eye to blue.[25]

The bonding molecular orbitals in Te_4^{2+} as well as Hg_4^{6-} have already been examined.[25] It is clear that the bond order based on the MO picture is 1.25, with five filled bonding (a_{1g}, b_{2g}, e_u, a_{2u}) and two filled and substantially nonbonding molecular orbitals (e_g) for the four edges. This high bonding order gives the ion shorter Bi–Bi bonds (2.939 Å av) than in Bi_9^{5+} where the bonds range from 3.078 (6) to 3.286 (12) Å[27,28] or the polymeric BiI, where the range is 3.04–3.06 Å.[29]

Recently the phase $Ca_{11}Bi_{10}$ was reported to contain more or less isolated Bi_2 and Bi_4 groups,[30] with the same arrangement appearing in the isostructural $Ca_{11}Sb_{10}$,[30] $Yb_{11}Sb_{10}$,[31] and $Ho_{11}Ge_{10}$.[32] The square units appear to bear a definite relationship to Bi_4^{2-}. With $Z = 4$ the unit cell of $Ca_{11}Bi_{10}$ contains 16 isolated Bi atoms, eight Bi_2 groups (3.15 Å bond length), and two Bi_4 rings (with D_{4h} site symmetry). The Bi_4 groups exhibit 3.20 Å Bi–Bi bonds compared with 2.94 Å in Bi_4^{2-} and 3.07 (×3) plus 3.53 (×3) Å in Bi metal.[33] All eight of the Bi_2 groups are distributed 3.34 Å away from the Bi_4 unit so as to maintain D_{4h} symmetry, as is shown in the diagonal section through one Bi_4 group.



As a zeroth approximation the 88 electrons from the calcium might be distributed by considering the isolated Bi atoms to be Bi^{3-}, the Bi_2 groups to be Bi_2^{4-} anions, isoelectronic with I_2, and the Bi_4 rings to be Bi_4^{4-} anions, the least reduced of the lot. In this scheme, the two additional electrons in the Bi_4^{4-} group would go into the lowest antibonding π orbital (b_{2u}[26]), which effect would reduce the bond order from 1.25 to 1.0 and probably lengthen the bonds to about 3.05 Å. This distance might also serve as a suitable approximation for singly bonded Bi_2^{4-} groups, although the higher field of the calcium ions likely serves to lengthen the bonds.

Such an assignment of all the valence electrons from calcium of course represents an unlikely extreme even for a polar intermetallic phase, but there are several likely routes for delocalizing charge back onto these cations, a process which should also lengthen bonds in what in the limit were termed Bi_4^{4-} and Bi_2^{4-} ions. Each of the so-called Bi_2^{4-} ions is surrounded symmetrically in a π-like manner (D_{2h}) by four calcium ions at 3.25 Å in a plane which comes within 0.08 Å of including the two atoms in Bi_2, and these calcium atoms are in turn all 3.26 Å from two isolated Bi plus more Ca atoms. The first four calcium atoms have the same symmetry as and would be expected to withdraw some charge from both the π and π^* orbitals of the Bi_2^{4-} ion, in the same manner as postulated for charge reduction of the square "anion" in Na_6Hg_4.[26]

For the Bi_4^{4-} group, the π orbitals (a_{2u}, e_g (nonbonding), and b_{2u}) are all in a position to lose charge to a pair of calcium ions immediately above and below the ring on the fourfold axis ($d_{Ca-Bi} = 3.6$ Å) or, perhaps even more likely in view of the remarkable geometry, into the σ^* orbitals of the formal Bi_2^{4-} ion. The 3.34 Å separation between the Bi_4 groups and eight symmetrically disposed Bi_2 units would seem to reflect a significant interaction, although this distance does not shorten on conversion to $Ca_{11}Sb_{10}$, in contrast to distances in the antimony dimer and tetramer groups. The fact that no atoms approach close to the Bi_4 square in or near its plane is consistent with the earlier observation[6] that this direction is a likely route for donation of charge from basic anions into vacant low-energy orbitals in the Te_4^{2+} and Se_4^{2+} ions.

The above description provides at least a heuristic approximation of the bismuth–bismuth bonding in $Ca_{11}Bi_{10}$, as well as in the related antimony and germanium phases, the starting point emphasizing the simplicity of localized MO descriptions and recognizing the fact that sufficient localization is present to define some direct covalent bonding. However, no basically ionic and localized description can be expected to well describe a presumably conducting intermetallic phase of this nature.

Acknowledgment. We thank Professor R. A. Jacobson and his group for assistance in the use of the diffractometer. This work was supported by the U.S. Energy Research and Development Administration, Division of Physical Research.

Supplementary Material Available: Table IV, the light-atom distances and angles for the cation, and the listing of the structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

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Structural Characterization of the Bioligomeric Triphenyltelluronium Thiocyanate Salt, $((C_6H_5)_3Te(NCS))_4((C_6H_5)_3Te(NCS))_2$

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Received March 25, 1977 AIC70223N

The crystal and molecular structure of triphenyltelluronium thiocyanate, $(C_6H_5)_3Te(NCS)$, has been determined from three-dimensional x-ray data collected by counter techniques. The structure was refined by full-matrix least-squares methods. The refinement was carried out using 5543 nonzero reflections for which $F > \sigma(F)$ and assuming anisotropic thermal motion for all nonhydrogen atoms. The least-squares refinement led to a final value of the conventional R factor (on F) of 0.039. Crystal data are as follows: space group $P\bar{1}$; $a = 13.339$ (12), $b = 13.885$ (10), $c = 14.796$ (11) Å; $\alpha = 82.53$ (6), $\beta = 76.53$ (7), $\gamma = 78.20$ (7)° (23 °C); $V = 2599$ Å^3. Triphenyltelluronium thiocyanate is bioligomeric in the solid state. The unit cell ($Z = 6$) consists of one dimer and one tetramer separated by van der Waals distances. The oligomers are predominantly ionic with tellurium–nitrogen and tellurium–sulfur distances significantly shorter than respective van der Waals distances. Te–N distances range from 2.963 (8) to 3.182 (8) Å; the Te–S distances range from 3.256 (4) to 3.616 (4) Å. Both end-to-end and terminally bridging NCS groups are present. The central eight-membered ring of the dimer is puckered and has a chair configuration with a dihedral angle of 93.2°. The overall configuration of the tetramer is that of a step with a dihedral angle of 99.9°. Five- and six-coordinate tellurium atoms are present in distorted square-pyramidal and distorted octahedral geometries, respectively. The three crystallographically independent triphenyltelluronium cations have a trigonal-pyramidal shape but possess no symmetry, due to the conformation adopted by the phenyl rings. The mean Te–C distance is 2.13 (2) Å and the mean C–Te–C angle is 97.3 (6)°. The thiocyanate groups are ionic with mean N–C and C–S distances of 1.15 (2) and 1.64 (1) Å, respectively.

Introduction

Organochalcogenonium salts, R_3XY (X = S, Se, Te; Y = anion), have been known for at least a century and are generally thought of as simple ionic solids of the $R_3X^+Y^-$ form.[2-6] Structural studies of $(CH_3)_3SI$[7] and $(CH_3)_3SeI$,[8] however, show that the compounds consist of isolated ion pairs having X···I distances shorter than respective van der Waals distances. Likewise, in the structure of the telluronium salt, $[(CH_3)_3Te]^+[CH_3TeI_4]^-$, four weak tellurium–iodine interactions occur.[9] This type of interaction, which frequently causes the chalcogen to have a coordination number higher than would be expected from the stoichiometry of the system, is called secondary bonding and has been reviewed by Alcock.[10]

During our investigation of the interaction of ambidentate nitrogen-containing pseudohalide ions with triorganotelluronium and triorganoselenonium ions, we found spectroscopic evidence suggesting structures for these compounds more complicated than the $R_3X^+Y^-$ ion-pair model.[11,12] $(C_6H_5)_3TeX$ (X = N_3, NCO, NCS, NCSe) compounds, for example, show multiple C–N or N–N stretching vibrations in the 2000–2200-cm^{-1} region of their infrared spectra.[11] As part of our effort to determine the structural relationships among these compounds[13,14] we have determined the crystal structure of triphenyltelluronium thiocyanate, $(C_6H_5)_3Te(NCS)$. The structural results reported herein have appeared in preliminary form.[15]

Experimental Section

The compound was prepared as a precipitate by mixing aqueous solutions of $(C_6H_5)_3TeCl$ and excess NaNCS.[11] The $(C_6H_5)_3Te(NCS)$, after being collected, was washed with water and recrystallized from 2-propanol.

Intensity data were collected by Molecular Structure Corporation (College Station, Texas) on a Syntex $P\bar{1}$ automatic diffractometer using graphite monochromatized Mo Kα radiation. The prism used for data collection measured 0.25 × 0.29 × 0.39 mm.

Unit cell parameters for $(C_6H_5)_3Te(NCS)$ obtained by computer-centering 25 reflections followed by least-squares refinement of the setting angles are as follows: $a = 13.339$ (12), $b = 13.885$ (10), $c = 14.796$ (11) Å; $\alpha = 82.53$ (6), $\beta = 76.53$ (7), $\gamma = 78.20$ (7)°; $V = 2599$ Å^3 (temperature 23 °C). Reduction of the cell revealed no hidden symmetry, and the cell axes, obtained from the Baloshov and Ursell algorithm,[16] represent the three shortest noncoplanar translations (Dirichlet triplet). The measured density of 1.597 (10)