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The Crystal Structure of Bismuth Subchloride. Identification of the Ion Bi_3^{5+}

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The stoichiometric formula of the lower chloride formed in the BiCl_3 -Bi system has been established as $\text{Bi}_{12}\text{Cl}_{14}(\text{BiCl}_{1.167})$ through a single crystal, X-ray determination of its structure. The unit cell is orthorhombic, with $a_0 = 23.057 \pm 0.002$, $b_0 = 15.040 \pm 0.007$, $c_0 = 8.761 \pm 0.003$ Å, and space group Pnmm. The experimental density of 6.54 ± 0.05 g. cc.⁻¹ agrees well with the value of 6.56 g. cc.⁻¹ calculated for 48 Bi and 56 Cl atoms in the unit cell. Bismuth positions were deduced from the three-dimensional Patterson map computed on the basis of 1957 observed reflections, while the number and positions of the chlorine atoms were obtained and confirmed by three-dimensional Fourier and difference Fourier maps. Refinement with isotropic temperature factors gave a final value for the residual R_1 of 0.156. Each unit cell of $\text{Bi}_{12}\text{Cl}_{14}$ contains 4 Bi_3^{5+} , 8 BiCl_3^{2-} , and 2 $\text{Bi}_2\text{Cl}_5^{2-}$ groups. The cation has the shape of a tripyramid, a trigonal prism with a Bi atom projecting from each face, with the geometry somewhat distorted by the unsymmetric environment of neighboring anions. The latter can be classified as separate tetragonal pyramids (BiCl_3^{2-}) and as pairs of such pyramids sharing a basal edge ($\text{Bi}_2\text{Cl}_5^{2-}$), with one half of the BiCl_3^{2-} groups considerably distorted. Previous studies of the BiCl_3 -Bi system are re-examined in the light of the structural results.

Introduction

Many aspects of the enigmatic BiCl_3 -Bi system have recently received attention in various laboratories. The dilute solutions of the metal in the molten trichloride have been investigated by several means, but with rather inconsistent results. Cryoscopic studies of solutions containing up to 24 mole % metal indicate a solute $(\text{BiCl})_2$ (or Bi_2^{2+}),² while solvent vapor pressure measurements up to 24% Bi have been interpreted in terms of metal atoms,³ or ideal solutions of the tetramer $(\text{BiCl})_4$,⁴ or a mixture of $(\text{BiCl})_2$ and Bi_2 .⁵ Concentration cell data indicate the presence of the monomer BiCl (or Bi^+) in dilute solution, $(\text{BiCl})_4$ above 0.1 to 0.6% metal, and then an apparent decrease in polymerization above about 7 to 10% Bi.⁶ A careful spectrophotometric study of the system demonstrates that only two species are present in the range 0.01 to 6% metal, and that their behavior with concentration is consistent with the foregoing e.m.f. conclusions.⁷ Solutions containing 7.4 to 28.5% metal have been shown to be diamagnetic.⁸

Phase studies on more concentrated solutions of metal in the trichloride resulted in the separation of the so-called bismuth monochloride and led to the present work. The first indication of the compound appeared in the 1908 phase diagram of Eggink,⁹ who observed that an intermediate solid phase separates from the

salt- and metal-rich liquid phases at about 320°. Ether extraction of the excess trihalide from a mixture of the two chlorides gave a product which analyzed very close to BiCl . A later study by Sokolova¹⁰ qualitatively confirmed the main features of the earlier phase diagram, although subsequent conclusions¹¹ regarding the stability and structure of BiCl on the basis of powder X-ray data have been disproved.¹² The most thorough study of the phase relationships is due to Yosim, *et al.*,¹³ who found that the intermediate, then-unidentified lower chloride disproportionates at 320° to liquid phases containing about 45 and 98% metal. Similar results have been published for the bismuth bromide and iodide systems with a lower halide apparently formed in each case.¹⁴

The first characterization of this lower bismuth subchloride was due to Corbett,¹² who obtained samples containing 98-99% BiCl by vacuum sublimation or benzene extraction of the excess BiCl_3 from the mixtures. The composition of the new phase was taken to be that which was just short of the composition at which diffraction lines of metal appeared in powder patterns of the samples as trichloride was removed; the limited sensitivity of this technique is evident from the structural results to be presented. The black product was found to be apparently insoluble or unstable in all solvents except BiCl_3 . The diamagnetism of the compound as well as the high viscosity,¹⁵ slow equilibration,¹³ and considerable supercooling of the concentrated solutions all point to some form of association of the subhalide.¹² In the gas phase, however, the

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(2) S. W. Mayer, S. J. Yosim, and L. E. Topol, *J. Phys. Chem.*, **64**, 238 (1960).

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stoichiometric monomer BiCl apparently predominates in the reaction of BiCl₃(g) with Bi(l).¹⁶

Finally, results of an X-ray examination¹⁷ of powdered and liquid Bi(AlCl₄)¹⁸ (albeit only partially characterized) point to an association of Bi atoms in the shape of equilateral triangles, with Bi-Bi distances equal to 3.04 Å. Single crystals of the same compound have been found to be rhombohedral; their space group symmetry (R3c) and the calculated $Z \sim 6$ are compatible with the triangular configuration.¹⁹

Experimental

Preparation of Crystals.—Mixtures containing up to 75% BiCl were synthesized in a sealed, evacuated Pyrex tube by equilibration of BiCl₃ with excess metal at 325°, followed by reduction of the temperature to 270° over a period of 1–2 weeks. The cooled tube was opened in an inert atmosphere and single crystals of BiCl projecting from the matrix were picked out manually. The compound crystallizes in the form of shiny black prisms with a flattened, hexagonal cross section; the crystals were found to decompose slowly on contact with the atmosphere.

The most suitable specimen was selected on the basis of preliminary Weissenberg photographs. It was shaped to a 320 × 98 μ cylinder by rolling over emery paper in order to facilitate absorption correction and was then sealed in an evacuated, thin-walled capillary. The same specimen was used for all diffraction work.

Determination of Density.—The crystals were too heavy for the floatation technique and too scarce for the normal pycnometric method. Macromolecular measurements on BiCl–BiCl₃ mixtures require a presumption as to the composition of the reduced product in order to correct for BiCl₃ (or Bi) impurities, although such measurements indicated the density to be near 6.5 g. cc.⁻¹. Therefore a micropycnometric method was developed which has very good precision and requires only a few milligrams of material.

The micropycnometer was constructed from a 15-mm. length of capillary tubing (5.5 mm. o.d., 0.678 mm. i.d.). One end was sealed and flattened, and the open end was ground to the usual cone shape for clean drainage. After its volume (ca. 5 μl.) had been determined, the pycnometer was cleaned, weighed on a microbalance, loaded with crystals, and reweighed. This assembly was then placed in an evacuable sample container to which an L-shaped side arm filled with 1-bromonaphthalene was attached through a ground glass joint. The density of 1-bromonaphthalene, selected for its low vapor pressure and chemical inertness, was measured with the same pycnometer and found to be 1.500 ± 0.003 g. cc.⁻¹ at 25°, compared with a literature value²⁰ of 1.478 g. cc.⁻¹. The container was evacuated to remove all traces of air from the crystals and liquid alike, and the 1-bromonaphthalene was allowed to enter the pycnometer by turning the side arm upward. In the last step, the micropycnometer containing crystals and liquid was removed from the sample container, wiped clean of excess liquid, and weighed. The average value of individual density determinations on five batches of crystals was 6.54 ± 0.05 g. cc.⁻¹.

Diffraction Data.—Preliminary Weissenberg and precession photographs indicated an orthorhombic unit cell. Lack of systematic extinctions for the *hkl* and *hk0* data, in conjunction

with the extinctions $h + l = 2n + 1$ for *h0l* data and $k + l = 2n + 1$ for the *0kl* data, allowed the choice of space groups Pnn and Pnmm. Precision lattice constants were measured by the conventional Weissenberg back-reflection method²¹ with unfiltered Cu, Cr, and Co radiation. The final values are $a_0 = 23.057 \pm 0.002$ Å., $b_0 = 15.040 \pm 0.007$ Å., c_0 (the needle axis) = 8.761 ± 0.003 Å.

All intensity data were obtained with Cu Kα radiation. Multiple film Weissenberg photographs were taken for layers *hk0* through *hk5* by the equiinclination technique.²¹ Exposure times varied between 120 and 180 hr. Timed-exposure, precession photographs were also taken of layers *h0l*, *h1l*, and *0kl* in order to supplement the Weissenberg data at low angles. Films were judged visually and each spot was rechecked until the estimate of values from different films in the pack agreed to within 10%. In all, 1957 observed reflections were judged. The 548 unobserved reflections which were not subject to systematic extinctions were assigned a value equal to 60% of the lowest observable intensity for that layer.

Treatment of Intensities.—Lorentz and polarization corrections were applied by means of the IBM 650 computer according to INCOR-IM, a locally-modified version of the INCOR-I program.²² Precession data were handled with the aid of Olson's²³ correction program. Weissenberg data were corrected for absorption according to Bond's approach²⁴ and sharpened according to the method proposed by Patterson²⁵ and developed by Lipson and Cochran.²⁶ The latter step consists of multiplying each corrected intensity by the factor $(\sum_j z_j / \sum_j f_j)^2$, where z_j is the atomic number and f_j , the corresponding, dispersion-corrected scattering factor of atom j . The calculations were again performed on the IBM 650 computer by means of a program written for this purpose.²⁷ Precession intensities were corrected for absorption graphically using corrected Weissenberg data. At this stage all corrected intensities were placed on the absolute scale.

Structure Determination

The trial model was obtained by the "heavy atom" technique which relies on the correct assignment of bismuth positions. The latter were deduced from a three-dimensional Patterson map. Fourier and difference Fourier maps were used to locate chlorine atoms.

Vector (Patterson) Maps.—A sharpened, three-dimensional Patterson function was summed on the IBM 650 computer according to the TDF-2 program of Fitzwater and Williams.²⁸ Results were tabulated and printed directly on a $1/80 \times 1/40 \times 1/40$ grid, suitable for plotting contours, by a special technique developed by Williams.²⁹ The absolute scale factor k and the average temperature factor B were evaluated from a plot of $\log \langle F_o^2 / \sum f_o^2 \rangle$ vs. $\langle (\sin^2 \theta / \lambda^2) \rangle$ according to Wilson's method.³⁰ On the basis of these two quantities all the Patterson peak heights were expressed in terms of products of the electron densities of the contributing atoms.

(21) M. J. Buerger, "X-Ray Crystallography," J. Wiley and Sons, New York, N. Y., 1942.

(22) A. Salkin and R. E. Jones, "The INCOR-I Intensity Correction Program," Univ. of California, Berkeley, 1957.

(23) D. H. Olson, Iowa State Univ., private communication, 1960.

(24) W. L. Bond, *Acta Cryst.*, **12**, 375 (1959).

(25) A. L. Patterson, *Z. Krist.*, **90**, 517 (1935).

(26) H. Lipson and W. Cochran, "The Determination of Crystal Structures," G. Bell and Sons, London, 1957, p. 170.

(27) A. Hershaft, "The ACS Absorption and Sharpening Program," available from D. R. Fitzwater, Iowa State Univ., 1960.

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(30) A. J. C. Wilson, *Nature*, **150**, 152 (1942).

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(17) H. A. Levy, M. A. Bredig, M. D. Danford, and P. A. Argon, *ibid.*, **64**, 1959 (1960).

(18) J. D. Corbett and R. K. McMullan, *J. Am. Chem. Soc.*, **78**, 2906 (1956).

(19) H. A. Levy, P. A. Argon, M. D. Danford, and R. D. Ellison, *Acta Cryst.*, **14**, 549 (1961).

(20) M. Jones and A. Lapworth, *J. Chem. Soc.*, **105**, 1804 (1914).

Discovery of large peaks along the P(00Z) line section, indicating the presence of atoms with the same x and y coordinates, gave first experimental proof of the presence of a mirror plane in the c direction. It thus justified the heretofore arbitrary choice of Pn \bar{m} as the correct space group and confirmed the presence of a center of symmetry. Subsequently, a negative piezoelectric test for BiCl reported by Okaya and Pepinsky³¹ did not deny the presence of a center of symmetry. The absence of a peak at $1/2, 1/2, 1/2$ limited the choice of positions to one type each of eightfold and fourfold sets.

The three-dimensional Patterson map was interpreted directly and systematically. Possible sets of the atomic coordinates x, y, z were found by inspection of the P($X^{1/2}Z$), P($1/2YZ$), and P(XOZ) sections, respectively, and checked against the presence of peaks corresponding to other vectors within the same set. One eightfold position was found by elimination after checking all the interset peaks at $r_{\text{Bi-Bi}}$ from the Patterson origin. Final screening was performed by inspection of peaks corresponding to vectors between members of different symmetry sets. Three eightfold and six fourfold symmetry sets were located for a total of 48 Bi positions.

Calculation of Structure Factors.—Atomic scattering factors for Bi⁺ and Cl⁻ were obtained from Ibers.³² Before their introduction into structural calculations the Bi⁺ scattering factors were approximately corrected for anomalous dispersion according to Templeton³³ by subtracting the constant value of 5 at all angles. The correction of Cl⁻ factors was not considered significant. Structure factors were calculated on the IBM 650 computer with the aid of the LS-IIM2 program, a locally expanded version of the LS-II least squares program of Senko and Templeton.³⁴

Electron Density Maps.—The three-dimensional electron density functions were computed on the IBM 650 computer with the aid of the TDF-2 program, and the results for one octant were compiled and printed directly on an $1/80 \times 1/80 \times 1/40$ grid as before. Partially refined Bi parameters and temperature factors were used; reflections below a certain minimum and those for which $F_o \gg F_c$ were excluded. Aside from the original 12 Bi positions, 21 new peaks appeared. Some of these were dismissed on the basis of bond length considerations as ripples due to series termination effects of nearby Bi atoms.

To clarify the model a three-dimensional difference Fourier (error synthesis) was summed and plotted in a manner similar to that of a regular Fourier series. Partially refined Bi parameters and temperature factors and only reflections above a certain minimum value and

with $F_o/F_c < 3$ were used. The 14 positive peaks which appeared were interpreted as Cl positions, whereas the smaller negative peaks were regarded as due to anisotropic thermal motions of the Bi atoms. Thus the unit cell was found to contain 48 Bi and 56 Cl atoms for a composition of BiCl_{1.167}. The 6.56 g. cc.⁻¹ density value calculated on this basis compared favorably with the 6.54 ± 0.05 g. cc.⁻¹ experimental value.

Structure Refinement and Functional Analysis

Structure Refinement.—The structure was refined by the method of least squares on the IBM 704 computer at the Midwest Universities Research Association according to the program of Busing and Levy.³⁵ Five cycles were run with isotropic temperature factors and weighted diffraction intensities.³⁶ The refinement dropped the residual $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ from an initial value of 0.26 to 0.156.³⁷ The refined atomic positions and temperature factors are listed in Table I along with their respective standard deviations. A drawing of one-quarter of the unit cell projected onto the (001) plane is given in Fig. 1.

Throughout the refinement no grounds appeared for dismissing any of the Cl positions. As a further check on their validity a (001) difference Fourier was computed on the basis of the refined Bi parameters alone. The height ratios of the Cl peaks established both the absence of a disorder in Cl atoms and the presence of a c -normal mirror plane to generate the eightfold Cl sets as well as the one fourfold set (Cl_x) that does not lie on this plane. Finally, a three-dimensional difference Fourier, computed on the basis of the refined Bi and Cl parameters, gave final confirmation of the correct assignment of all atomic positions. The (001) composite of the latter is shown in Fig. 2 relative to the Bi positions (Fig. 1). Small positive peaks symmetrically distributed around the Bi atoms give an indication of (only) the apparent extent and direction of thermal vibrations of the Bi atoms.

Functional Analysis.—Interatomic distances and angles, along with their respective standard deviations, were evaluated on the IBM 704 with the aid of the Crystallographic Function and Error program.³⁸ A partial list is given in Tables II and III; the most pertinent bonding distances are also indicated in Fig. 1.

(35) W. R. Busing and H. A. Levy, Oak Ridge National Laboratory Report ORNL 59-4-37, Oak Ridge, Tenn., 1959.

(36) A. Hershaf, Ph.D. Thesis, Iowa State University, 1961. For observed intensities equal to or greater than the mid-point of the best judged range (I_b), where a precision of 10% was estimated, $\sigma(F_o) = 0.05F_o$. For weaker reflections the expression $\sigma(F_o) = 0.05(I_b/I)^{3/4}F_o$ was found to satisfy the statistical relationship for the change in standard deviation with observation on a decreasing number of films and to coincide with a reasonable estimate for the error of the lowest observable intensity. These deviations and the resultant weighting factor were calculated prior to the application of what were sometimes rather large absorption corrections.

(37) Tables of calculated and observed structure factors are deposited as Document No. 7623 with the American Documentation Institute, Auxiliary Publication Project, Photo Duplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and remitting in advance \$2.50 for photoprints or \$1.75 for 35-mm. microfilm payable to: Chief, Photoduplication Service, Library of Congress.

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(33) D. H. Templeton, *Acta Cryst.*, **8**, 842 (1955).

(34) M. E. Senko and D. H. Templeton, "The I.S.-II Least Squares Program," University of California, Berkeley, 1957.

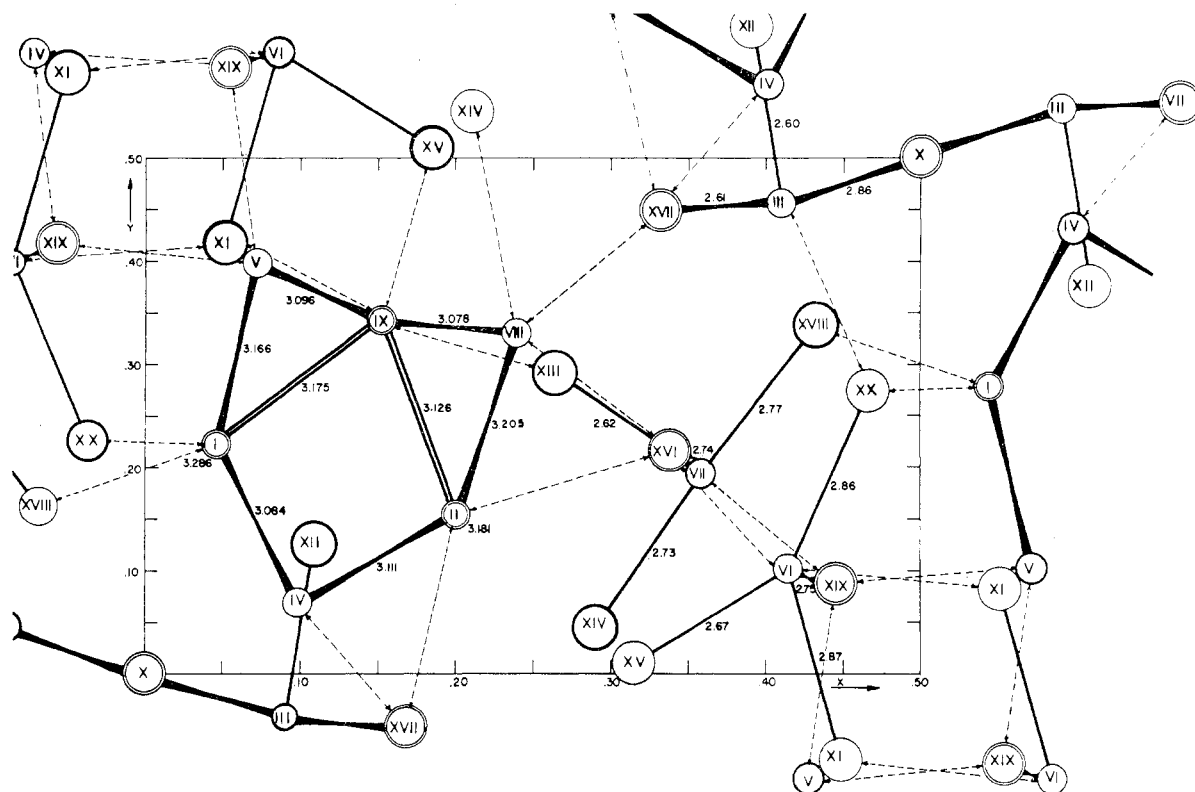


Fig. 1.—The structure of $\text{BiCl}_{1.167}$ projected onto the (001) plane. Small circles represent bismuth; large circles, chlorine. Single atoms are at $z = 0.00$ or 0.50 , with the latter heavier; double atoms are at ± 0.2 to 0.3 .

TABLE I
FINAL ATOMIC PARAMETERS FOR $\text{BiCl}_{1.167}^a$

Atom no.		Positions			
		x	y	z	B
Bi	I	0.0459 ± 0.0002	0.2229 ± 0.0003	$\pm(0.1876 \pm 0.0007)$	3.25 ± 0.07
	II	$.2002 \pm .0002$	$.1544 \pm .0002$	$\pm(.1815 \pm .0006)$	$2.96 \pm .07$
	III	$.4101 \pm .0002$	$.4550 \pm .0003$	0	$2.07 \pm .07$
	IV	$.0984 \pm .0002$	$.0692 \pm .0003$	0	$2.52 \pm .07$
	V	$.0723 \pm .0003$	$.3982 \pm .0004$	0	$3.70 \pm .10$
	VI	$.4139 \pm .0002$	$.1009 \pm .0004$	0	$3.39 \pm .10$
	VII	$.3578 \pm .0002$	$.1930 \pm .0002$	$1/2$	$1.75 \pm .06$
	VIII	$.2390 \pm .0002$	$.3296 \pm .0003$	0	$2.25 \pm .07$
	IX	$.1525 \pm .0002$	$.3425 \pm .0003$	$\pm(0.2669 \pm 0.0007)$	$3.43 \pm .08$
Cl	X	0	0	$\pm(.288 \pm .005)$	$2.3 \pm .4$
	XI	0.052 ± 0.001	0.418 ± 0.002	$1/2$	$3.1 \pm .5$
	XII	$.109 \pm .001$	$.126 \pm .002$	$1/2$	$2.6 \pm .4$
	XIII	$.264 \pm .002$	$.291 \pm .003$	$1/2$	$5.0 \pm .8$
	XIV	$.290 \pm .001$	$.044 \pm .002$	$1/2$	$3.6 \pm .5$
	XV	$.315 \pm .001$	$.010 \pm .002$	0	$3.5 \pm .5$
	XVI	$.338 \pm .001$	$.216 \pm .002$	$\pm(0.194 \pm 0.004)$	$3.4 \pm .4$
	XVII	$.332 \pm .001$	$.449 \pm .002$	$\pm(.216 \pm .004)$	$3.4 \pm .4$
	XVIII	$.433 \pm .001$	$.337 \pm .001$	$1/2$	$1.8 \pm .3$
	XIX	$.445 \pm .001$	$.086 \pm .002$	$\pm(0.302 \pm 0.005)$	$4.5 \pm .5$
	XX	$.466 \pm .001$	$.274 \pm .001$	0	$1.2 \pm .3$

^a $K_0 = 12.72$, $K_1 = 12.00$, $K_2 = 13.50$, $K_3 = 12.34$, $K_4 = 12.71$, $K_5 = 13.20$.

Discussion

Interpretation of Structure.—The unit cell of bismuth “monochloride” contains four Bi_9 polyhedra and an array of Bi and Cl atoms which can be cataloged as eight BiCl_5 (Bi_{VI} , Bi_{VIII}) and two Bi_2Cl_3 (Bi_{III}) units (Fig. 1). The Bi_9 polyhedron has the form of a slightly distorted trigonal prism with atoms Bi_{IV} and Bi_{IX} (2)

projecting from its faces. In BiCl_5 the Cl atoms form a distorted tetragonal pyramid about Bi; in Bi_2Cl_3 two such pyramids share a basal edge. Weak Bi-Cl interactions form the only links between these groups; those shorter than 3.5 \AA . are indicated by dashed lines in Fig. 1.

Each atom in the Bi_9 unit has four nearest neighbors

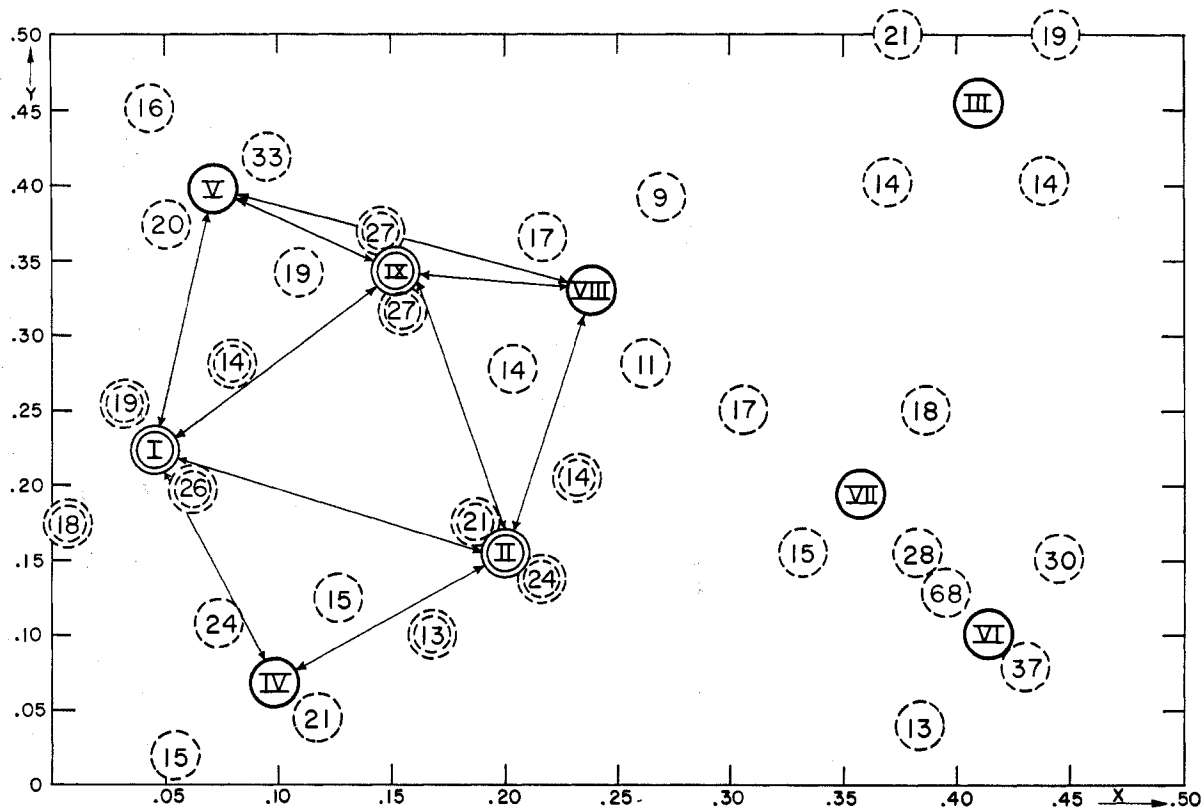


Fig. 2.—The (001) projection of the peaks derived from the three-dimensional difference Fourier with final Bi and Cl parameters (dashed circles) together with the Bi positions (solid circles). The scale of the peak heights given corresponds to a bismuth atom at *ca.* 450. The *z* parameters (not given) for the dashed peaks are the same as for the originating Bi atoms except for the eightfold I, II, and IX.

TABLE II
INTERATOMIC DISTANCES IN BiCl_{1.167}

Atom no.	Distance, Å.	Atom no.	Distance, Å.
I-I	3.286 ± 0.012	VII-XIII	2.617 ± 0.050
I-II	3.704 ± .005	VII-XIV	2.730 ± .034
I-IV	3.084 ± .006	VII-XVI	2.743 ± .037
I-V	3.166 ± .007	VII-XVIII	2.775 ± .021
I-IX	3.125 ± .006	VII-XIX	3.100 ± .037
I-X	3.625 ± .011	VIII-IX	3.078 ± .006
I-XII	3.424 ± .017	VIII-XIV	3.296 ± .034
I-XVIII	3.215 ± .018	VIII-XVI	3.311 ± .029
I-XX	3.297 ± .011	VIII-XVII	3.378 ± .028
II-II	3.181 ± .011	IX-XI	3.297 ± .024
II-IV	3.111 ± .006	IX-XIII	3.373 ± .040
II-VIII	3.205 ± .005	X-XII	3.64 ± .03
II-IX	3.126 ± .006	X-XVIII	3.84 ± .03
II-XII	3.525 ± .017	XI-XI	3.43 ± .06
II-XIII	3.763 ± .034	XI-XV	3.38 ± .05
II-XVI	3.305 ± .025	XI-XX	3.84 ± .03
II-XVII	3.306 ± .025	XIII-XVI	3.36 ± .05
III-X	2.860 ± .028	XIV-XVII	3.68 ± .04
III-XII	2.605 ± .027	XVI-XVI	3.40 ± .08
III-XVII	2.606 ± .032	XVI-XIV	3.29 ± .04
III-XX	3.017 ± .018	XVII-XVII	3.78 ± .07
IV-X	3.553 ± .030	XVII-XVIII	3.79 ± .03
IV-XVII	3.470 ± .031	XIX-XIX	3.46 ± .09
V-VIII	3.979 ± .007	XIX-XIX	3.63 ± .06
V-IX	3.096 ± .007		
V-XIX	3.418 ± .037		
V-XIX	3.337 ± .036		
VI-XI	3.185 ± .031		
VI-XV	2.870 ± .031		
VI-XV	2.666 ± .035		
VI-XVI	3.000 ± .030		
VI-XIX	2.753 ± .046		
VI-XX	2.865 ± .018		

TABLE III
INTERATOMIC ANGLES IN BiCl_{1.167}

Atom no. ^a	Angle, deg.	Atom no.	Angle, deg.
I-I-V	58.7 ± 0.1	XV-VI-XX	145.8 ± 0.9
II-I-V	92.3 ± .2	XIX-XI-XIX	148.5 ± 1.4
I-II-VIII	92.7 ± .1	XIII-VII-XIV	89.3 ± 1.3
X-III-X	80.7 ± 1.3	XIII-VII-XVIII	77.7 ± 0.6
X-III-XII	83.5 ± 0.5	XIII-VII-XVIII	94.2 ± 1.2
X-III-XVII	92.2 ± .9	XIV-VII-XVIII	176.5 ± 0.8
XII-III-XVII	85.4 ± .7	XVI-VII-XVI	155.4 ± 1.1
XVII-III-XVII	92.8 ± 1.3	II-VIII-V	86.8 ± 0.1
I-IV-II	73.4 ± 0.1	I-IV-VIII	107.7 ± .2
I-IV-II	105.1 ± .2	II-IX-V	105.9 ± .2
I-V-I	62.5 ± .1	V-IX-VIII	80.2 ± .2
I-V-VIII	88.3 ± .2		
XI-VI-XV	75.2 ± 1.0		
XI-VI-XIX	81.4 ± 0.7		
XI-VI-XX	139.0 ± .7		

^a Central atom is vertex.

at 3.08 to 3.29 Å., grouped at 3.17 to 3.29 Å. between the equivalent atoms forming the trigonal prism (Bi_{VIII} and Bi_{II}(2), Bi_V and Bi_I(2)) and at 3.08 to 3.13 Å. between these and the atoms that project from the faces. These compare to the 3.10 Å. between bismuth and its three nearest neighbors in the metal. The reason for the somewhat shorter Bi-Bi distances to the apical atoms is not clear, although their relationship to other like atoms is more symmetric than that about atoms defining the prism.

Comparison of the Bi₉ geometry with that of a regular arrangement of nine atoms equidistant from a central atom shows that the height of the trigonal prism (I-II) in this case is shortened about 10% and the apical angles at Bi_{IV} and Bi_{IX} are correspondingly altered. All other angles are within 2° of the 60° for the regular

geometry, except that I-IV-I is 64° . Further distortion of the Bi_9 group may be viewed as arising from electrostatic interactions with the chlorine environment which is at distances (3.22 to 3.42 Å.) that average very close to the sum of the estimated ionic (or van der Waals) radii of Bi^+ (~ 1.4 Å.) and Cl^- . The unsymmetric arrangement of these nearest neighbors apparently is the source of the increase of nearly 0.3 Å. in the $\text{Bi}_{\text{V}}-\text{Bi}_{\text{VIII}}$ distance relative to $\text{Bi}_{\text{I}}-\text{Bi}_{\text{II}}$, while the close approach of Cl_{XVIII} (3.22 Å.) is possibly the reason for the somewhat larger $\text{Bi}_{\text{I}}-\text{Bi}_{\text{I}}$ separation.

Assignment of a collective charge of $5+$ to the Bi_9 unit follows from charge conservation and the stoichiometry once it is concluded that the other three bismuth atoms present in the quadrant illustrated must be in the normal, tripositive state. That this is the case is indicated by the observed Bi-Cl distances, 2.61 to 2.78 Å. in $\text{Bi}_2\text{Cl}_8^{2-}$ and $\text{Bi}_{\text{VII}}\text{Cl}_5^{2-}$ and up to 2.87 Å. in $\text{Bi}_{\text{IV}}\text{Cl}_5^{2-}$, as compared to a Bi-Cl distance of 2.71 Å. reported for the five-coordination metal atom in BiSCl .³⁹ It should be noted that an odd charge on the complexation, and an odd oxidation number for bismuth in the anions, is to be expected from the diamagnetism of the compound. A molecular orbital treatment is doubtlessly necessary to explain the charge distribution and bonding within this unusual cation.

The geometry observed for the $\text{Bi}_{\text{VII}}\text{Cl}_5^{2-}$ anion and for the *trans* $\text{Bi}_2\text{Cl}_8^{2-}$ group (Bi_{II}) can be described as a regular square pyramid and two such pyramids sharing a basal edge, respectively, or the equivalent figures derived from octahedra with one atom removed. In each case the vacant position presumably is occupied by the nonbonding electron pair derived from the $6s^2$ configuration of the free Bi^{3+} ion. Although no halo complexes of bismuth(III) are known structurally, the arrangements found here are quite similar to those found for SbCl_5^{2-} ,⁴⁰ SbF_5^{2-} ,⁴¹ and the single bridged $(\text{SbF}_4^-)_n$ ⁴²; in all of these complexes the metal atom is found somewhat below the basal plane of the square pyramid, perhaps due to the more demanding spatial requirements of the nonbonding pair on Sb^{3+} and Bi^{3+} .

The other BiCl_5^{2-} ion about Bi_{VI} is the most distorted, perhaps due to packing requirements, and this gives an additional, more distant chlorine atom at 3.19 Å. (Cl_{XI}) and somewhat longer distances within the group. The two BiCl_5^{2-} ions within the quadrant are displaced by $1/2c_0$ from one another so that each of these Bi atoms also has two additional, more distant (3.0 to 3.1 Å.) chlorine neighbors in the other ion (XVI or XIX). The result is to link the BiCl_5^{2-} groups into a kinked, infinite chain in the z direction; two such chains are also more weakly connected by the $\text{Bi}_{\text{VI}}-\text{Cl}_{\text{XI}}$ interaction noted above. The geometry of these bridging chlorine atoms about bismuth is as

predicted by Orgel⁴³ on the basis of the spatial requirements of the nonbonding electron pair.⁴⁴

Reliability of the Model.—The consistency of Bi-Bi vectors with the observed Patterson peaks, the agreement between observed and calculated structure factors, the satisfactory progress of refinement, and the plausibility of the resulting configurations and interatomic distances all serve to ensure that the proposed model is essentially correct. According to Lipson and Cochran,⁴⁵ the only valid basis for the assessment of the correctness (as distinct from accuracy) of a structure lies in the agreement for individual reflections. For reflections which are reasonably strong and thus reliably estimated, the observed and calculated structure factors should agree to within 40%, most of them being much better than this. In the present case the structure factors of the 55 strongest reflections agree, on the average, within 11% and only two show a discrepancy greater than 20%.

The final value of 15.6% for the R_1 residual is not as low as might be desired, chiefly because of the necessarily inadequate compensation for absorption and secondary extinction by the heavy bismuth atoms. In addition, isotropic temperature factors were forced on the refinement despite the thermal anisotropy noted above. As indicated by the positional standard deviations give in Table I, the stronger diffracting bismuth atoms have been located more reliably than the lighter chlorine atoms.

Discussion of Other Studies.—The composition $\text{BiCl}_{1.167}$ is notably different from the 1:1 ratio of chlorine to bismuth that was first estimated¹² and that has usually been assumed in the study of this system. Knowledge of atomic configurations in the solid compound also offers a valuable insight into the possible nature of species formed when bismuth metal or $\text{BiCl}_{1.167}$ is dissolved in liquid BiCl_3 . Of course, there is no compelling reason to expect that species present in dilute solutions will be of the complexity found in the reduced solid, and, in fact, recent data indicate quite clearly that at least two simpler units are present instead.^{6,7} However, the present findings do suggest caution should be exercised in the interpretation of solution data solely in terms of the simple-valent $(\text{BiCl})_n$ or Bi_n^{n+} . In addition, interpretations based primarily on the assumption of a well behaved activity

(43) L. Orgel, *J. Chem. Soc.*, 3815 (1959).

(44) A referee has kindly pointed out that the chlorine environment about Bi_{VI} may also be viewed as that of a distorted dodecahedron (triangular faces), the same as found for chlorine about the $d^{10}s^2$ ion Ga^+ in $\text{Ga}(\text{GaCl}_4)$ (G. Garton and H. M. Powell, *J. Inorg. Nucl. Chem.*, **4**, 84 (1957)). Thus although the shortest distances appear to define a (badly distorted) BiCl_5^{2-} ion quite well, inclusion of the three more distant neighbors (XI and $\text{XVI}(2)$) makes the arrangement appear less unusual. Following the description of Hoard and Silverton (*Inorg. Chem.*, **2**, 235 (1963)) the figure may be seen as the interlocking chlorine trapezoids XV-XI(2)-XX and XIX-XVI(2)-XIX (B-A(2)-B) with the 4 axis bisecting the two A-A edges. The Bi-Cl group of distances M-B (notation of H. and S.) show a range of 0.19 Å. and are uniformly shorter, as is generally the case, than M-A, which include one Bi-Cl "bond" and three longer "bridges." The distortion of the dodecahedron is not unusual considering the BiCl_5^{2-} ion forced into it. It should be noted that Bi_{VI} and Bi_{III} are only seven and six coordinate, respectively, on inclusion of next nearest neighbors.

(45) H. Lipson and W. Cochran, "The Determination of Crystal Structures," G. Bell and Sons, London, 1957, p. 147.

(39) R. Wyckoff, "Crystal Structures," Vol. I, Interscience Publishers, Inc., New York, N. Y., Chapter 4, p. 52d.

(40) M. Edstrand, M. Inge, and N. Ingri, *Acta Chem. Scand.*, **9**, 122 (1955).

(41) A. Byström and K. Wilhelmi, *Arkiv. Kemi*, **3**, 461 (1951).

(42) A. Byström, S. Bäcklund, and K. Wilhelmi, *ibid.*, **6**, 77 (1953).

for the BiCl_3 solvent in these dilute solutions²⁻⁵ are hazardous in view of the probable ionization of chloride from the product to form chlorobismuthate complexes such as are found in the solid, since other investigations have shown rather drastic nonideality of BiCl_3 in such cases.⁴⁶

It would appear highly probable that the species Bi_9^{5+} will become important in the more concentrated solutions of metal in BiCl_3 at the lower temperatures, although no direct evidence for this or any other entity has been published. However, in the study of the oxidation-reduction process in solution by means of concentration cells,⁶ the strange decrease in the Nernst n from 8 to about 2 over the range of about 8 to 22% Bi may be a result of increasing partition of the solute

(46) L. E. Topol, S. W. Mayer, and L. D. Ransom, *J. Phys. Chem.*, **64**, 862 (1960).

into species such as Bi_9^{5+} that are not in equilibrium with Bi^{3+} at the electrodes. The properties of the concentrated solutions, that is, the high viscosity, slow equilibration, and pronounced supercooling at the BiCl_3 ,¹⁶⁷ peritectic, are also indicative of the presence of large groups. A study of the X-ray scattering by these solutions may elucidate something of the nature of the solute.

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Structure of the Polyanions of the Transition Metals in Aqueous Solution: The Hexatantalate¹

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Alkaline solutions of tantalum(V) have been studied by spectrophotometric, e.m.f., and light scattering techniques. The position of the charge-transfer band at about 2000 Å. did not change as the total tantalum concentration was varied from 1.2 to $60 \times 10^{-4} M$ or as the hydroxide ion concentration was varied from 6 to $350 \times 10^{-4} M$. The e.m.f. measurements indicated that the compound $\text{K}_5\text{Ta}_6\text{O}_{19} \cdot 16\text{H}_2\text{O}$ dissolves in dilute KOH solutions without appreciable protonation. The experimental value for the number of protons bound per tantalum was constant in the pH range 10 to 13 and had a value of 0.12. These data indicate that the dissolved solute has essentially the same stoichiometry as the crystalline $\text{K}_5\text{Ta}_6\text{O}_{19}$ and that neither protonation-deprotonation reactions nor the concomitant condensation-depolymerization processes are occurring in the range $13 \geq \text{pH} \geq 10$. The light scattering investigation indicated that the solute species contains about 6 tantalum atoms, that this value was pH independent in the range studied, and that the species charge is reduced appreciably by the binding of counter-ions from the 1 M KCl medium used in the measurements. The scattering of potassium 12-tungstosilicate was also studied as a check on our procedure. On the basis of the results, it appears very likely that the tantalate solutions contain a monodisperse species and that this anionic species has the same structure as the $[\text{Ta}_6\text{O}_{19}]^{-8}$ anion found in tantalate crystals. An examination of the structure and bonding of this anion indicates that it should be somewhat resistant to protonation. Comparisons are made with structures for other poly-cations and anions which are found at high concentrations in monodisperse systems.

Introduction

Recently there has been some interest in the isopoly-anions formed in aqueous solutions of the transition metals, primarily with the group V-A and VI-A elements. Studies on solutions of vanadium(V) by e.m.f. techniques have indicated that a decavanadate $[\text{V}_{10}\text{O}_{28}]^{-6}$ exists in aqueous solutions together with the protonated species $[\text{HV}_{10}\text{O}_{28}]^{-5}$ and $[\text{H}_2\text{V}_{10}\text{O}_{28}]^{-4}$ in the range of hydrogen ion concentration 10^{-4} to 10^{-6}

M .^{2,3} Studies by other experimental methods including measurements of the visible absorption spectrum,⁴ ultracentrifugation,⁵ and cryoscopic studies^{6,7} have tended to confirm these results. E.m.f. studies have also indicated that the smaller poly- and mononuclear anions $[\text{V}_3\text{O}_9]^{-3}$, $[\text{HV}_2\text{O}_7]^{-2}$, and $[\text{HVO}_4]^{-2}$ also exist in solutions in the pH range 8 to 10.⁸ Unfortunately, because of the very complicated stereochemistry of

(2) F. J. C. Rossotti and H. S. Rossotti, *Acta Chem. Scand.*, **10**, 957 (1956).

(3) J. Meier and G. Schwarzenbach, *Chimia (Aarau)*, **12**, 328 (1958).

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(5) E. Priesler, Dissertation, Göttingen, 1958; O. Glensner and E. Priesler, *Naturwiss.*, **46**, 474 (1959).

(6) G. Parissakis and G. Schwarzenbach, *Helv. Chim. Acta*, **41**, 2042 (1958).

(7) K. F. Jahr and L. Schoepp, *Z. Naturforsch.*, **14b**, 461 (1959).

(8) N. Ingri and F. Brito, *Acta Chem. Scand.*, **13**, 1971 (1959).

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