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Homopolyatomic Ions of the Heavy Post-Transition Elements. The Preparation, Properties, and Bonding of $\text{Bi}_5(\text{AlCl}_4)_3$ and $\text{Bi}_4(\text{AlCl}_4)^1$

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The compounds $\text{Bi}_5(\text{AlCl}_4)_3$ and $\text{Bi}_4(\text{AlCl}_4)$ may be conveniently crystallized from liquid NaAlCl_4 following reduction of the composition $\text{BiCl}_3 \cdot \text{AlCl}_3$ by a stoichiometric or an excess quantity of bismuth metal, respectively. The relationships of the two compounds in the pseudo-binary system $\text{BiCl}_3 \cdot 3\text{AlCl}_3\text{-Bi}$ are also described, $\text{Bi}_5(\text{AlCl}_4)_3$ melting congruently at 326° and $\text{Bi}_4(\text{AlCl}_4)$, with irreversible decomposition, at about 398° . The intrusion of an intermediate, substantially amorphous phase above 249° causes the latter behavior and effectively prevents direct reduction to Bi_4AlCl_4 unless excess AlCl_3 is employed. Mull and reflectance spectra of the two diamagnetic compounds show a considerable resemblance to those reported for Bi_5^{3+} and Bi_8^{2+} in dilute melts, respectively, and it is concluded that these ions together with the relatively inert AlCl_4^- anion are present in the respective solids. LCAO-MO calculations including overlap for a variety of conceivable configurations lead to unambiguous predictions of trigonal-bipyramidal (D_{3h}) and square-antiprismatic (D_{3d}) arrangements for Bi_5^{3+} and Bi_8^{2+} , respectively. Relationships among these and the Bi_9^{5+} previously described are considered. The bonding in the polybismuth cations is found to show a considerable similarity to that within the polyborane cages, specifically $\text{B}_3\text{C}_2\text{H}_5$, $\text{B}_3\text{H}_8^{2-}$, and $\text{B}_9\text{H}_9^{2-}$, when it is recognized that only 6p is important for bonding with bismuth.

Introduction

A considerable chemistry for bismuth with oxidation states less than that of the familiar bismuth(III) appears to be realized in or *via* melt reactions. The first insight into these was obtained with solutions of the metal in BiCl_3 . Although early studies² appeared contradictory as to species, two of the most direct and thorough are in good accord that two reduced products are formed up to about 6 mole % dissolved metal. An emf study³ of concentration cells showed that Bi^+ , or $\text{Bi}^+ \cdot n\text{Bi}^{3+}$ generally, was present in dilute solution and that at higher concentrations this was converted to a second species $\text{Bi}_3^+ \cdot m\text{Bi}^{3+}$. A spectrophotometric study⁴ of the same system confirmed the presence of just two species in this composition region and furthermore demonstrated that the stoichiometric relationship between them was consistent with the products deduced in the emf investigation. Very little is known about species in the more concentrated solution of metal in BiCl_3 , although eventually a rather complex solid phase is obtained. This was first thought to be the stoichiometrically simple BiCl ,⁵ suggesting species such as Bi_n^{n+} might be formed in dilute solution as well. However, a structural study⁶ showed that the compound contained the unusual ion Bi_9^{5+} , with approximately D_{3h} symmetry, and that this together with two types of chlorobismuth(III) anions resulted in the stoichiometry $\text{Bi}_{12}\text{Cl}_{14}$. A molecular orbital treatment of the bonding in the cation has subsequently been provided.⁷

At about the time "BiCl" was first studied, the sub-

stantial effect of "acid-stabilization" on cadmium(I) compounds had been realized, wherein the replacement of halide by the AlX_4^- anion was found to yield the stable solids $\text{Cd}_2(\text{AlX}_4)_2$.⁸ A few experiments on "BiCl" suggested that "BiAlCl₄" could be obtained likewise.⁹ Subsequently others have reported a radial distribution analysis of the X-ray scattering by liquid and powdered samples of this composition¹⁰ as well as its powder pattern data and the space group of a single crystal.¹¹ All were found to be consistent with the presence of triangular bismuth units ($d_{\text{Bi-Bi}} = 3.04 \text{ \AA}$) which were then formulated as Bi_3^{3+} ions in accordance with the reported stoichiometry.

Actually such a Bi_3^{3+} unit does not have a reasonable bonding scheme for a diamagnetic product since the a_1' , a_2'' , and e' MO's are all strongly bonding,⁷ thus accommodating two more electrons than indicated. The present study was prompted by the recognition that the obvious Bi_3^+ would also be compatible with the above X-ray results as well as with solution studies in BiCl_3 .¹² Notwithstanding, the trimeric species does not appear to exist as a solid tetrachloroaluminate, but, as already briefly noted,¹³ two solid phases with the compositions $\text{Bi}_5(\text{AlCl}_4)_3$ and Bi_4AlCl_4 are instead formed. These solids will also be seen to show a considerable spectral resemblance to the ions Bi_5^{3+} and Bi_8^{2+} recently identified in dilute solution in NaCl-AlCl_3 and KCl-ZnCl_2 solvents by Bjerrum, *et al.*^{14,15}

(8) J. D. Corbett, W. J. Burkhard, and L. F. Druding, *J. Am. Chem. Soc.*, **83**, 76 (1961).

(9) J. D. Corbett and R. K. McMullan, *ibid.*, **78**, 2906 (1956).

(10) H. A. Levy, M. A. Bredig, M. D. Danford, and P. A. Agron, *J. Phys. Chem.*, **64**, 1959 (1960).

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

(12) J. D. Corbett, F. A. Albers, and R. A. Sallach, *Inorg. Chim. Acta*, in press.

(13) J. D. Corbett, *Inorg. Nucl. Chem. Letters*, **3**, 173 (1967).

(14) N. J. Bjerrum, C. R. Boston, G. P. Smith, and H. L. Davis, *ibid.*, **1**, 141 (1965); N. J. Bjerrum, C. R. Boston, and G. P. Smith, *Inorg. Chem.*, **6**, 1162 (1967).

(15) N. J. Bjerrum and G. P. Smith, *Inorg. Nucl. Chem. Letters*, **3**, 165 (1967); *Inorg. Chem.*, **6**, 1908 (1967).

(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Presented at the 153rd National Meeting of The American Chemical Society, Miami, Fla., April 10-14, 1967.

(2) Reviewed by J. D. Corbett in "Molten Salts," B. R. Sundheim, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1964, pp 382-385.

(3) L. E. Topol, S. J. Yosim, and R. A. Osteryoung, *J. Phys. Chem.*, **65**, 1511 (1961).

(4) C. R. Boston, G. P. Smith, and L. C. Howick, *ibid.*, **67**, 1849 (1963).

(5) J. D. Corbett, *J. Am. Chem. Soc.*, **80**, 4757 (1958).

(6) A. Hershafit and J. D. Corbett, *Inorg. Chem.*, **2**, 979 (1963).

(7) J. D. Corbett and R. E. Rundle, *ibid.*, **3**, 1408 (1964).

The predictions and correlations provided by MO calculations on these species will also be considered.

Experimental Section

Because of the sensitivity of the compounds and their component salts to moisture, they were handled by the usual vacuum-line and drybox techniques and were stored and allowed to react in sealed containers.

Materials.—The bismuth employed was an American Smelting and Refining grade reported to be 99.999%. Spectrographic analysis revealed Cu and Ag at the "trace" level, Pb, Fe, and Si as "faint trace," with B, Al, Sb, Sn, and Zn undetected. Some early experiments were also carried out with a "reactor grade" material which was comparable except that the above iron and silver levels were reversed. The metal was broken up, vacuum fused to allow physical removal or decomposition of such as oxide and carbon impurities, and then rebroken into small pieces. Aluminum wire used as a reductant was stated to be 99.99% (A. D. MacKay).

Bismuth trichloride was prepared from the elements either by passing chlorine over the heated metal or in a sealed apparatus with the Cl_2 at -80 or -33° and the metal at up to 750° . Even under these rather drastic conditions the reaction is relatively slow. With care the vacuum-sublimed product obtained was white, unlike the carbon-contaminated material obtained from commercial BiCl_3 . The AlCl_3 used was usually the result of two sublimations of the commercial material. The solvent NaAlCl_4 was prepared by fusion of the component salts (with a 5% excess of AlCl_3), digestion in fused silica at 400° for 1 or 2 days, and then filtration through a coarse-grade Vycor frit to remove traces of carbon. The AlCl_3 used in this case was prepared from metal and high-purity HCl (Precision Gas Products).

Synthesis of Reduced Phases.—The starting material for reduction was the composition $\text{BiCl}_3 \cdot 3\text{AlCl}_3$ or " $\text{Bi}(\text{AlCl}_4)_3$ " which melts incongruently at 155 – 160° to yield solid AlCl_3 . Because of the incongruent melting property and low apparent stability of the compound formed in the BiCl_3 – AlCl_3 system, it was difficult to assure a uniform composition throughout such a sample. Consequently a partial reduction was usually effected at the same time, as this greatly reduced the tendency of the mixture to lose AlCl_3 (and to a lesser extent, BiCl_3) on cooling. Stock solutions containing 50–86.2 (saturation) mole % Bi in $\text{BiCl}_3 \cdot 3\text{AlCl}_3$ were prepared directly, adding 4–10 g of BiCl_3 and the appropriate amount of AlCl_3 , each weighed to 10 mg in the drybox, to previously weighed metal in a fused-silica container which was then evacuated and sealed off. Reaction of the bismuth metal takes from about 2 hr at 410° for saturation to 36 hr at lower temperatures necessary for the safe containment of less reduced melts. A few compositions were also prepared by cautious execution in a sealed tube of the stoichiometric reaction $4\text{BiCl}_3 + 3\text{Al} \rightarrow \text{BiCl}_3 + 3\text{AlCl}_3 + 3\text{Bi}$, the products of which then react further to give the 75% solution or greater if more metal is initially added, but this reaction was abandoned as too wasteful of the relatively dear BiCl_3 .

The reduced melts were found to attack Pyrex glass slowly above 300° , producing a lower melting phase in which Si and B were detected by emission spectroscopy. For this reason all reactions were carried out in sealed, fused-silica (not Vycor) containers. A very small amount of attack, evidenced by wetting of the walls, is still found on prolonged heating above about 350° . Molybdenum is a thoroughly satisfactory though obvious less convenient alternate.

Synthesis in and crystallization of the new phases from NaAlCl_4 solvent were accomplished in a fused-silica container constructed of two short, collinear lengths of 12- and 25-mm tubing which was closed at the smaller end and connected through 8-mm tubing to a ball joint at the large end. A 1×12 mm diameter disk of fused silica with several short 1-mm notches cut into one side was sealed into the apparatus near the midpoint to aid separation of the crystals from solvent. (The melt would not flow through a coarse-grade Vycor frit.) Lateral vanes of silica were also used

in the large end to separate different batches of product. Excess bismuth necessary for production of the lowest phase was first fused to assist in its later removal. In this case amounts of the order of 10 g of NaAlCl_4 and 6–7 g of the saturated (86%) solution of Bi in $\text{BiCl}_3 \cdot 3\text{AlCl}_3$ (or equivalent) were added in the drybox, and the apparatus was evacuated and sealed off. The container held by insulation in a glass jacket was positioned in a long tube furnace with the larger end slightly lower. After equilibration at 200 – 220° for several hours with agitation, the crystals were grown from the saturation point down to about 160° by lowering the temperature 0.5 to 2° hr^{-1} , and the process was terminated by tipping the furnace so as to pour the solvent through the barrier into the smaller end. Continuous rather than off-on temperature control is nearly essential for good crystals. The Bi_4AlCl_4 separates congruently from the solution in equilibrium with metal and has a moderate solubility therein, about 7.2 mole % Bi_4AlCl_4 at 194° and 3.2% at 160° .

Production of the intermediate phase $\text{Bi}_5(\text{AlCl}_4)_3$ is accomplished similarly. The solubility is somewhat lower, *e.g.*, about 0.6 mole % at 155° , and apparently has a larger temperature coefficient so that a smaller amount of solvent and a somewhat larger proportion of solute can be used for the same yield. The amount of metal added was sufficient to give the equivalent of a 70–78% solution in $\text{BiCl}_3 \cdot 3\text{AlCl}_3$ (80% is stoichiometric for $\text{Bi}_5(\text{AlCl}_4)_3$) so as to avoid possible contamination with the lowest phase. The intermediate phase has also been obtained from KAlCl_4 over the range 270 – 250° . The relative solubilities of the two reduced phases in this solvent appear reversed relative to NaAlCl_4 .

Thermal Analysis.—The fused-silica containers, of 30×15 mm diameter, had a closed, 5-mm length of 2-mm tubing sealed inwardly through the bottom for a thermocouple well. These were filled and sealed as before and jacketed in a second tube together with a differential couple. Fairly slow heating and cooling rates were necessary with the compact solids to avoid fracture of the container at the major transformations at 313 , 249 , and 149° ; even so, the majority of the samples were ultimately lost in this way.

Spectra.—Diffuse-reflectance data *vs.* NaAlCl_4 were obtained for samples diluted with NaAlCl_4 using a Beckman DU spectrophotometer and No. 2580 reflectance attachment. Mull spectra were run in Nujol on a Cary Model 14 instrument.

X-Ray Data.—Powder diffraction data were secured with samples sealed in 0.15–0.25 mm i.d. Pyrex capillaries in a Debye-Scherrer camera of 11.46-cm radius using Ni-filtered $\text{Cu K}\alpha$ radiation. The spacings given are uncorrected although absorption doubling was sometimes observed at low angles. Intensities were estimated visually based on 10 for the strongest diffraction.

Data reported¹¹ for " BiAlCl_4 " agree well with those obtained here for $\text{Bi}_5(\text{AlCl}_4)_3$ except that the diffraction reported at 5.09 \AA was not observed. Additional lines (in Å) suitable for identification, with intensities in parentheses, are: 5.6 (2), 2.30 (2), 2.09 (3), 1.989 br (6), 1.852 (2), 1.829 (2), 1.706 (3), 1.638 (3), and 1.460 (4). The principal powder diffractions of $\text{Bi}_4(\text{AlCl}_4)$ are: 8.75 (6), 7.25 (10), 3.88 (5), 3.55 (3), 3.41 (4), 3.25 (4), 3.10 (6), 2.98 (3), 2.84 (6), 2.54 (8), 2.172 (3), 2.110 (5), 2.002 (3), 1.958 br (6), 1.455 (3), and 1.378 br (5).

Analyses.—The lower phases lose a small amount of HCl when added directly to water although the hydrolysis is still relatively mild for compounds containing AlCl_3 . Analytic samples were sealed under vacuum in short lengths of 8-mm tubing, briefly fused to reduce the surface area and reactivity, weighed, quickly dropped into water after the tubing had been cracked, and then taken into solution with HNO_3 .

Bismuth was determined as before⁶ by EDTA titration with thiourea indicator. Since aluminum and, to a lesser extent, chloride interfere slightly with this determination, aliquots were heated with concentrated perchloric acid until fuming, then diluted, and the bismuth was extracted into hexane with isooctyl thioglycolate,¹⁶

(16) J. S. Fritz, R. K. Gillette, and H. E. Mishmash, *Anal. Chem.*, **38**, 1896 (1966).

back-extracted into 6 M HCl, and then evaporated again with HClO₄ before titration. The unextracted aluminum was determined by back-titration with standard zinc solution using NAS indicator¹⁷ after the solution had been heated near the boiling point at pH 2 with excess EDTA. Chloride was determined gravimetrically from 50% acetone solution.

The analysis of samples crystallized from NaAlCl₄ requires correction for the saturated solvent physically retained by them. This amounts to 8–10 wt % for Bi₅(AlCl₄)₃ but is a 30–35% correction for Bi₄AlCl₄, presumably because of its sheet-like crystal habit. Accordingly, a relatively accurate sodium determination for both the crystals and the filtrate is required, particularly with the lowest phase. Originally sodium was determined by flame photometry; however, the high nitric acid content of the solutions containing bismuth seriously affected the accuracy. That this rather than gross contamination was the cause of the erratic results and poor recoveries at this point was indicated by the relative invariance of the Cl/Al ratios from 4. The photometry values used (for some of the Bi₅(AlCl₄)₃ analyses where the correction is less critical) were subsequently corrected to $\pm 10\%$ with standards containing comparable amounts of acid. The best sodium results were obtained by atomic absorption utilizing the less intense 3092-Å line; the precision and accuracy were both of the order of 1%.

Correction of the crystal analysis for solvent retained is based on the sodium content of each portion, according to

$$M_i(\text{cor}) = M_i(\text{crystals}) - M_i(\text{filtrate})[M_{\text{Na}}(\text{crystals})/M_{\text{Na}}(\text{filtrate})]$$

where M_i is the moles of element i or the sample weight. For example, the following millimolar contents of the crystals (3.7142 g, 99.64% recovery) and filtrate (1.87825 g, 99.61%) give the percentages shown below for Bi₄AlCl₄ (2.4045 g net). The relatively

	Na	Bi	Al	Cl
Crystals	4.768	11.05	7.469	30.462
Filtrate	6.838	2.156	7.490	29.925
Cor	0	9.550	2.247	9.596
Wt %		83.0	2.52	14.15

large correction required here emphasizes any deficiency in total recovery as well as any errors in the sodium analysis. In the above example an uncertainty in the sodium content of the crude crystals of $\pm 1.5\%$ (the range observed) alters the final bismuth and chlorine contents by 0.47 and -0.33% , respectively. The recoveries for all crystal and filtrate samples were in the range of 99.6–100.3%.

Molecular Orbital Calculations.—The LCAO–MO treatments were carried out the same as before.⁷ Symmetry orbitals were deduced according to standard group theory, and overlap was evaluated using the previous integrals⁷ and an improved scaling parameter $\rho (= \xi d/a_0)$ of 17.76. Second and, where important, third nearest neighbors were included, with a cutoff at about 3% of the largest overlap. Generally all Bi–Bi distances were set at the 3.04-Å distance indicated for Bi₃⁸⁺¹⁰ (see Results section), though this is no case critical. Overlap was retained in one-electron, Hückel-type calculations, where H_{ij} terms were again set equal to $S_{ij}\beta_0$, and the energy parameter x was evaluated such that $E = \alpha + x(\beta_0 - \alpha)$, where α and β_0 are unevaluated constants.

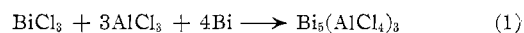
Results

Although the reduced bismuth tetrachloroaluminates were first recognized in studies in the pseudo-binary system BiCl₃·3AlCl₃–Bi, their identification therein is complicated by two factors. First is the usual problem of deducing the composition of an intermediate such as Bi₅(AlCl₄)₃ once formed by thermal analysis and the interpolation of X-ray data. Second, a particular problem in this system is the very slow attain-

(17) J. S. Fritz, J. E. Abbink, and M. A. Payne, *Anal. Chem.*, **33**, 1381 (1961).

ment of equilibrium which makes thermal analysis of limited value and which essentially prevents complete reduction to the lowest phase. As will be seen, this latter problem may be overcome by reduction of compositions lying in the general ternary system. However, these results are better presented after the identity of the new phases has been established. Fortunately both of these may also be obtained in a more classical manner by synthesis in and crystallization from a foreign solvent. Although the usual molecular solvents are quite generally too basic and cause disproportionation of products of this sort, melt solvents such as NaAlCl₄ and KAlCl₄ are ideal for this purpose since the aim was to prepare salts of the relatively inert AlCl₄⁻ ion. The former was chosen for most of the work because of its lower melting point, 151 vs. 256°.¹⁸

Crystallization from NaAlCl₄.—As described in the Experimental Section, crystals of the intermediate phases are readily obtained on cooling of an NaAlCl₄ solution of BiCl₃·3AlCl₃ plus slightly less than the theoretical amount of metal, the product being formed according to the reaction



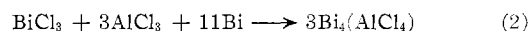
The solution and the crystals are dark red-brown, lighter when ground and peach-colored when highly diluted with NaAlCl₄. The analytical data for five different preparations after correction for solvent retained are given in Table I. The phase has also been obtained from KAlCl₄ solvent.

TABLE I
ANALYTICAL DATA FOR Bi₅(AlCl₄)₃
CRYSTALLIZED FROM NaAlCl₄

Na method ^a	Bi	Al	Cl	Σ
FP	67.52	5.30	27.36	100.2
FP	67.50	5.11	27.06	99.7
AA	67.01	5.21	27.59	99.8
FP	67.06	...	27.33	
AA	67.74	5.16	27.34	100.24
Theory	67.36	5.22	27.42	100.00

^a FP, flame photometry; AA, atomic absorption (see Experimental Section).

A solution of BiCl₃·3AlCl₃ in NaAlCl₄ may be quantitatively reduced to the composition Bi₄AlCl₄ by excess metal at about 200°, according to



Two determinations of the ratio of metal reacted to BiCl₃ present gave values of 10.6 and 11.5, the precision being limited by an uncertainty of about 0.5% in the amount of the starting salts weighed in the drybox. Bjerrum and Smith¹⁵ have likewise determined the metal coefficient with greater precision in dilute solutions in NaAlCl₄–AlCl₃ compositions. Cooling the solutions in NaAlCl₄ results in the separation of black, shale-like sheets with the composition Bi₄AlCl₄. The analytical data for four preparations from NaAlCl₄ are

(18) W. Fischer and A.-L. Simon, *Z. Anorg. Allgem. Chem.*, **306**, 1 (1960).

given in Table II; the source of the last two entries will be described later. Because of the relatively large correction for the saturated solvent retained by the crystals, the bismuth, aluminum, and chlorine values may be uncertain by about 0.3, 0.1, and 0.2%, respectively. The solubility of $\text{Bi}_2(\text{AlCl}_4)$ in a solvent of the composition NaAl_2Cl_7 is very much larger, owing perhaps to the low concentration of the common ion AlCl_4^- .

TABLE II
ANALYTICAL DATA FOR Bi_4AlCl_4

Source	Bi	Al	Cl	Σ
NaAlCl_4	83.55	2.82	13.8	100.2
NaAlCl_4	83.0	2.71	13.8	99.5
NaAlCl_4	83.0	2.52	14.15	99.7
NaAlCl_4	83.7	2.70	14.06	100.4
$\text{BiCl}_3 \cdot 3.6\text{AlCl}_3$	83.17	...	14.45	
$\text{BiCl}_3 \cdot 4\text{AlCl}_3$	83.19	2.69	14.16	100.04
Theory	83.20	2.69	14.11	100.00

The System $\text{BiCl}_3 \cdot 3\text{AlCl}_3$ -Bi.—The choice of the starting composition $\text{BiCl}_3 \cdot 3\text{AlCl}_3$ is dictated by the desire to convert all chloride to tetrachloroaluminate ions, at least on formation of the larger and less acidic, reduced cations. Whether the intermediate compound formed between BiCl_3 and AlCl_3 has the 1:3 composition or a tetrachloroaluminate formulation has not been investigated, but the X-ray data suggest that the compound either contains less AlCl_3 than this or loses this component easily on normal cooling. A 1:1 phase has been reported in the bromide system.¹⁹

The phase diagram for the metal-rich portion of the $\text{BiCl}_3 \cdot 3\text{AlCl}_3$ -Bi pseudo-binary section is illustrated in Figure 1. Supercooling is a general problem in this system, so that the equilibrium temperatures of affected liquidus and eutectic transitions often can be located well only by inspection or, better, by a bracketing procedure, carrying out repeated equilibrations at increasing temperatures followed by thermal analysis to detect the supercooled effect, if any. All points shown in the figure are best estimates of the equilibrium values.

The mixture $\text{BiCl}_3 \cdot 3\text{AlCl}_3$ melts at 160° to give solid AlCl_3 plus liquid. The composition of first eutectic obtained on reduction also contains less than 3AlCl_3 per BiCl_3 and therefore lies outside of the pseudo-binary section. This means that the primary separation of AlCl_3 from the solutions persists on reduction past the first eutectic and in the region shown gives rise to an additional effect at 170° above the eutectic at 149° . The liquidus curvature found between 50 and 80% metal probably results from substantial non-ideality, as is commonly found between an "ionic" salt and a fairly molecular component. Annealed or quenched samples containing 50–70% metal gave no X-ray evidence for the formation of any other phase in this region. In retrospect, the specious " BiAlCl_4 " composition reported earlier⁹ is close to the liquidus composition at the temperature used. Finally, the

(19) J. Kendall, E. D. Crittenden, and H. K. Miller, *J. Am. Chem. Soc.*, **45**, 963 (1923); W. Isbekow, *Z. Anorg. Allgem. Chem.*, **143**, 80 (1925).

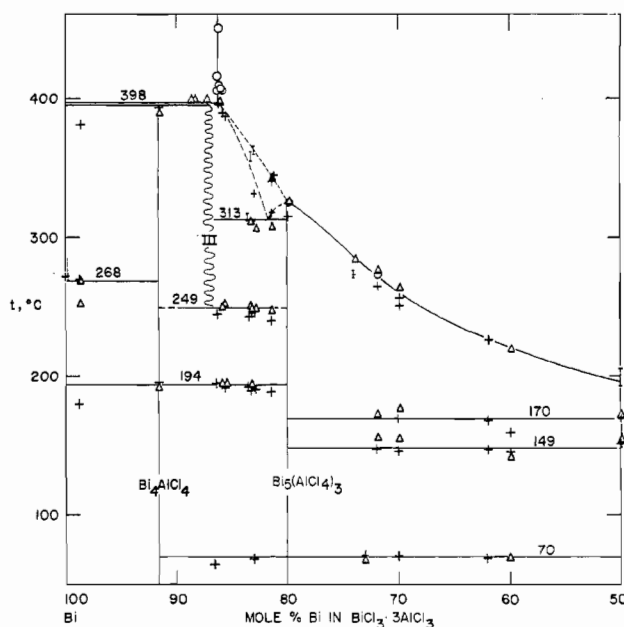


Figure 1.—The phase diagram for the metal-rich portion of the system $\text{BiCl}_3 \cdot 3\text{AlCl}_3$ -Bi: +, thermal analysis on cooling; Δ , on heating; O, equilibration followed by analysis.

thermally small effects at 70° shown in Figure 1 as well as 194° for compositions more reduced than $\text{Bi}_5(\text{AlCl}_4)_3$ appear to result from polymorphic transitions in the two new phases; no changes could be detected in the powder patterns of samples quenched from above these temperatures.

The phase $\text{Bi}_5(\text{AlCl}_4)_3$ melts evidently congruently at $326 \pm 1^\circ$, and hence may be prepared directly in this system. Solidification usually involves up to 50° supercooling. The region between $\text{Bi}_5(\text{AlCl}_4)_3$ and $\text{Bi}_4(\text{AlCl}_4)$ and 250 – 400° is complicated by an unusual, intermediate phase (marked III), and it is this that is apparently responsible for the inability to form the lowest phase by direct reduction. This region is best considered in order, starting at the top.

The amount of metal taken up by the $\text{BiCl}_3 \cdot 3\text{AlCl}_3$ composition on equilibration with Bi(l) is remarkably large, 86.2 mole % (64.6 wt %), at 410 – 450° , and an intermediate phase (III) separates from this at about 398° . The properties of the latter are such as to make its substantial characterization extremely difficult, as attested by the following observations. The dashed "liquidus" shown between 398 and 326° , the melting point of $\text{Bi}_5(\text{AlCl}_4)_3$, represents a transition at which the effect of shaking on the temperature record during cooling also disappears for compositions containing more than about 82.5% Bi, but which at 81–82% is reasonably normal for a liquidus point. An apparent eutectic is also found at about $313 \pm 4^\circ$ up to at least 84% metal, a substantial transition which supercools 35 – 40° and therefore is located well only by bracketing. A large thermal arrest is also found in this region at 249° , supercooled up to 70° but rather sharp on heating and increasing in magnitude on reduction. Samples containing 83–87.5% Bi which have been rapidly quenched from either 310 or 365 to -80° are black, very

hard, and stable at room temperature and yield poor powder patterns showing only a few diffuse, low-angle lines of the title phases. On the other hand such compositions annealed down slowly, cooled at the normal rate for thermal analysis, or quenched from 240° or lower are brown, friable, and give normal X-ray data for the appropriate mixture. Pure Bi_4AlCl_4 quenched from 346° is also normal.

The presence of another phase between $\text{Bi}_5(\text{AlCl}_4)_3$ and Bi_4AlCl_4 implied by the above is very effective in frustrating the anticipated reaction between melt and excess metal below 398° to produce the lowest phase. Equilibration of small salt samples with large excesses of metal at 370 or 390° for up to 15 days gives products containing only up to 87–88 mole % metal or having Bi/AlCl₄ ratios of 2.6–2.8. Such samples were visually observed to melt over a range of only 5–8°, also contrary to what would be expected if Bi_4AlCl_4 were the direct product of reduction.

The above findings strongly suggest, in fact probably require, that another phase is interposed between the two known phases above 249°. Its character and relationships in the diagram are still relatively abstruse, largely because of very appreciable kinetic difficulties associated with heterogeneous equilibria in this region together with a substantially useless X-ray pattern for the intermediate. Although many of the properties suggest that a glass-forming region is involved, this is not reasonable in view of the reversibility of the transition between III and the other phases at 249°, which must then be taken to be the peritectoid disproportionation of phase III on cooling. It is evident that an additional solidus (or liquidus) line between 313 and 398°, such as the one shown dashed, has not been observed, although this is not surprising in view of the kinetic problems. The constancy of the 313 and 249° arrest over the range studied also suggests the absence of solid solutions in $\text{Bi}_5(\text{AlCl}_4)_3$; the region between III and Bi_4AlCl_4 cannot be investigated directly. A substantial homogeneity range for phase III (below 398°) would best account for the phase and X-ray data, presumably with a highly disordered structure but not quite the character of a glass insofar as it is reversibly related to better behaved crystalline phases. Phase III may also lie somewhat outside the section considered. Although this part of the system is not completely understood, further attempts to characterize it by the above and related methods seem relatively profitless.

Experiments in which the proportion of BiCl_3 and AlCl_3 in the mixture reduced was varied from 1:3 in order to confirm that AlCl_4^- was the anion in the phase also gave a solution to the dilemma of direct reduction to Bi_4AlCl_4 . First, the 398° melting point was found to be noticeably depressed with samples containing a 10% excess or deficiency in the amount of AlCl_3 used. At the same time it was observed that the apparent limit of reduction increased appreciably in the presence of excess AlCl_3 and that the products obtained were noticeably more crystalline. The use of 20 or 33% excess AlCl_3 was found to allow complete reduction to

$\text{Bi}_4(\text{AlCl}_4)$ at 270–320°, the weight loss in metal corresponding to an uptake of 91.7 and 91.95 mole % bismuth (91.67% theory), or coefficients of 11.06 and 11.4 for the metal in eq 2, respectively. The last two entries in Table II are the analyses of such products after the excess AlCl_3 had been removed under vacuum at $\leq 195^\circ$. The role of AlCl_3 here can be viewed as that of a flux, although it may be that the formation of phase III is simply by-passed by operation in the general ternary; the fluidity of these samples at the equilibration temperature is much greater than with the AlCl_4^- composition.

The thermal analysis data shown in Figure 1 for $\text{Bi}_4(\text{AlCl}_4)$ were obtained with samples prepared in this manner. As far as can be determined, the phase melts within a few degrees of that ascribed to III, as shown; the two can have the same decomposition point if III lies outside the binary section considered. The transition at 249° and the metal fusion at 268° are observed only *after* such a Bi_4AlCl_4 sample has been melted, producing the substantially irreversible disproportionation to metal and the 86% solution. It is interesting that the metal in such a mixture supercools by about 60° and its solidification appears to "set off" the decomposition of III. The depression of the equilibrium fusion point of the metal is about 3°, compared to 3.7° in the BiCl_3 -Bi system.²⁰

Spectra of the Reduced Phases.—The spectra of the solids $\text{Bi}_5(\text{AlCl}_4)_3$ and $\text{Bi}_4(\text{AlCl}_4)$ are particularly informative when compared with those of the ions Bi_5^{3+} and Bi_5^{2+} recently obtained by Bjerrum, *et al.*,^{14,15} in the NaAlCl_4 - AlCl_3 eutectic melt. The principal change in their solvent from the AlCl_4^- environment present here is thought to be the conversion of about 70% of the anions to Al_2Cl_7^- , thereby buffering the melt at an even lower pCl.

The diffuse-reflectance and mull spectra of solid $\text{Bi}_5(\text{AlCl}_4)_3$ are compared with the solution spectrum¹⁴ of Bi_5^{3+} in Figure 2. Of course, intensity comparisons are not meaningful because of the undefined, variable effective path length with the solid; to some extent this is a blessing as the weaker absorptions are enhanced by a greater penetration at these wavelengths. A generally good agreement as to the energies of absorption is found within the range of small shifts that often occur on transition to the solid state and with these methods. The two weak, low-energy bands in the melt appear shifted to slightly higher energy but are not resolved. In the melt data two bands seem to be present on the low-energy side of the prominent 390-m μ feature, and these appear resolved with the solids near 455 and 540 m μ . The melt spectrum below about 375 m μ is inaccessible because of BiCl_3 absorption; in addition, the reflectance data below 325–350 m μ are probably not very meaningful because of low sensitivity and poor reproducibility.

Although the spectra of black solids are often rather uninformative, that of $\text{Bi}_4(\text{AlCl}_4)$ also bears a consider-

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

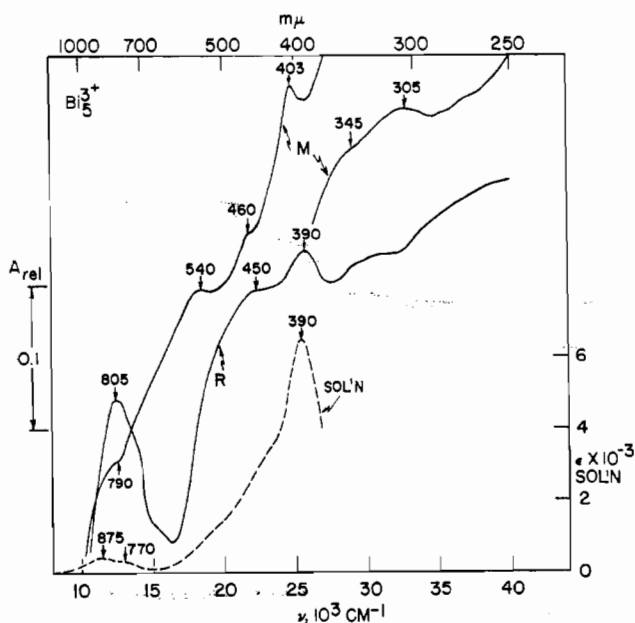


Figure 2.—The reflectance (R) and mull (M) spectra of $\text{Bi}_5(\text{AlCl}_4)_3$ and the solution spectrum of Bi_5^{3+} (dashed curve¹⁴).

able resemblance to the spectrum of Bi_5^{2+} recently obtained in dilute melts,¹⁵ as illustrated in Figure 3. At first glance the reflectance spectrum (R) appears relatively featureless; however, six different samples exhibited small but highly reproducible inflections at 335–345, 440–450, and 525–540 $\text{m}\mu$, in reasonable agreement with the melt data. Fortunately the mull spectrum (M) shows these somewhat better resolved. The source of the lower energy absorption in the solid (675 $\text{m}\mu$ in reflectance, 620 and 725 $\text{m}\mu$ in mull) is not clear, although something like this may actually be unresolved in the rather long, low-energy tail in the melt spectrum. Finally, the peak observed at 390 $\text{m}\mu$ in reflectance is believed to result from a slight decomposition to Bi_5^{3+} caused by adventitious traces of impurities since this absorption was not observed with most samples and either grew in or increased over a relatively long period of time. In fact, both the mull and reflectance samples of $\text{Bi}_4(\text{AlCl}_4)$ show an orange-brown and then a black band growing inwardly from the edges after standing, suggesting decomposition proceeds first to $\text{Bi}_3(\text{AlCl}_4)_3$ and then to (visible) bismuth metal.

Bonding and Configurations of the Reduced Cations.—Both $\text{Bi}_5(\text{AlCl}_4)_3$ and Bi_4AlCl_4 are definitely diamagnetic at room temperature. Though this contributes little for the former, it suggests some degree of polymerization to $\text{Bi}_{8n}(\text{AlCl}_4)_{2n}$ for the latter since the simple Bi_4^+ ion contains an odd number of electrons. The simplest case, $n = 1$, is suggested by the foregoing spectral correspondence with Bi_5^{2+} in the melt, and this will be assumed hereafter. Resistance measurements on pure powdered Bi_4AlCl_4 as well as on crystals grown from NaAlCl_4 give no indication that the material should be considered as other than a typical, insulating salt.

A fairly obvious question arises at this point as to whether it should be possible to predict the configura-

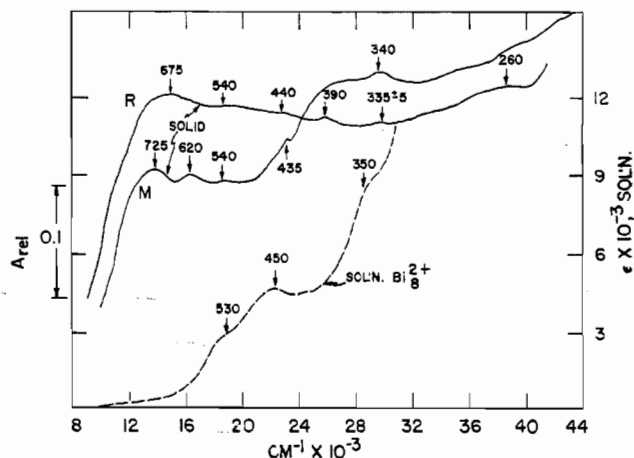


Figure 3.—The reflectance (R) and mull (M) spectra of $\text{Bi}_4(\text{AlCl}_4)$ and the solution spectrum of Bi_5^{2+} (dashed curve¹⁵).

tions of the electron-deficient ions Bi_5^{3+} and Bi_5^{2+} on the basis of simple bonding considerations. For the present purposes it will also be assumed that the simple bismuth cations are involved, as opposed to groups wherein the anions directly and significantly participate in the bonding of bismuth. *A priori* this is what would be expected for AlCl_4^- , and the spectra seem to support this notion in the absence of a discernible effect when the solvent is changed from NaCl-AlCl_3 (37:63) (or $\text{NaAlCl}_4\text{-NaAl}_2\text{Cl}_7$, 30:70) to KCl-ZnCl_2 (28:72) for Bi_5^{3+} and from the first to NaCl-AlCl_3 (50.4:49.6) (or $\text{NaAlCl}_4\text{-NaCl}$, 98.4:1.6) for Bi_5^{2+} .^{14,15,21} Further, there seems to be little change from the first solvent to the solids containing only AlCl_4^- . The only other observation directly bearing on the inertness of AlCl_4^- is that it is not measurably perturbed from T_d symmetry in a melt with Cd_2^{2+} and Cd^{2+} cations according to the Raman spectrum.²²

As noted earlier,⁷ MO bonding arguments for such homonuclear species have a particular simplicity as well as a probably greater credibility because of the formal identity of the atoms involved, even when these are not all equivalent by symmetry and hence in their bonding. In addition, the very substantial 6s–6p and 6p–6d separations⁷ for bismuth justify a still simpler, isoorbital treatment in terms of only the 6p basis set, with 6s² taken as an inert core. The procedure followed in this inquiry has been to make calculations for all polyhedra which appear feasible for five and for eight atoms to see which will accommodate the indicated 12 and 22 electrons, respectively, in a closed-shell configuration. Although no claim can be made that all arrangements have been surveyed, in each case the calculations give an unambiguous conclusion for the models considered.

The most regular configuration expected for five atoms, the regular trigonal bipyramid (D_{3h}), gives a satisfactory bonding scheme for Bi_5^{3+} . The results are shown in Figure 4 for a range of overlap about the estimated value. The indicated 12 electrons are ac-

(21) G. P. Smith, private communication.

(22) J. D. Corbett, *Inorg. Chem.*, **1**, 700 (1962).

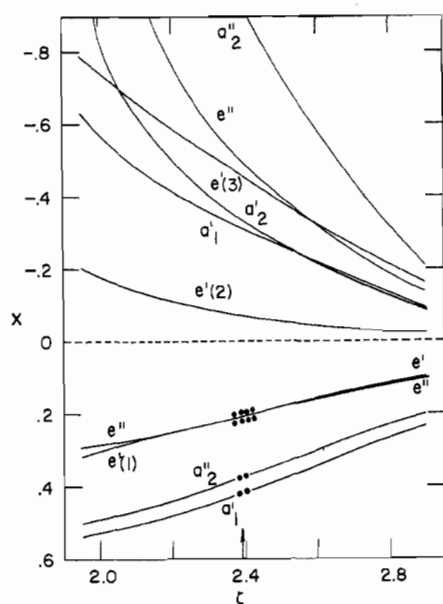


Figure 4.—Energy parameters x calculated for trigonal-bipyramidal Bi_3^{3+} as a function of overlap scaling; $E = \alpha + x(\beta_0 - \alpha)$.

commodated in the bonding a_1' , a_2'' , e' , and e'' MO's, with the gap between the highest bonding (e' , e'') and the lowest antibonding (e') levels comparable to that obtained for Bi_3^{5+} .⁷ This separation is probably a minimum and would be expected to be increased by small distortions; a like change would be expected to result from a more nearly exact treatment of the poly-electronic problem with perturbations such as configuration interaction since the levels in question are part of the same irreducible representation (e') and have the smallest energy separation of such by a factor of 2.5.

On the other hand, the regular square pyramid (C_{4v}) does not give a satisfactory solution for the present problem since 14 electrons would be necessary to fill the bonding orbitals. In decreasing energy these are ordered a_1 , e , b_2 , a_1 , and e^{23} with no seeming ambiguity that would accommodate only the indicated 12; the total binding energy is also less with this arrangement. It would appear that substantial distortions of either model to lower symmetry (e.g., to C_{2v}) would be required to obviate the above conclusions. The regular pentagon (D_{5h}) is also unsuitable, the slightly bonding e_1'' ($x = 0.03$) above bonding a_1' , e_2' , e_1' , and a_2'' indicating either a 10- or a 14-electron solution. The centered, tetrahedral model is certainly unsuitable, with only t_2 really bonding because of the large (~ 5 -Å) separation of the outer atoms.

The trigonal-bipyramidal configuration indicated for Bi_3^{3+} is nicely consistent with the rather conclusive deduction of a triangular (D_{3h}) Bi_3 unit in " BiAlCl_4 " by Levy, *et al.*¹⁰ (see Introduction). According to the phase diagram, Figure 1, five-sixths of the strongly diffracting metal is present as $\text{Bi}_6(\text{AlCl}_4)_3$ at this composition, and the unreduced mixture $\text{BiCl}_3 \cdot 3\text{AlCl}_3$ is not

detectable in the powder patterns. Of course, all faces of the regular bipyramid are triangular, and the only other pair distance within this figure is the apical one, which probably would not have been resolved as it occurs at nearly 5 Å and amounts to only one-tenth of the intramolecular pairs. This may not be true of the 4.3-Å base diagonal of a square pyramid which also occurs with twice as great a frequency.

The calculated energies for eight atoms at the corners of a cube (O_h),²⁴ an Archimedean antiprism (D_{4d}), and the regular,²⁵ triangular-faced dodecahedron or bis-disphenoid (D_{2d}) are given in Table III. Only the antiprism gives a satisfactory solution for 22 electrons. The cube clearly requires 24 electrons (or a paramagnetic product), and the dodecahedron 20 or a paramagnetic product if the very slightly antibonding e level were to be occupied. The total binding energy for either 20 or 22 electrons is greatest for the antiprism by 2 and 6%, respectively; 24 electrons would give a neutral species. Inspection of the symmetry orbitals for the end-capped trigonal prism⁷ (D_{3h}) indicates either 20 or 24 electrons will be needed for bonding.

TABLE III
ENERGY PARAMETERS FOR Bi_8 UNITS WITH O_h , D_{4d} ,
AND D_{2d} POINT SYMMETRY, $E = \alpha + x(\beta_0 - \alpha)$

Cube (O_h)		Regular antiprism (D_{4d})		Regular dodecahedron (D_{2d})	
Irr reprn	x	Irr reprn	x	Irr reprn	x
				e	-0.735
				b_1	-0.530
		a_2	-0.822	a_1	-0.470
		e_3	-0.618	e	-0.435
		e_2	-0.473	a_2	-0.426
t_{1u}	-0.878	b_2	-0.388	e	-0.367
a_{2u}	-0.718	b_1	-0.382	b_2	-0.350
e_u	-0.656	e_2	-0.380	a_1	-0.311
t_{1g}	-0.486	e_3	-0.361	b_2	-0.245
t_{2g}	-0.360	e_1	-0.360	e	-0.073
t_{2g}	0.123	e_1	0.046	a_2	0.120
t_{2u}	0.226	b_2	0.224	b_2	0.191
t_{1u}	0.230	e_3	0.242	e	0.247
e_g	0.318	a_1	0.292	b_1	0.272
a_{1g}	0.381	e_1	0.313	e	0.297
		e_2	0.337	b_2	0.312
		a_1	0.400	a_1	0.335
				a_2	0.366

Some consideration has been given to the effect that distortions might have on the conclusions just reached. Generally, moderate distortions within the same point group will not be significant, such as elongation or compression of the antiprism (or bipyramid) along the principal axis to produce unequal edges. A sizable elongation of the regular dodecahedron along the S_4 axis would be necessary to make the critical bonding a_2 become antibonding. (This distortion, changing only the " b " distances,²⁵ might seem otherwise attractive in the absence of a central atom since it increases the coordination of the "B" atoms, but it adversely influences the bonding of the others.) A likewise large

(23) For the regular square pyramid the energy parameters x are: a_1 , 0.394, 0.168, -0.438; a_2 , -0.572; b_1 , -0.148, -0.468; b_2 , 0.267; e , 0.273, 0.113, -0.295, -0.470.

(24) The irreducible representations were kindly supplied by D. S. Martin, Jr.

(25) J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963).

elongation of the cube (to D_{4h}) would be required to make a b_{2g} level (from t_{2g}) become antibonding; a compression would be less pertinent. The orbital correlation diagram between the antiprism and the other eight-atom configurations considered in Table III also allows a measure of the extent to which the former bonding scheme for 22 electrons remains unambiguous on distortion toward the others. Rotation of the square faces of the antiprism with respect to one another carries D_{4h} to D_4 to O_h and, in the critical region, $e_g^*(2) + e_g(2) + b_1^*$ to t_{2g} and e_u^* . Assuming an approximately linear change with rotation, it would appear that such a distortion of 15 to 20° could occur before a ground-state problem would arise, and even more before the critical b_1 level in D_4 descending from $e_g(2)$ to t_{2g} becomes bonding. Distortion of the antiprism to the regular dodecahedron (*via* D_4) gives a similar effect, the antibonding $e_g(2)$ going to the antibonding $a_1(3)$ and bonding a_2 . Although in this case the transformation is geometrically not as direct, perhaps one-third to one-half of the necessary twist and fold of the square faces of the antiprism could take place before ambiguities arise from the descending a_2 (or b_2). Crystal structure studies now underway should give a direct test of the foregoing predictions.

Experience has shown that the sort of one-electron MO calculations employed here to deduce the probable configurations of the polybismuth cations give at least qualitatively correct descriptions of bonding in a great number of situations, even when more severe approximations are applied because of the presence of heteroatoms and a more diverse set of basis orbitals. In the present case the qualitative predictions are sufficiently unambiguous that no great concern is needed concerning small deviations from the highest symmetry, differences in atoms unrelated by symmetry, and probably spin-orbit coupling and polyelectronic effects. However, the inherent simplicity of the present homoatomic situation tempts a far more speculative inquiry into the possible correlation between the calculated energy diagram and the observed spectrum of Bi_3^{3+} . A direct comparison shows that a moderately good correlation between observed and predicted energies for allowed electric dipole transitions can be obtained with an arbitrary scaling parameter $\beta_0 - \alpha$. However, the two lowest energy transitions originating from the bonding e' and e'' levels (Figure 4) are predicted to be accidentally degenerate whereas the experimental data show these split by about 1600 cm^{-1} (Figure 2). It was noted at the time the MO calculations were presented that the relative e' energies were probably the least reliably placed and that their separation was probably minimal. Presuming that this alone is responsible for the observed splitting (there are other ways), the first absorption may be assigned to the transitions of an electron from e'' to $e'(2)$ ($A_1' \rightarrow A_2''$) and the second, $e'(1)$ to $e'(2)$ ($A_1' \rightarrow E'$). Proceeding in this manner it is found that the entire observed spectrum can be accounted for well with small and plausible adjustments in the relative positions of *only* the e'

levels. The correlation given in Table IV results from the empirical values of $-37,600\text{ cm}^{-1}$ for the scaling parameter $\beta_0 - \alpha$ and changes in the α parameters of e' (1, 2, 3) of $+0.053$, -0.019 , and -0.010 , respectively (the last is gilding the lily). Although only the first five transitions are at all well established experimentally, two tentative observations with the mull are also accounted for. Because of the high background, the two missing transitions would have to be only a little weaker to be unobservable with the solid. The results are really too good to be true considering the simplicity of the model and so are presented more as an interesting observation; at the very least the energy diagram is consistent with the spectrum within the uncertainty of the calculation.

TABLE IV
CALCULATED AND OBSERVED ELECTRIC DIPOLE
TRANSITIONS FOR Bi_3^{3+} (D_{3h})

Transition	Calcd, $m\mu$	Obsd, ^a $m\mu$
$e'' \rightarrow e'(2)$ (A_2'')	901	875 ± 5
$e'(1) \rightarrow e'(2)$ (E')	765	790 ± 5
$a_1' \rightarrow e'(2)$ (E')	525	540 ± 8
$e'(1) \rightarrow a_1'$ (E')	462	455 ± 8
$e'(1) \rightarrow a_2'$ (E')	445	
$e'' \rightarrow e'(3)$ (A_2'')	390	390 ± 3
$a_2'' \rightarrow a_1'$ (A_2'')	388	...
$e'' \rightarrow e''$ (E')	376	
$e' \rightarrow e'(3)$ (E')	362	...
$e'(1) \rightarrow e''$ (A_2'')	350	345 ± 6
$a_2'' \rightarrow e''$ (E')	304	305 ± 4
$a_1' \rightarrow e''$ (E')	298	
$e'' \rightarrow a_2''$ (E')	232	...

^a Figure 2, with estimated uncertainty in measurement.

Discussion

The two polybismuth species reported here not only make the former Bi_3^{5+} appear a good deal less of an oddity but also indicate that bismuth has a good deal more diverse chemistry involving metal-metal bonding than has been suspected. Before relating this property to the chemistry of other elements, it is worthwhile to make some comparisons within the known compounds.

At present five reduced, cationic states are known for bismuth: those in the three solids plus Bi^+ and Bi_3^+ (or equivalent—see Introduction) in dilute solution in $BiCl_3$. In addition, Bi^+ is well established in $NaCl-AICl_3$ solvents.¹⁴ The apparent symmetries of the most stable cations, D_{3h} for Bi_3^{3+} , D_{4d} for Bi_3^{2+} , and D_{3h} for Bi_3^{5+} , are relatively familiar for species with a central force field, *i.e.*, complex ions ML_n^q , where antibonding repulsions between nonbonded ligands are important and may be used for prediction and explanation of their configurations.²⁶ In the latter the dodecahedral and antiprismatic conformations are nearly equivalent for eight-coordinate complexes²⁵ and may be expected to interconvert readily.^{27, 28} This is

(26) R. J. Gillespie, *Can. J. Chem.*, **38**, 818 (1960).

(27) E. L. Muetterties, *Inorg. Chem.*, **4**, 769 (1965).

(28) E. L. Muetterties and C. M. Wright, *Quart. Rev. (London)*, **21**, 109 (1967).

not true for such as the bismuth polyhedra as the two arrangements require different numbers of bonding electrons. In general, the direct bonding attractions between atoms in the "empty" cages may be expected to give considerably stiffer configurations which have a negligible causal relationship to the more familiar complex ions. For the present examples it may be observed that the same arrangements generally also lead to the greatest average number of nearest bonding neighbors, but not necessarily to the highest equivalence and hence symmetry. Thus there is an average of 3.6 nearest neighbors for 5 atoms in D_{3h} vs. 3.2 in C_{4v} or 2.0 in D_{5h} symmetry, and 4.0 for 8 atoms with D_{4d} vs. 3 with O_h or 3.5 in D_{2d} symmetry (plus about 0.3 more for the 25% longer "b"²⁵ distances based on the relative σ overlap), and in each case the arrangement with the highest coordination has the highest binding energy for the regular polyhedron. An additional, important criterion for stability of such polyatomic ions in general would seem to be that the preferred arrangement should have a fairly uniform distribution of the bonding and hence of the total charge.

An interesting relationship exists between Bi_3^{2+} and Bi_9^{5+} in that they are isoelectronic (in p electrons) and thereby differ only by a Bi^{3+} ion. The general high sensitivity of these ions toward nucleophiles presumably requires the presence of anions of low basicity or a low pCl. The differences found in the counteranions, $AlCl_4^-$ for Bi_3^{2+} and $BiCl_5^{2-}$ and $Bi_2Cl_5^{2-}$ for Bi_9^{5+} , with no evidence of an alternation, suggests that higher charge density in the latter cation requires larger anions of lower field and higher polarizability. Intrusion of the more stable Bi_5^{3+} with $AlCl_4^-$ could also be responsible for the absence of Bi_9^{5+} with the simpler anion. Conversion of Bi_3^{2+} to Bi_9^{5+} may be viewed as a capping of a square face followed by a small rearrangement;²⁹ the second step, leading to Bi_{10}^{8+} (D_{4d}), gives a plausible bonding scheme but results in an improbably high charge unless the new nonbonding levels b_2 and e_3 are occupied.³⁰ Both Bi^+ and Bi_3^+ (or equivalent) would be favored by dilution and probably by an increase in pCl, as in $BiCl_3$ at small reduction. Both are doubtlessly unstable with respect to disproportionation and condensation to higher species, and there is not much hope of isolating them in pure compounds.

The expanding array of polynuclear bismuth compounds suggests that a general class of homopolyatomic species may exist in a hitherto unsuspected region of the periodic table, far removed from other elements showing any comparable behavior. Even with the few examples now available a definite relationship is already discernible. Although such a comparison is necessarily somewhat speculative, it is valuable in showing not only that relationships exist in diverse

chemistries but also in pointing out the directions in which future discoveries may go.

The number of discrete homopolyatomic clusters formed by normally metallic elements is severely limited. Of course, the electron-deficient bonding in these cages or clusters is also a fundamental characteristic of metals as well,³² but one would not expect to find neutral species in condensed systems, Bi_4 for example, even though the isoelectronic P_4 is well known and may be treated well on a similar basis with only p orbitals.³¹ Arsenic, antimony, and bismuth do, however, exhibit structures suggestive of somewhat more localized bonding,³³ but generally one must consider ions in order to keep the delocalized bonding at the same time localized in discrete units, and because of the properties of metals, the formation of cations is more likely than anions. The best known examples elsewhere are the simple Hg_2^{2+} and Cd_2^{2+} , where bonding arises largely from atomic s orbitals.²² Many examples of metal-metal bonding are to be found in compounds of the transition metals,³⁴ but here a plethora of orbitals also serves to bind anions to give either solid polymers or stable heteroatomic ions such as $M_6X_{12}^{n+}$ ($M = Nb, Ta$; $X = Cl, Br, I$; $n = 2, 3, 4$).³⁵ As far as the present bismuth species are concerned, it is particularly noteworthy that a close analogy to their bonding is apparently provided by a more distant element well known for electron-deficient bonding, boron, and specifically by the remarkable polyboranes $B_nH_n^{2-}$ and the related carboranes $B_{n-2}C_2H_{n-2}R_2$ ($R = H, CH_3$).

Comparison with Polyboranes.—In each of the boron compounds considered an evidently normal (two-electron) bond (or an equivalent delocalized set) is directed outward from each atom of the framework to a hydrogen atom or another substituent, so that the comparison to be made is concerned with only the configuration of and bonding within the cluster or cage. The heteroatoms or exosubstituents in the carboranes should not have a substantial effect on the bonding within the polyhedron; for present purposes this assumption is necessary only in the five-atom case and the apparent high symmetry there makes it even less of a problem.

For the five-atom comparison there is the known $B_5C_2H_5$, probably D_{3h} on the basis of nmr and ir spectra,³⁶ as well as an MO calculation predicting the same trigonal bipyramid for $B_5H_5^{2-}$.³⁷ The nine-atom analogs are $B_9H_9^{2-}$,²⁹ known to have the D_{3h} symmetry of the tripyramid in the solid state,³⁸ and $B_7C_2H_7(CH_3)_2$,³⁹ both compounds having nmr data consistent only with the same configuration in solution. The situation with the octaborane(8) anion requires more dis-

(32) R. E. Rundle, *Acta Cryst.*, **1**, 180 (1948), *J. Chem. Phys.*, **17**, 671 (1949).

(33) E. g., H. Krebs, *Angew. Chem.*, **70**, 615 (1958).

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(35) E. g., P. B. Fleming, L. A. Mueller, and R. E. McCavley, *Inorg. Chem.*, **6**, 1 (1967).

(36) I. Shapiro, C. D. Good, and R. E. Williams, *J. Am. Chem. Soc.*, **84**, 3837 (1962).

(37) E. B. Moore, L. L. Lohr, and W. N. Lipscomb, *J. Chem. Phys.*, **35**, 1329 (1961).

(38) L. J. Guggenberger, private communication.

(39) F. N. Tebbe, P. M. Garrett, D. C. Young, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **88**, 609 (1966).

(29) F. Klanberg and E. L. Muettterties, *Inorg. Chem.*, **5**, 1955 (1966).

(30) In the same way, the formation of Bi_3^{3+} may be viewed as a capping by Bi^{3+} of one face of tetrahedral Bi_4^0 , analogous to P_4 .³¹ In this case, the bonding $e \rightarrow e'$, $t_2 \rightarrow a_2' + e'$, $a_1 \rightarrow a_1'$, and new antibonding solutions e' and a_1' appear.

(31) R. A. Hart, M. B. Robin, and N. A. Kuebler, *J. Chem. Phys.*, **42**, 3631 (1965).

discussion. The anion in solid $[\text{Zn}(\text{NH}_3)_4]^{2+}[\text{B}_8\text{H}_8]^{2-}$ has recently been shown to have D_{2d} point symmetry, albeit somewhat distorted from the regular dodecahedron, while its nmr spectrum in solution shows only a single boron environment more suggestive of an antiprismatic configuration.⁴⁰ The latter could arise not only from an actual change in structure on solution but also from a relatively small nonequivalence of the two types of boron sites in a dodecahedron or, less likely, from a rearrangement that is rapid compared to the time scale of the measurement.⁴⁰ The same uncertainty thus pertains to the interpretation of the nmr data for $\text{B}_8\text{C}_2\text{H}_6(\text{CH}_3)_2$.^{39,41} One-electron, MO calculations for the octaborane in a variety of point groups indicated that all of these would properly accommodate the 34 bonding electrons for the same position of the gap. In total bonding energy the antiprism was found to be about 0.4% more stable than the regular dodecahedron by these approximations. This difference was decreased somewhat when the observed distortion of the latter was included, and the same time the bonding within the cage increased noticeably and the hydrogen populations became more nearly equivalent.

For the purposes of comparison a simple process can be imagined to relate the polybismuth and polyborane species with the same number of atoms in the cluster. Removal of n protons from $\text{B}_n\text{H}_n^{2-}$, conversion of the electron pair left on each boron atom to a nonbonding s^2 state, and then an increase of the nuclear charge of each atom by 2 to give a reasonably low charge yields $(\text{M}^{\text{V}})_n^{n-2}$, or specifically, Bi_n^{n-2} , with an invariant $2n + 2$ electrons bonding the cages. Of course, there is a substantial change of four periods as well from boron to bismuth, and the conversion envisioned implies that the principal function of the s orbitals qualitatively is to generate a set of outward-pointing orbitals (sp hybrids in one approximation) for bonding hydrogen. This is, of course, not true rigorously; although the s orbitals (and the hydrogen atoms) transform as do radially directed p orbitals on the framework atoms, many of these representations also contain symmetry orbitals from other of the p orbitals on the framework atoms, and in any case inclusion of s would be expected to alter details of the bonding within the cage as well as the eigenvalues. Nonetheless the qualitative view that addition of s to the basis set mainly serves to bind n protons to a bismuth-like cage does not appear to be very far from the truth.

According to the above scheme the framework bonding in $\text{B}_3\text{C}_2\text{H}_5$ and Bi_3^{3+} involves 12 electrons delocalized in the same irreducible representations of the trigonal bipyramid. However, the same relationship predicts a $+7$ charge for Bi_3^{5+} and a $+6$ charge (and perhaps D_{2d} symmetry) for Bi_3^{2+} , and differences between predicted charges for other configurations are also found. However, these disparities appear to be only a logical consequence of comparing anions with

cations. The MO calculations for octaborane in a number of point groups and for the nonaborane with D_{3h} symmetry^{38,40} all indicate that the requisite number of electrons for the observed -2 charge could be accommodated in a diamagnetic ground state if the levels up to about -9 eV were filled. However, in the real situation the position of the gap and the energies themselves must depend not only on the atoms involved but also on the charge of the species considered, so that bonding (negative) levels in the one-electron approximation could be left vacant in the polyborane anions but all occupied with the bismuth cations. *All differences in calculated and observed properties between the boron and bismuth cages with eight or nine atoms can be understood if the highest bonding level in the bismuth cation is left vacant in the polyborane anion.* For eight atoms these have the representations t_{2g} in O_h , e_1 in D_{4d} , a_2 in D_{2d} (Table III), and, for nine atoms, a_2'' in D_{3h} symmetry;⁷ the lowest unfilled orbitals in the polyborane calculations are precisely these³⁸ and would be occupied if the (somewhat larger) gap were instead between -3 and -6 eV. The fact that these levels do not all have the same degeneracy thus allows a distinction to be made between several possible configurations for Bi_8^{2+} that is evidently not possible for $\text{B}_8\text{H}_8^{2-}$. The reduction of $\text{B}_8\text{H}_8^{2-}$ or $\text{B}_9\text{H}_9^{2-}$, thereby populating the a_2 or a_2'' levels, evidently does not take place at all readily, but rather oxidation is more prevalent.^{29,40} It would be extremely interesting to examine the reduction of the analogous, neutral carboranes.

Except for the above distinctions the bonding representations calculated for the boranes are those for the bismuth cages plus one each of just those representations in which s (and H) occur, an equal number appearing as strongly antibonding levels. A comparison of the distribution of eigenvalues for bismuth and boron in each of the above polyhedra plus those available^{37,42} for five atoms in D_{3h} and ten in D_{4d} symmetry also indicates that the *relative* energies of the above critical levels show a general trend toward less bonding with boron that is plausible and perhaps even predictable. First, eigenvalues for representations in which s does not occur generally (and properly) become relatively less bonding (or antibonding) on the transition from bismuth to boron. The a_2 level for the D_{2d} model is in this category.⁴³ A regularity is also observed with the slightly bonding or antibonding results with bismuth for representations in which s mixes. This pertains then to the middle of three eigenvalues in a_2'' for Bi_5^{5+} (D_{3h}), e_1 for Bi_6^{2+} (D_{4d}), $e'(2)$ for Bi_6^{3+} (D_{3h}), and b_2 for the bicapped antiprism (D_{4d}), as well as to $e_3(2)$ in the last and t_{2g} for the cube, all with $x \leq \pm 0.12$. The transition to boron apparently always causes these to become substantially antibonding as an additional

(42) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179 (1962). The defined energy parameters are related to those employed here as $\pi/(1-x)$.

(43) Calculations for Bi_8^{2+} with the same relative distortion found for $\text{B}_8\text{H}_8^{2-}$ ⁴⁰ show that it would be noticeably less stable unless the 1-2 distance were to be substantially less than the 3.04 Å values used; however, it is interesting that the same a_2 level becomes substantially nonbonding in the process.

(40) F. Klanberg, D. R. Eaton, L. J. Guggenberger, and E. L. Muetterties, *Inorg. Chem.*, **6**, 1271 (1967).

(41) R. E. Williams and F. J. Gerhart, *J. Am. Chem. Soc.*, **87**, 3513 (1965).

orbital is generated which in part serves to bond hydrogen. Evaluation of the symmetry orbital coefficients in the first two cases, the most important in the present discussion, shows that those orbitals which contribute the principal positive overlap and hence bonding to these intermediate solutions are also those which have the greatest overlap with the *s* orbital. Addition of *s* to the basis set will thus be expected to increase the contributions of these symmetry orbitals in the strongly bonding solutions and therefore to lessen their contribution in and raise the energy of the middle eigenvalue, as observed. The prediction is weakest for the t_{2g} orbital in the cube as the t_{2u} and e_g solutions (where *s* does not mix) are only slightly lower in energy.⁴⁰ The lack of a change in the number of electrons in ground state for the two five-atom cages (D_{3h}) appears to result from the fact that the highest bonding solution (e' , no *s*) is more strongly bonding (Figure 4). In addition, a boron cation would be obtained if this were to go antibonding; the presence of carbon in the known $B_3C_2H_5$ may play an important role in increasing the electron affinity as well as in reducing the charge.

The presence of the large *s*-*p* and *p*-*d* separations in bismuth, *e.g.*, 9.5 and 10 eV to the lowest sp^3 (6S) and s^2p^2d (3D) states in Bi^+ , respectively,⁷ would appear to be of paramount importance for the existence of these compounds as well as for their remarkable resemblance to the polyborane anions just considered since this causes the bonding to be derived from substantially *p* orbitals only. The implications that certain bonding arrangements are preferred with such diverse elements is not entirely surprising. The relative surplus of orbitals over electrons with transition elements thus appears to require tight binding of anions as well.

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The Thermodynamic Properties of Bismuth(I) Bromide and Bismuth(III) Bromide¹

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Literature data on the vaporization of $BiBr_3$ were reevaluated by a second-law method to derive the enthalpy and entropy of sublimation (27.56 kcal/mole and 43.36 eu, respectively, at 298°K). The absolute entropy of the solid (45.5 eu) was derived from the latter value and the absolute entropy of the gas as calculated from molecular constants. The free energy functions for the condensed phases up to 1000°K are tabulated. The enthalpy of formation of solid $BiBr_3$ was measured by solution calorimetry and found to be -66.0 kcal/mole at 298°K. This leads to a value of 168.1 kcal/mole for the enthalpy of atomization of gaseous $BiBr_3$ at 298°K. A second-law treatment of literature data on the equilibrium among $BiBr_3$, Bi , and $BiBr$ led to a dissociation energy of 63.9 kcal/mole, for gaseous $BiBr$, in good agreement with the literature spectroscopic value. A value of 72 eu was derived for the absolute entropy of gaseous $BiBr$.

Introduction

The present work started as a reevaluation of our earlier study² of the equilibrium $2/3Bi(l) + 1/3BiBr_3(g) = BiBr(g)$ similar to that made for the chloride system.³ The vibration frequencies of $BiBr_3$ have recently been determined⁴ and so have the enthalpy increment data⁵ for the solid above room temperature. As the evaluation proceeded it became apparent that a measurement of the enthalpy of formation of solid $BiBr_3$ would serve as a check on the enthalpies of for-

mation based only on the spectroscopic dissociation energy of $BiBr$. Accordingly, enthalpies of solution of Bi , Br_2 , and $BiBr_3$ were measured in an aqueous Br_2 - HBr solvent.

The Enthalpy of Formation of $BiBr_3$

Calorimeter.—A simple solution calorimeter was made from a 1-pint Pyrex dewar with a thermistor as a thermometer. The solution was stirred by a Teflon lift stirrer operated by a chain drive and constant-speed dc motor. The dewar top was closed by a cork which supported two 15-mm glass tubes, closed by rubber stoppers. The substances to be added to the solvent in the dewar were contained in those tubes, and the rubber stoppers were pushed out with glass rods when it was time to mix the components. The dewar as-

(1) This work was supported by the Research Division of the U. S. Atomic Energy Commission under Contract No. AT(04-3)-106.

(2) D. Cubicciotti, *J. Phys. Chem.*, **64**, 1506 (1960).

(3) D. Cubicciotti, *ibid.*, **71**, 3066 (1967).

(4) T. R. Manley and D. A. Williams, *Spectrochim. Acta*, **21**, 1467 (1965). The molecular constants used were specified in Table I of this reference. No electronic contribution to the entropy was assumed.

(5) D. Cubicciotti and H. Eding, *J. Chem. Eng. Data*, in press.