53011-62-4; $(CH_3)_3N{\cdot}BH_3$, 75-22-9.

References and Notes

(1) NSF-CNRS, U. S.–France Exchange Scholar, 1973–1974.

(2) (a) P. S. Bryan and R. L. Kuczkowski, *Inorg. Chem.*, **11**, 553 (1972); (b) J. R. Durig, Y. S. Li, L. A. Carreira, and J. D. Odom, *J. Amer. Chem. Soc.*, **95**, 2491 (1973).

(3) R. L. Kuczkowski and D. R. Lide, Jr., *J. Chem. Phys.*, **46**, 357 (1967).

(4) J. P. Pasinski and R. L. Kuczkowski, *J. Chem. Phys.*, **54**, 1903 (1971).

(5) D. R. Lide, Jr., R. W. Taft, Jr., and P. Love, *J. Chem. Phys.*, **31**, 561 (1959); S. Geller, *ibid.*, **32**, 1569 (1960); D. R. Lide, Jr., *ibid.*, **32**, 1570 (1960).

(6) P. S. Bryan and R. L. Kuczkowski, *Inorg. Chem.*, **10**, 200 (1971).

(7) S. H. Bauer, *J. Amer. Chem. Soc.*, **59**, 1804 (1937).

(8) H. G. Schirdewahn, Doctoral Thesis, University of Freiburg, 1965.

(9) J. R. Durig, Y. S. Li, and J. D. Odom, *J. Mol. Struct.*, **16**, 443 (1973).

(10) Both ref 8 and 9 report spectra for the ^{10}B and ^{11}B isotopes of the $(CH_3)_3N{\cdot}BH_3$, $(CH_3)_3N{\cdot}BD_3$, $(CD_3)_3N{\cdot}BH_3$, and $(CD_3)_3N{\cdot}BD_3$ species. Reference 9 also reports on the $(CH_3)_3N{\cdot}^{11}BD_2H$ and $(^{13}CH_3)(^{12}CH_3)_2N{\cdot}^{11}BH_3$ species.

(11) L. Pierce, *J. Mol. Spectrosc.*, **3**, 575 (1969).

(12) A. B. Burg and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **59**, 780 (1937).

(13) Two measurements (for transitions 1 and 9 in Table I) differed by +0.64 and −0.76 MHz. Fortunately, however, this does not seem to affect markedly the calculations in ref 9, except possibly the dipole moment evaluation.

(14) W. H. Kirchhoff, *J. Amer. Chem. Soc.*, **89**, 1312 (1967).

(15) J. S. Muenter, *J. Chem. Phys.*, **48**, 4544 (1968).

(16) J. Kraitchman, *Amer. J. Phys.*, **21**, 17 (1953).

(17) $\mu = M\Delta M/(M + \Delta M)$ where ΔM is the change in mass upon substitution and M is the mass of the parent species.

(18) L. C. Krisher and L. Pierce, *J. Chem. Phys.*, **32**, 1619 (1960).

(19) A. P. Cox and J. M. Riveros, *J. Chem. Phys.*, **42**, 3106 (1966).

(20) L. C. Krisher and L. Pierce, *J. Chem. Phys.*, **31**, 875 (1959).

(21) M is the mass of the parent species; $\Delta M = {}^{15}N$ mass $- {}^{14}N$ mass; $\mu = M\Delta M/(M + \Delta M)$; $\mu' = M' \Delta M/(M' + \Delta M)$, where M' is the mass of the substituted species used in eq 1.

(22) Previously:[9] $d(CN) = 1.495$ Å; $\angle CNB = 110.9°$.

(23) J. E. Wollrab and V. W. Laurie, *J. Chem. Phys.*, **51**, 1580 (1969).

(24) The value of 4.90 D in ref 8 was corrected for the newer dipole moment value of OCS in ref 15.

(25) N. Noth and H. Beyer, *Chem. Ber.*, **93**, 939 (1960).

(26) C. H. Bax, A. R. Katritzky, and L. E. Sutton, *J. Chem. Soc.*, 1258 (1958).

(27) This conclusion seems warranted based on the reports in ref 28 and 29, assuming that irreversible decomposition of the $Me_3N{\cdot}BH_3$ adduct at the temperatures employed can be neglected.

(28) J. M. Miller and M. Onyszchuk, *Can. J. Chem.*, **41**, 2898 (1963).

(29) W. A. G. Graham and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **3**, 164 (1956).

(30) T. D. Coyle and F. G. A. Stone, *Progr. Boron Chem.*, **1**, 83 (1964).

(31) R. E. McCoy and S. H. Bauer, *J. Amer. Chem. Soc.*, **78**, 2061 (1956).

(32) S. R. Gunn, *J. Phys. Chem.*, **69**, 1010 (1965).

(33) For original literature references, see H. D. Johnson, II, and S. G. Shore, *Fortschr. Chem. Forsch.*, **15**, 94 (1970).

(34) H. C. Brown and R. R. Holmes, *J. Amer. Chem. Soc.*, **78**, 2173 (1956).

(35) H. C. Brown and L. Domash, *J. Amer. Chem. Soc.*, **78**, 5384 (1956).

(36) The interpretation that BH_3 is a better acid than BF_3 toward Me_3N has also been drawn from studies on their nmr spectra,[37,38] mass spectra,[39] and dipole moments.[26] However, these studies are measuring effects more related to the intrinsic properties of the complexes after formation and do not necessarily indicate which adduct is more stable to dissociation as evaluated by ΔH_G.

(37) J. M. Miller and M. Onyszchuk, *Can. J. Chem.*, **42**, 1518 (1964).

(38) T. D. Coyle and F. G. A. Stone, *J. Amer. Chem. Soc.*, **83**, 4138 (1961).

(39) G. F. Lantier and J. M. Miller, *J. Chem. Soc. A*, 346 (1971).

(40) F. A. Cotton and J. R. Leto, *J. Chem. Phys.*, **30**, 993 (1959).

(41) B. Swanson, D. F. Shriver, and J. A. Ibers, *Inorg. Chem.*, **8**, 2182 (1969).

(42) S. Geller and J. L. Hoard, *Acta Crystallogr.*, **3**, 121 (1950); **4**, 399 (1951).

(43) J. L. Hoard, S. Geller, and T. B. Owen, *Acta Crystallogr.*, **4**, 408 (1951).

(44) Z. V. Zvonkova, *Kristollografiya*, **1**, 73 (1960); *Sov. Phys.—Crystallogr.*, **2**, 403 (1957).

(45) A similar viewpoint was stated recently by R. W. Rudolph and R. W. Parry, *J. Amer. Chem. Soc.*, **89**, 1621 (1967).

(46) E. R. Alton, Ph.D. Thesis, University of Michigan, 1960.

(47) An MO estimate of the deformation energy of BF_3 gave 48 kcal.[40] However, no estimate for BH_3 was given.

(48) P. S. Ganguli and H. A. McGee, Jr., *J. Chem. Phys.*, **50**, 4658 (1969).

(49) For example, the nmr experiments[39,40] which show small differences for the two adducts lend support for this assumption. On the other hand, some unpublished data in this laboratory seem to indicate that the B–N force constants may be different. This would not be readily reconciled with the assumption although it is possible that the force constants do not reflect similar bond energies. This point deserves further investigation.

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Structural Chemistry of the Polysulfides Ba_2S_3 and BaS_3

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The crystal structures of Ba_2S_3 and BaS_3 were determined from three-dimensional single-crystal X-ray diffraction data. Ba_2S_3 is tetragonal, $I4_1md$, $a = b = 6.112$ (1) Å, $c = 15.950$ (2) Å, $Z = 4$, and BaS_3 is tetragonal, $P\bar{4}2_1m$, $a = b = 6.871$ (2) Å, $c = 4.1681$ (4) Å, $Z = 2$. Least-squares refinement gave final R's of 0.0623 for 174 observed reflections and 0.028 for 151 observed reflections, respectively. Ba_2S_3 contains a sulfide ion and a S_2^{2-} polysulfide ion. The S–S distance in the polysulfide ion is 2.32 (9) Å. One barium ion is in the center of a distorted trigonal prism whose corners are occupied by the S_2 ions. The distances between Ba^{2+} and the nearest sulfur of the dumbbell-shaped ions are 3.11 and 3.91 Å with three additional S^{2-} capping the rectangular faces at 3.15 and 3.24 Å. The second barium ion has an irregular polyhedron of nine sulfur atoms around it. Three of the vertices are occupied by S^{2-} at 3.14 and 3.72 Å and six vertices are occupied by S_2 ions. The nearest sulfur atoms of the polysulfide ion are at 3.21 and 3.42 Å from barium. In BaS_3 the polysulfide anion is S_3^{2-} with S–S = 2.074 Å and the S–S–S angle is 114.8°. Barium is in 12-fold coordination with Ba–S distances varying from 3.204 to 3.541 Å.

Introduction

During high-pressure investigations of the systems Ba–Ge–S and Ba–Mn–S we frequently observed lemon yellow crystals in the reaction products. They were birefringent and X-ray diffraction powder patterns could not be matched with known patterns. Single-crystal X-ray structural investigations were carried out to determine the stoichiometries of these phases and they proved to be Ba_2S_3 and BaS_3. The existence of BaS_3 had been reported by Miller and King[1] and the powder pattern due to this phase was probably not identified in our experiments because BaS_3 was a minor constituent in a multiphase reaction product. These authors deduced an incorrect unit cell and space group from their X-ray powder diffraction data but their proposed structure is remarkably accurate. The phase Ba_2S_3 is new and its structure was determined in this investigation.

Experimental Section

A single crystal of what proved to be Ba_2S_3 was selected from the product resulting from a high-pressure experiment carried out in a tetrahedral press at about 50 kbars and 800° on a mixture of 3BaS + Ge + 2S. The crystal had a lemon yellow color and was ap-

Table I. Atomic Parameters for Ba_2S_3 ($\times 10^4$)

Atom	x	y	z	B_{11}[a]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ba(1)	0	0	−2031 (24)[b]	118 (19)	603 (42)	39 (3)	0	0	0
Ba(2)	0	0	2051 (23)	327 (24)	74 (15)	13 (1)	0	0	0
S(1)	0	0	0	270 (83)	−38 (51)	30 (5)	0	0	0
S(2)	0	3101 (101)	6426 (29)	162 (39)	1755 (311)	77 (18)	0	0	305 (62)

[a] Coefficients in the temperature factor: $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. [b] The number in parentheses is the standard error in terms of the last digits, as derived from the variance–covariance matrix.

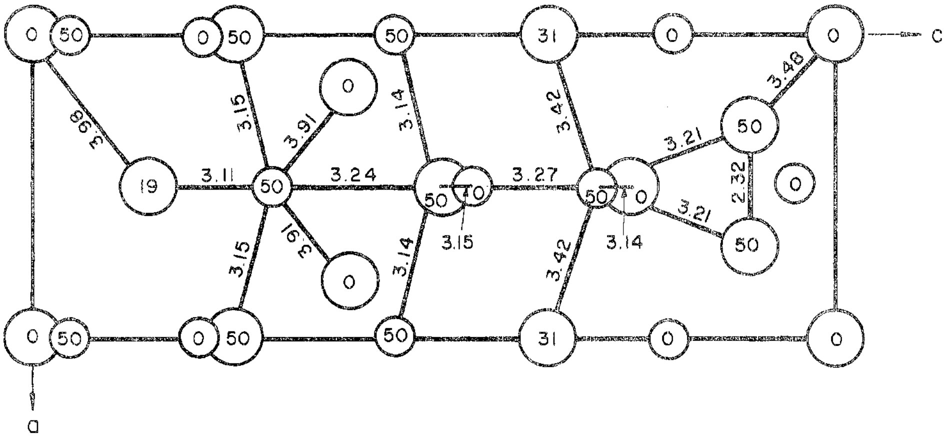

Figure 1. Projection of the structure of Ba_2S_3 on (010). The large circles are S and the small circles are Ba. The numbers denote fractional heights along the axis of projection and where no number is shown the atom is in the plane of projection.

proximately 50 × 41 × 29 μ in size. Weissenberg and precession diagrams showed that it was tetragonal with systematic absences for hkl, $h + k + l = 2n + 1$, hhl, $2h + l = 4n + 2$, and $hk0$, $h = 2n + 1$, so that the space group was uniquely determined as $I4_1/amd$. Lattice constants were determined from a least-squares refinement of precise 2θ values of 11 reflections between 21 and 31° from a crystal mounted on a single-crystal diffractometer with the instrument set at a 1° takeoff angle and a 0.05° slit in front of the scintillation counter and using Mo radiation, λ_1 0.70926 Å, λ_2 0.71354 Å. The lattice constants at room temperature were $a = 6.112$ (1) Å and $c = 15.950$ (2) Å, $\rho_{calcd} = 4.13$ g/cm^3.

The single crystal of what proved to be BaS_3 was found in the reaction product of a high-pressure experiment in the system BaS + Mn + S. A lemon yellow crystal was selected and Weissenberg and precession diagrams showed that it was tetragonal with the only systematic absences $h00$, $h = 2n + 1$, consistent with the space groups $P\bar{4}2_1m$ and $P42_12$, of which the first one turned out to be correct. A least-squares refinement of 24 2θ measurements under the identical conditions as above yielded the lattice parameters $a = 6.871$ (2) Å and $c = 4.1681$ (4) Å, $\rho_{calcd} = 3.94$ g/cm^3.

Intensity data were collected by the stationary-crystal, stationary-counter method with the instrument set at a 5° takeoff angle and no aperture in front of the counter. The pulse height discriminator was set to accept 80% of the incident Mo Kα radiation; balanced Zr–Y filters were used. For Ba_2S_3 211 independent reflections were measured to a maximum $2\theta = 55°$. Each reflection was counted for 40 sec and only reflections which exceeded background by 8 counts were considered observed; this criterion reduced the final number to 174. The same procedure was used to measure 163 reflections from BaS_3 except that the counting interval was 20 sec and the peak count had to exceed background by 15 counts. The number of reflections exceeding background was 151. Both sets of intensity data were corrected in the usual manner for Lorentz, polarization, and absorption to obtain the structure factors. Standard deviations were assigned using the formula

$$\sigma(|F|) = \tfrac{1}{2}\left[K\left(1 + \frac{I_Y}{I_{Zr}}\bigg/1 - \frac{I_Y}{I_{Zr}}\right)\right]^{1/2}$$

where K is the product of all correction factors and I_Y and I_{Zr} are the counts with the respective filters in the diffracted beam path.

Structure Determination

Although the atomic compositions and stoichiometries of the crystals were unknown, the structures were easily solved from the three-dimensional Patterson function. In the case of Ba_2S_3 some difficulties were initially encountered. The interpretation of the Patterson function required the location of a S atom in position 16(h) of $I4_1/amd$ and this led to an unreasonably short S–S distance in the symmetry related atoms. The removal of the center of symmetry and considerations based on the construction of various models showed that $I4_1md$ was the correct space group. It can be seen from Table I that Ba(1), Ba(2), and S(1) atomic positions are centrically related and only S(2) positions destroy the center. The location of three of the four atoms in the asymmetric unit in special position 4(a) of $I4_1md$ means that $hk0$ reflections are observed only for $h = 2n$ so that $I4_1/amd$ is simulated by the diffraction data.

A least-squares refinement using anisotropic temperature factors converged to $R = 0.0623$ and $R_w = 0.0473$ for the 174 observed structure factors ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2}$). Scattering factors for Ba, S^{2-}, and S^-, for sulfur in 8(b), were used[2] and, after the stoichiometry was known, the absorption correction was calculated by approximating the crystal shape with 11 faces. The final atomic parameters are listed in Table I and the observed and calculated structure factors are listed in Table II. The rather large standard deviations of the parameters are due to the small size of the crystal and the resultant low intensities of the reflections. A final difference Fourier map showed no peaks greater than 1 e Å^{-3}.

The least-squares refinement of the observed 151 BaS_3 structure factors converged to $R = 0.028$ and $R_w = 0.032$. The structure factors are listed in Table III and the atomic parameters in Table IV. Scattering factors for Ba^{2+} and S^- were used in the calculation. The final difference Fourier map did not have any peaks exceeding 1 e Å^{-3}. The programs used in the structure determination and their authors were as follows: ORFLS, W. R. Busing and H. A. Levy; INCON, R. E. Davis; DAESD, D. R. Harris; RFOUR, S. T. Rao; XRDSET, P. J. Shapiro; LSLAT, K. N. Trueblood; ORABS, J. Williams.

Discussion

Projections of the structures are shown in Figures 1 and 2 and interatomic distances are shown in Tables V and VI.

Two different types of sulfur are present in Ba_2S_3, S^{2-}, and S_2^{2-}, with the former in the 4(a) and the latter in the 8(b) positions of the space group. S(1) is surrounded by three Ba(1) and three Ba(2) atoms at distances of 3.14–3.27 Å, essentially the sum of the ionic radii; the S(2) atoms are 2.32 Å apart. It should be noted that the vibration ellipsoid of S(2) is strongly elongated along the S–S bond direction.

Ba(1) is in the center of a distorted trigonal prism whose corners are occupied by six S_2 ions and the three rectangular faces are capped by three S ions. The prisms form infinite

Table IV. Atomic Parameters for BaS_3 ($\times 10^4$)

Atom	x	y	z	B_{11}[a]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ba	0	0	0	44 (4)[b]	44	186 (7)	0	0	0
S(1)	0	$^1/_2$	2060 (15)	38 (14)	38	141 (32)	1 (16)	0	0
S(2)	1797 (8)	6797	4760 (17)	28 (9)	28	235 (28)	−13 (7)	−2 (30)	2

[a] Coefficients in the temperature factor: $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. Symmetry-related values are indicated by the omission of the standard deviations. [b] The number in parentheses is the standard error in terms of the last digits, as derived from the variance-covariance matrix.

Table V. Bond Distances in Ba_2S_3

Atoms	Distance, Å	Atoms	Distance, Å
Ba(1)-1[a]S(1)	3.24 (4)[b]	Ba(2)-1S(1)	3.27 (4)
2S(1)	3.15 (1)	2S(1)	3.14 (1)
2S(2)	3.11 (9)	2S(2)	3.21 (7)
4S(2)	3.91 (5)	4S(2)	3.42 (3)
S(1)-S(2)	3.98 (5)	S(2)-S(2)	2.32 (9)

[a] The number to the left of the S atom shows the number of bonds from the Ba ion. [b] The number in parentheses is the standard deviation.

Table VI. Bond Distances in BaS_3

Atoms	Distance, Å	Atoms	Distance, Å
Ba-4S(1)	3.541 (1)	S(1)-S(2)	3.388 (7)
4S(2)	3.204 (7)	S(1)-S(2)	2.074 (7)
4S(2)	3.344 (7)		

columns by sharing the triangular faces and two types of columns are present; one has its long axis parallel to *a* and the other parallel to *b* and they are interconnected by sharing corners. Ba(2) is surrounded by three S and six S_2 ions which form an irregular polyhedron.

Sulfur exists as the S_3^{2-} anion in the structure of BaS_3. The S–S distance is 2.074 Å, and the S(2)–S(1)–S(2) angle is 114.8 (5)°. The S_3 ions form columns and the closest distance between sulfur atoms of adjacent columns is 3.388 Å. Barium is surrounded by eight S(2) atoms at the corners of a slightly distorted cube; *i.e.*, if the *z* parameter of S(2) were $^1/_2$, it would be a perfect cube. The Ba–S(2) distances differ, therefore, and are 3.20 and 3.34 Å. Four additional S(1) atoms are at 3.54 Å so that Ba can be considered to have 12-fold coordination. Miller and King[1] indexed their powder patterns on the basis of an orthorhombic unit cell in which their *a* and *b* axes are related to our tetragonal *a* axis by the relation $\vec{a}_t + \vec{b}_t \approx \vec{b}_o$ and $c_t \approx {}^1/_2 a_o$. They deduced the presence of the S_3 ion in the structure with S–S = 2.15 Å and the S–S–S angle as 103°.

The S–S distance of 2.32 Å in the S_2^{2-} ion is considerably longer than the usual values of 2.0–2.15 Å[3-5] although a 2.39-Å length is reported for the dithionate ion in $Na_2S_2O_4$. However, the large error in our bond length, 0.09 Å, does not permit us to say that this value differs significantly from those previously reported. The S–S length of 2.074 Å in the S_3^{2-} ion agrees with previously reported values although the angle of 115° is significantly larger than the values of about 103° reported in the literature. However, the literature values are for angles in polysulfide ions other than free S_3^{2-}, or, in the case of $(CF_3)_2S_3$ and similar molecules, the sulfur atoms are bonded to additional groups which probably affect the S–S–S angle.

The Ba_2S_3 phase apparently forms only at elevated pressure but BaS_3 was initially formed by Miller and King in evacuated ampoules and we have reproduced their results as well as recovered it from high-pressure runs.

We have calculated the volume available per sulfur atom by subtracting the volume of Ba^{2+} (r = 1.35 Å) from the unit cell volumes of BaS, Ba_2S_3, and BaS_3 and get 54.84, 42.78, and 29.37 Å^3, respectively. Thus at high pressure the formation of polysulfide anions is favored because more of the available volume is utilized by the sulfur atoms. The percentage change in volume $\Delta V/V_{\text{reactants}}$ for the reactions BaS + $^1/_2$S → $^1/_2Ba_2S_3$ and Ba_2S_3 + 3S → $2BaS_3$ is −4.56% and −13.04%, respectively, and is in accordance with expectations for the formation of compounds found at higher pressures.

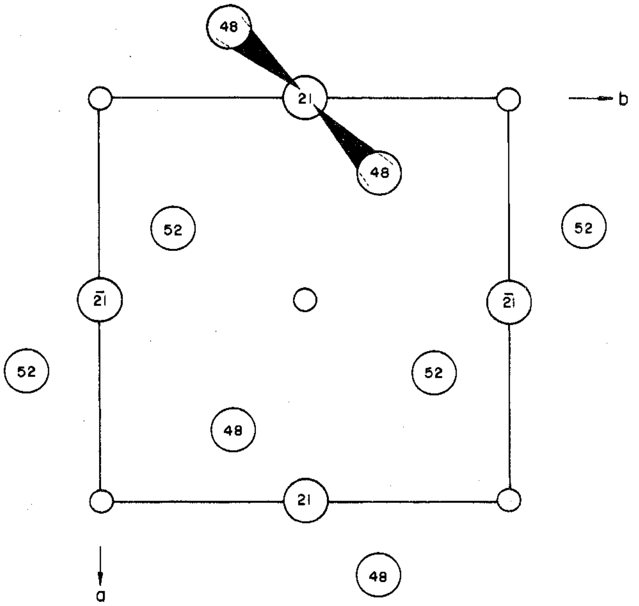

Figure 2. Projection of the structure of BaS_3 on (001). The symbology of Figure 1 applies here also. Bonds outlining one S_3 unit are shown.

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Registry No. Ba_2S_3, 53111-28-7; BaS_3, 12231-01-5.

Supplementary Material Available. Tables II and III, listings of structure factor amplitudes for Ba_2S_3 and BaS_3, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number AIC40475D.

References and Notes

(1) W. S. Miller and A. J. King, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **94**, 441 (1936).
(2) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962.
(3) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Interscience, New York, N. Y., 1972.
(4) "Tables of Interatomic Distances and Configuration of Molecules and Ions," The Chemical Society, London, 1958.
(5) R. W. G. Wyckoff, "Crystal Structures," Vol. I, Interscience, New York, N. Y., 1963.