CONTRIBUTION FROM LEDGEMONT LABORATORY, KENNECOTT COPPER CORPORATION,
LEXINGTON, MASSACHUSETTS 02173

# On the Preparation, Properties, and Structure of Cuprous Ammonium Thiomolybdate[1]

BY W. P. BINNIE, M. J. REDMAN, AND W. J. MALLIO

*Received June 5, 1969*

The preparation and characterization of cuprous ammonium thiomolybdate, $CuNH_4MoS_4$, are described. The compound could only be prepared as a fine crystalline precipitate so that its crystal structure was determined from the geometry and intensity of X-ray scattering as recorded by powder techniques. The intensity was placed on an absolute scale experimentally by the methods of mixtures and substitution. Electron diffraction studies of single crystallites indicated the systematic absences. The compound crystallizes in the tetragonal space group $I\bar{4}$ with unit cell dimensions of $a = 8.000 \pm 0.004$ Å and $c = 5.409 \pm 0.003$ Å. Measured and calculated densities for two molecules per unit cell are $2.94 \pm 0.02$ and 2.93 g $cm^{-3}$, respectively. The X-ray intensity data for 13 unique reflections and 27 overlapped reflections led to a trial structure which was refined by least-squares methods to a conventional $R$ factor of 0.08. Each metal atom is coordinated tetrahedrally with sulfur atoms. These different tetrahedra are stacked alternately along the $c$ direction, each one sharing opposite edges with two neighboring tetrahedra to form infinite chains between which the ammonium ions are distributed. Each ammonium ion is surrounded by 12 sulfur atoms which occupy the vertices of a slightly distorted cuboctahedron. The shortest N–S distance suggests the possibility of N–H···S hydrogen bonds but the angular distribution of these sulfur atoms about the ammonium ion is not favorable for their formation. The cuboctahedra and the tetrahedra share edges only, giving rise to open packing of polyhedra in this structure. Substitution of various metals for the copper, molybdenum, or ammonium ion was unsuccessful.

A compound reported by Debray[2] has been shown to be cuprous ammonium thiomolybdate, $CuNH_4MoS_4$. This compound was prepared and studied because we are interested in the coordination of sulfur with metal atoms.

## Experimental Methods

**Preparations.**—The compound has been prepared by the three methods described below. (i) By a method similar to that used by Debray, *viz.*, a solution of ammonium sulfide was prepared by saturating concentrated aqueous ammonia with hydrogen sulfide gas. To 150 ml of this solution at room temperature was added an equal volume of a solution consisting of 75 ml of concentrated ammonia, 75 ml of water, 20 g of ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, and 15 g of cupric sulfate pentahydrate. A precipitate separated out and then redissolved almost immediately to form a deep red solution. On (a) boiling for 2–3 min or (b) standing for 3–4 hr, a crystalline precipitate formed, dichroic green in reflected light and purplish red in transmitted light. The precipitate was washed with ammonia solution and then with ethanol and allowed to dry in air and then in a desiccator.

(ii) Excess hydrogen sulfide was passed into an ammoniacal solution (8% $NH_3$) of cupric sulfate (100 g/l.) and molybdenum trioxide (140 g/l.) at room temperature. The precipitate was filtered, washed, and dried as above.

(iii) Ammoniacal ammonium molybdate solution (100 g/l.) was saturated with hydrogen sulfide and freshly precipitated cupric sulfide was added. Excess sulfide was filtered off to give a deep red solution. Upon (a) standing for 3–4 hr or (b) acidification to pH 5, a precipitate appeared. The product from (b) was a finely divided reddish powder.

Of the preparative methods, the best yield (over 90%) is obtained by use of method ii; yields from method iii are poor while moderate yields are obtained from method i. Material obtained by the use of method iii is impure; products from methods i and ii are of comparable purity. A typical analysis gave a composition $Cu(NH_4)_{1.07}Mo_{1.05}S_{4.09}$. *Anal.* Calcd for $CuNH_4MoS_4$: Cu, 20.79; Mo, 31.38, S, 41.97; $NH_4$, 5.89. Found: Cu, 19.80; Mo, 31.39; S, 40.78; $NH_4$ (determined as $NH_3$), 5.98. The remaining material (2%) is possibly retained moisture. The copper, molybdenum, and ammonia were determined by conventional wet analytical techniques. The sulfur was determined as barium sulfate after oxidation with bromine.

**Physical Measurements.**—Infrared spectra of potassium bromide pellets containing 0.1% of sample were taken on Perkin-Elmer spectrophotometers, Models 337 and 137G. Determination of diamagnetism or paramagnetism was made using the Faraday method with a Varian magnet and a Cahn RG microbalance. The density was measured pycnometrically using carbon tetrachloride as the fluid medium.

**Diffraction Techniques.**—Since the material could only be prepared as a precipitate with an average crystallite size of <5 μ, only X-ray powder methods were employed. Iron-filtered Co K$\alpha$ radiation [$\lambda(K\alpha_1)$ 1.7889 Å, $\lambda(K\alpha_2)$ 1.7928 Å] was used throughout the X-ray work. The geometric distribution of scattering was measured on a Straumanis-type powder film, diameter 114.6 mm, using material contained in a 0.2-mm glass capillary, while the intensity distribution was recorded with a Norelco vertical diffractometer fitted with a sample spinner and a scintillation detector with pulse height analysis. For the latter procedure, a flat circular sample of 2-cm diameter and 0.1 cm thick was used.

The intensities were measured using material from preparation method i by the $\theta$–$2\theta$ scan technique with a 100-sec counting period at a scan rate of 1°/min. Net intensities were obtained by subtracting the sum of two background counts, each of 50 sec, taken at the beginning and end of each scan. These intensities were placed on an absolute scale experimentally by the methods of mixtures and substitution,[3,4] using finely powdered $\alpha$-aluminum oxide and silicon as standards. Four scans were made by these two methods using four different samples and the absolute intensities were averaged, giving values for 13 unique reflections and 27 overlapped reflections. The mean deviation in intensity from the average varied from 2% for strong reflections to 10% for weak reflections, indicating that preferred orientation had been essentially avoided in sample preparation. Corrections for absorption ($\mu = 441.8$ $cm^{-1}$ for the compound), Lorentz, polarization, and multiplicity factors were made.

---

[1] A preliminary report on this work was given at the American Crystallographic Association Winter Meeting, Seattle, Wash., March 23–28, 1969; see Abstract G8.

[2] M. Debray, *C. R. Acad. Sci.*, **96**, 1616 (1883).

[3] G. W. Brindley and F. W. Spiers, *Proc. Phys. Soc. London*, **50**, 17 (1938).

[4] J. C. M. Brentano, *ibid.*, **50**, 247 (1938).

A Hitachi HU-11A unit was used to obtain electron diffraction patterns of single crystallites in order to determine systematic absences. Continued exposure to a finely focused electron beam decomposed the crystallites so that powder diffraction rings were recorded.

## Results and Discussion

The main characteristics of the infrared spectra are the $NH_4^+$ absorption band at 1350–1400 $cm^{-1}$ and the absorption at 460 $cm^{-1}$ arising from the $MoS_4^{2-}$ group.[5,6] A small water peak is also present suggesting that the sample contained moisture.

The compound proved to be diamagnetic, suggesting that cuprous rather than cupric copper is present. Upon thermal decomposition in an inert atmosphere, sulfur is evolved and a mixture of molybdenum and cuprous sulfides remains, suggesting loss and decomposition of ammonium sulfide. The same products were recognized from powder diffraction rings when the material decomposed during the electron diffraction experiments. The material is stable in air to over 100°, but at 120° decomposition begins with the evolution of $SO_2$. The final decomposition product at 350–400° is cupric molybdate; anhydrous cupric sulfate and molybdenum trioxide were identified as intermediates.

The material is unaffected by dilute mineral acids. When treated with concentrated nitric acid, sulfur is liberated, and cupric and molybdate ions appear in solution. The material is decomposed but not solubilized by concentrated sulfuric and hydrochloric acids.

The X-ray powder pattern was readily indexed on the basis of a tetragonal unit cell with dimensions and standard deviations, calculated by a method of least squares, of $a = 8.000 \pm 0.004$ Å and $c = 5.409 \pm 0.003$ Å. The pycnometric density was 2.94 ± 0.02 g $cm^{-3}$ while the calculated density assuming two molecules per unit cell was 2.93 g $cm^{-3}$.

The electron diffraction plates showed that the chosen unit cell was body centered. No additional systematic absences were found but insufficient reflections of the type ($0kl$) or ($00l$) were recorded to enable the presence of a glide plane or screw axis to be determined. Consequently, from the observed systematic extinctions, the space group is one of the 13 listed under the crystal aspect numbers 24, 25, and 26 of the tetragonal system.[7] However, the density and lattice type require that the Cu, N, and Mo atoms occupy special twofold positions. The only possible space groups which can accommodate this number of such special positions in the unit cell are $I4$ (no. 82) and $I\bar{4}m2$ (no. 119),[8] each of which has four sets of twofold positions, their coordinates being the same in each space group. In $I\bar{4}m2$, the sulfur atoms would also occupy special positions with one known coordinate whereas in $I\bar{4}$ these atoms would occupy general positions.

From a comparison of the absolute observed and calculated structure factors, the space group $I\bar{4}$ was chosen as correct and the approximate coordinates of all atoms except hydrogen were obtained by trial and error methods. These coordinates along with the scale factor and isotropic thermal parameters were refined by least-squares methods for four cycles using J. Gvildys' modified ANL-FLS program. This program minimizes the function $\Sigma||F_o|^2 - |F_c|^2|^2$ and also accounts for overlapped powder diffraction data. The scale factor, which was refined, was initially the experimentally derived one. An isotropic thermal parameter of 2.5 Å$^2$, evaluated by Wilson's method,[9] was used initially for all atoms. Atomic scattering factors for $Cu^+$, N, and $S^{2-}$ were taken from ref 10 and that for $Mo^{6+}$ was from Cromer and Waber's compilation.[11] Full allowance was made for anomalous scattering by the copper, molybdenum, and sulfur atoms, the real and imaginary components being obtained for Co K$\alpha$ radiation by interpolation, using the values given by Cromer.[12] The use of these atomic scattering factors in the refinement resulted in a shift of the experimentally derived scale factor by 1%. When the atomic scattering factors for neutral atoms were used in the refinement, the corresponding shift was 5% but the atomic positional and thermal parameters were refined to the same values within one estimated standard deviation and two such deviations, respectively. Hydrogen contributions were not included.

The final positional and thermal parameters found by using the ionic scattering factors are listed in Table I and the structure amplitudes calculated from them are compared with observed values in Table II. The residual $R_{F^2}$, based on $F^2$ and defined by $R_{F^2} = \Sigma||F_o|^2 - |F_c|^2|/\Sigma|F_o|^2$, is 0.15 while the conventional $R$, based on $F$ and defined by $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, is 0.08 (with $|F_o|$ values of overlapped reflections apportioned according to their calculated values).

TABLE I

ATOMIC POSITIONAL AND ISOTROPIC THERMAL PARAMETERS[a]

| Atom | Position[b] | $x$ | $y$ | | $B$, Å$^2$ |
|---|---|---|---|---|---|
| Cu | 2b | 0 | 0 | 1/2 | 3.5 (8) |
| N | 2c | 0 | 1/2 | 1/4 | 3.3 (10) |
| Mo | 2a | 0 | 0 | 0 | 2.0 (4) |
| S | 8g | 0.195 (2) | 0.112 (2) | 0.232 (7) | 3.8 (7) |

[a] Numbers in parentheses are the standard deviations in the least significant digits. [b] See ref 8, p 172.

Projections of the structure along the crystallographic directions [001] and [$\bar{1}$10] are shown in Figures 1 and 2, respectively. The sulfur atoms are not drawn as they occupy the vertices of the tetrahedra in both diagrams. The numbering system refers to atoms between which interatomic distances and angles have been calculated. These are listed in Table III.

---

(5) G. M. Clark and W. P. Doyle, *J. Inorg. Nucl. Chem.*, **28**, 381 (1966).

(6) G. Gattow, A. Franke, and A. Mueller, *Naturwissenschaften*, **52**, 428 (1965).

(7) J. D. H. Donnay and G. Donnay, Ed., "Crystal Data," ACA Monograph No. 5, 2nd ed, American Crystallographic Association, Washington, D. C., 1963, p 1300.

(8) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1965, pp 172, 209.

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

(10) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1965, p 202.

(11) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(12) D. T. Cromer, *ibid.*, **18**, 17 (1965).

TABLE II

CALCULATED AND OBSERVED STRUCTURE AMPLITUDES FOR $CuNH_4MoS_4$

| HKL | $\|F_c\|$ | $\sqrt{\Sigma\|F_c\|^2}$[a] | $\sqrt{\Sigma\|F_o\|^2}$[a] |
|---|---|---|---|
| 110 | 137.7 | 137.7 | 130.5 |
| 200 | 90.5 | 90.5 | 94.1 |
| 211 | 99.2 | 102.6 | 102.5 |
| 121 | 26.3 | | |
| 220 | 100.6 | 100.6 | 93.6 |
| 310 | 101.2 | 102.1 | 89.6 |
| 130 | 13.6 | | |
| 112 | 85.7 | 85.7 | 64.9 |
| 202 | 105.6 | 105.6 | 117.9 |
| 400 | 68.3 | 68.3 | 61.7 |
| 222 | 86.1 | 86.1 | 91.4 |
| 330 | 102.5 | 102.5 | 105.0 |
| 312 | 78.5 | 162.1 | 176.1 |
| 132 | 141.8 | | |
| 420 | 138.1 | 156.1 | 159.2 |
| 240 | 72.8 | | |
| 213 | 55.0 | 106.7 | 112.9 |
| 123 | 31.2 | | |
| 402 | 86.0 | | |
| 510 | 70.4 | 108.2 | 104.1 |
| 150 | 82.1 | | |
| 332 | 53.0 | 53.0 | 59.0 |
| 501 | 53.0 | 78.7 | 82.6 |
| 431 | 24.0 | | |
| 341 | 53.0 | | |
| 303 | 30.6 | 80.8 | 70.4 |
| 422 | 19.7 | | |
| 242 | 72.1 | | |
| 530 | 70.0 | 90.0 | 92.5 |
| 350 | 56.6 | | |
| *512 | 60.1 | 92.7 | 103.1 |
| *152 | 50.1 | | |
| *004 | 99.4 | | |
| 600 | 62.6 | 62.6 | 59.8 |
| 413 | 19.2 | 72.8 | 80.7 |
| 143 | 27.3 | | |
| 114 | 64.7 | | |
| 204 | 49.6 | 58.9 | 55.1 |
| 611 | 21.3 | | |
| 161 | 23.6 | | |
| 620 | 40.2 | 100.9 | 87.8 |
| 260 | 92.5 | | |
| 442 | 58.1 | 58.1 | 62.2 |
| 532 | 45.7 | 94.9 | 83.2 |
| 352 | 56.7 | | |
| 224 | 52.7 | | |
| 541 | 24.6 | | |
| 451 | 18.0 | | |
| 503 | 38.5 | 93.6 | 107.2 |
| 433 | 12.5 | | |
| 343 | 38.5 | | |
| 602 | 48.8 | | |
| 314 | 53.8 | | |
| 134 | 19.3 | | |
| 631 | 37.5 | 43.3 | 44.5 |
| 361 | 21.7 | | |
| 523 | 15.9 | 68.7 | 62.8 |
| 253 | 19.1 | | |
| 622 | 61.4 | | |
| 262 | 18.1 | | |
| 710 | 17.7 | 65.5 | 55.9 |
| 170 | 60.5 | | |
| 550 | 17.8 | | |
| 404 | 39.9 | 45.5 | 39.5 |
| 701 | 21.9 | | |
| 640 | 49.4 | 58.9 | 55.3 |
| 460 | 32.1 | | |
| 334 | 55.5 | 55.5 | 58.3 |
| 424 | 70.7 | 86.8 | 95.4 |
| 244 | 42.2 | | |
| 721 | 16.9 | | |
| 271 | 21.6 | | |
| 730 | 40.4 | 60.1 | 58.4 |
| 370 | 44.5 | | |
| 712 | 67.0 | 99.9 | 100.5 |
| 172 | 31.6 | | |
| 552 | 67.0 | | |
| 811 | 17.2 | 47.3 | 38.6 |
| 181 | 27.6 | | |
| 741 | 20.2 | | |
| 471 | 27.7 | | |
| 534 | 40.8 | 53.4 | 47.5 |
| 354 | 34.5 | | |
| 604 | 36.8 | 36.8 | 31.5 |
| 723 | 22.4 | 43.1 | 35.0 |
| 273 | 13.8 | | |
| 802 | 34.1 | | |
| 750 | 44.3 | 56.9 | 56.2 |
| 570 | 35.7 | | |

[a] The summations apply specifically to overlapped reflections. In all cases, the individual reflections which overlap to give a single recorded reflection have the same multiplicities (and so are equally weighted in the summation) except for the reflections indicated by asterisks in which case the individual reflections are weighted in the ratio of their multiplicities.

TABLE III

INTERATOMIC DISTANCES AND ANGLES IN $CuNH_4MoS_4$[a]

| | | | |
|---|---|---|---|
| | (i) Distances, Å | | |
| Mo–S(1) | 2.19 (3) | S(1)–S(3) | 3.86 (4) |
| Cu–S(1) | 2.31 (3) | S(1)–S(4) | 3.60 (4) |
| N(1)–S(1) | 3.48 (3) | S(1)–S(2′) | 3.60 (4) |
| N(1)–S(2) | 3.68 (3) | S(1)–S(3′) | 3.60 (4) |
| N(1)–S(3) | 3.82 (3) | S(2)–S(3′) | 3.68 (4) |
| S(1)–S(2) | 3.58 (4) | S(2′)–S(3) | 3.68 (4) |
| | (ii) Angles, Deg | | |
| S(1)–Mo–S(4) | 110 (1) | S(2)–S(1)–S(3) | 93 (2) |
| S(1)–Mo–S(2) | 110 (1) | S(2′)–S(1)–S(3′) | 97 (2) |
| S(1)–Cu–S(4) | 102 (1) | S(2)–S(1)–S(3′) | 62 (2) |
| S(1)–Cu–S(3) | 113 (1) | S(2′)–S(1)–S(3) | 59 (2) |

[a] Standard deviations occurring in the last digit quoted for each distance and angle are given in parentheses.

Each metal atom is coordinated tetrahedrally with four sulfur atoms. The Mo–S distance is 2.19 (3) Å and the six S–Mo–S bond angles all have values of 110 (1)°. The Cu–S distance is 2.31 (3) Å and the six S–Cu–S bond angles consist of two equivalent values of 102 (1)° and four equivalent values of 113 (1)°. While the crystallographic symmetry of these different tetrahedra within this structure is only $\bar{4}$, the observed symmetry does not deviate significantly from that of a regular tetrahedron. These tetrahedral metal–sulfur bond values are comparable with those reported elsewhere for Cu[13] and Mo,[14] although no structures appear to have been studied fully in the case of the latter.

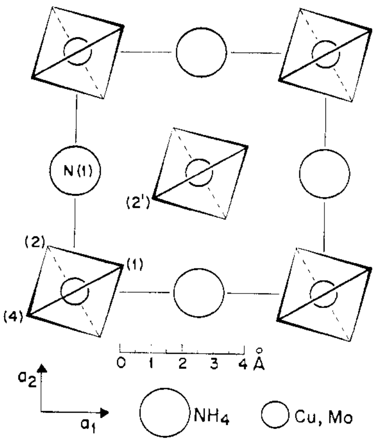

Figure 1.—A unit cell projection of the structure of $CuNH_4MoS_4$ along the [001] direction. Sulfur atoms are located at the vertices of the tetrahedra.

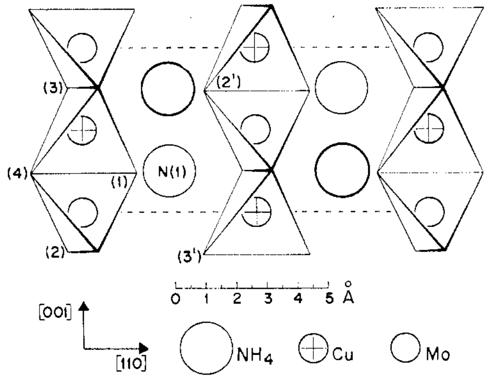

Figure 2.—A projection of the structure of $CuNH_4MoS_4$ along the [$\bar{1}10$] direction. Sulfur atoms are located at the vertices of the tetrahedra.

These different tetrahedra are stacked alternately along the *c* direction, each one sharing opposite edges with two neighboring tetrahedra to form infinite anionic chains. The electric charges on these chains are balanced by ammonium ions distributed between them. The periodicity along the chains is 5.409 Å, the *c* dimension. This same distance is found approximately as a unit cell parameter for such diverse compounds as $SiS_2$, $Cu_3VS_4$, and $KFeS_2$,[15] all of which have sulfur tetrahedra linked in this manner.

Packing contacts exist between neighboring chains and between chains and the ammonium ions. Between neighboring chains, the S–S distances for any sulfur atom consist of two equivalent values of 3.60 (4) Å and two equivalent values of 3.68 (4) Å. These are not significantly different from the average nonbonded distance between sulfur atoms within a chain, namely 3.68 (4) Å, and represent the van der Waals diameter of sulfur.[16] The smallest N–S distances are four equiv-

---

(13) L. Pauling and R. Hultgren, *Z. Kristallogr. Kristallogeometric Kristallphys. Kristallochem.*, **84**, 204 (1933).

(14) K. Sasvari, *Acta Crystallogr.*, **16**, 719 (1963).

(15) J. W. Boon and C. H. MacGillavry, *Rec. Trav. Chim. Pays-Bas*, **61**, 910 (1942).

(16) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

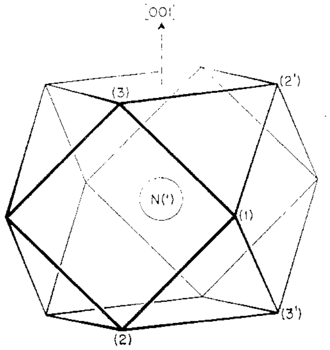

Figure 3.—A perspective view of the distribution of sulfur atoms around an ammonium ion, identifying the [001] direction. The sulfur atoms are located at the vertices of the slightly distorted cuboctahedron.

alent values of 3.48 (3) Å. In addition, there are two sets of four equivalent distances at the larger values of 3.68 (3) and 3.82 (3) Å. While the shortest N–S distance suggests the possibility of N–H· · ·S hydrogen bonds,[17] the angular distribution of these sulfur atoms about the ammonium ion is not favorable for their formation. The larger N–S distances are somewhat greater than the sum of the van der Waals radii of sulfur and nitrogen.[16] The four sulfur atoms nearest any nitrogen lie 0.10 Å in the [001] direction from the corners of a square, the plane of which is parallel to (001) and contains the nitrogen atom. These four sulfur atoms and the other eight can be considered as residing at the vertices of an approximate cuboctahedron which is slightly elongated in the *c* direction and surrounds the ammonium ion, as shown in Figure 3. The cuboctahedra and the tetrahedra share edges only, giving rise to open packing of polyhedra in this structure.[18]

The corresponding tungstate could not be prepared using any of the methods mentioned above. Neither could a nickel, cobalt, or silver ammonium thiomolybdate be obtained. Attempts were made to prepare a cuprous sodium or potassium thiomolybdate using method iii. Sodium or potassium thiomolybdate solutions were prepared by passage of hydrogen sulfide into a solution of molybdenum trioxide in caustic soda or potash. To these were added freshly precipitated cupric sulfide; a deeply colored liquid resulted. Acidification to pH 5 gave a reddish precipitate, difficult to filter, as reported by Debray.[2] The phases present in these precipitates could not be identified by X-ray diffraction due to poor crystallinity. Chemical analysis was not meaningful as the precipitates could not be washed well. Reduction of the cupric copper had probably taken place in the dissolution process. This does not appear to be the case when a 5% excess of cupric sulfate solution is added to ammonium thiomolybdate solution to form a black precipitate. Clark and Doyle[5] showed that this was not cupric thiomolybdate, $CuMoS_4$, as thought by Berzelius[19] but presumably a mixture of molybdenum and cupric sulfides. An unreported and unexplained event in this precipitation is that the pH drops to a final value of 2.0.

**Acknowledgments.**—We wish to thank Dr. W. W. Harvey for helpful discussions, Dr. R. H. Duff for taking the electron diffraction plates, J. R. Carter for assistance with the measurement of X-ray films, and S. I. Andersen for help with the chemical analysis.

(17) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, Inc., New York, N. Y., 1968, p 167.

(18) A. F. Wells, *Acta Crystallogr.*, **7**, 545 (1954).

(19) J. J. Berzelius, *Poggendorffs Ann.*, **7**, 261 (1826).

---

Contribution from the Departments of Chemistry, Wellesley College, Wellesley, Massachusetts 02181, and
Wayne State University, Detroit, Michigan 48202

# The Crystal and Molecular Structure of Hexadecaborane(20)

By LAWRENCE B. FRIEDMAN,[1a] RICHARD E. COOK,[1b] and MILTON D. GLICK[1b]

*Received June 30, 1969*

The boron hydride hexadecaborane(20), $B_{16}H_{20}$, crystallizes in the monoclinic space group $P2_1/c$ with $a = 5.849$ (9), $b = 13.67$ (2), $c = 16.75$ (3) Å, $\beta = 100.83$ (5)°, $Z = 4$, and $\rho_{\text{calcd}} = 0.975$ g/cm³. The $B_{16}H_{20}$ molecule may be described as an unsymmetrical fusion of a $B_{10}$ icosahedral fragment with a $B_8$ icosahedral fragment in which the component fragments open in opposite directions and, as such, is the first example of a neutral boron hydride without molecular symmetry. The structure was solved by direct methods and refined by least squares to a conventional $R$ factor of 5.4% for 1095 reflections which were collected by counter methods. Mechanisms for the formation of $B_{16}H_{20}$, chemical properties of $B_{16}H_{20}$, and possible new fused fragment boron hydrides are discussed.

## Introduction

The structures of 12 neutral boron hydrides have been determined[2] previously, and in ten of these compounds (all but $B_5H_9$ and $B_{10}H_{16}$) the boron atoms are arranged such that the frameworks, or portions thereof,

(1) (a) Department of Chemistry, Wellesley College, Wellesley, Mass. 02181; (b) Department of Chemistry, Wayne State University, Detroit, Mich. 48202.

(2) (a) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963; (b) R. M. Adams in "Boron, Metallo-Boron Compounds and Boranes," Interscience Publishers, New York, N. Y., 1964; (c) M. F. Hawthorne in "The Chemistry of Boron and Its Compounds," John Wiley and Sons, Inc., New York, N. Y., 1967.