JOURNAL OF SOLID STATE CHEMISTRY 9, 6–14 (1974)

Structural Chemistry of Ba_2CdS_3, Ba_2CdSe_3, $BaCdS_2$, $BaCu_2S_2$ and $BaCu_2Se_2$*

J. E. IGLESIAS,† K. E. PACHALI‡ AND H. STEINFINK

Materials Science Laboratories, Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712

Received January 29, 1973

The structures of all compounds were determined from three dimensional single crystal X-ray diffraction data and refined by least squares. Ba_2CdS_3 and Ba_2CdSe_3 are isostructural, *Pnma*, $a = 8.9145(6)$ Å, $b = 4.3356(2)$ Å, $c = 17.2439(9)$ Å for the former compound and $a = 9.2247$ Å, $b = 4.4823(6)$ Å, $c = 17.8706(11)$ Å for the latter, $z = 4$, $R = 0.0751$ and $R = 0.0462$, respectively. The compounds are isostructural with the previously reported Mn analogues and with K_2AgI_3. Cd ions are in tetrahedral environment and the tetrahedra form infinite linear chains by corner sharing. Ba ions are in 7-fold coordination in which 6 anions form a trigonal prism and 1 anion caps one of the rectangular faces. $BaCdS_2$, *Pnma*, $a = 7.2781(3)$ Å, $b = 4.1670(1)$ Å, $c = 13.9189(6)$ Å, $z = 4$, $R = 0.0685$. Cd ions can be considered to have a triangular planar coordination with Cd–S distances of 2.47 and 2.53 Å (twice). Two additional S ions are at 2.89 and 3.22 Å to complete a triangular bipyramidal configuration. Ba is in 7-fold coordination with the anions forming a trigonal prism which is capped on one rectangular face. The compound is isostructural with $BaCdO_2$ and is related to the structure of $BaMnS_2$. $BaCdSe_2$ could not be prepared. $BaCu_2S_2$ and $BaCu_2Se_2$ are isostructural, *Pnma*, $a = 9.3081(4)$ Å, $b = 4.0612(3)$ Å, $c = 10.4084(5)$ Å for the sulfide and $a = 9.5944(6)$ Å, $b = 4.2142(4)$ Å, $c = 10.7748(8)$ Å for the selenide, $z = 4$, $R = 0.0634$ and 0.0373, respectively. Ba ions are in the usual 7-fold, capped hexagonal prism, coordination. However, 9 Cu ions also can be considered to form a trigonal prism with all rectangular faces capped, around Ba since the Ba–Cu distances range from 3.24 to 3.54 Å for the sulfide and from 3.37 to 3.67 Å for the selenide. One of the Cu ions is in a very distorted tetrahedral environment and the second one is located in a more regular tetrahedral configuration of the anions. Two independent infinite chains of tetrahedra are present. They are formed by sharing of two adjacent edges of each tetrahedron and then these chains in turn are linked by corner sharing into a three-dimensional network of tetrahedra.

Introduction

In our investigation of the crystal chemistry of barium-transition metal chalcogenides we have reported on the structural features of Ni (*1*), Mn (*2*), Co (*2, 3*), Fe (*3, 4*), and Cu (*5*) containing compounds. In the continuation of this work we have investigated additional phases which form with Cd and with Cu and we report here the structures of Ba_2Cds_3, Ba_2CdSe_3, $BaCdS_2$, $BaCu_2S_2$, and $BaCu_2Se_2$.

Ba_2CdS_3, Ba_2CdSe_3, $BaCdS_2$

Mixtures of 2BaS:CdS and 2BaSe:CdSe were heated in evacuated Vycor ampoules and single phase Ba_2CdX_3 was obtained for the sulfide between 1000 and 1200°C and for the selenide between 700 and 900°C. Single phase material of $BaCdS_2$ was obtained by heating a mixture BaS:CdS at 900°C for 3 wk and many crystals with average dimensions of 0.2 mm were found in the reaction product. Similar attempts at synthesizing $BaCdSe_2$ at various temperatures resulted always in Ba_2CdSe_3 and CdSe.

Ba_2CdSe_3 single crystals grew as flat needles, needle axis [010], which are light brown in transmitted light and have a somewhat metallic luster when observed in reflected light. The color ranges to light olive green upon grinding. Ba_2CdS_3 crystals are also acicular and tend to form massive aggregates. Their color is light

---

* Research supported in part by the Robert A. Welch Foundation, Houston, TX, and in part by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Grant No. AFOSR 72-2199.

† Present address: Departmento Fisica del Solido, Universidad Autonoma, Bilbao, Spain.

‡ Present address: Institut fur Anorganische Chemie, Universitat Stuttgart, 7 Stuttgart 1, Schellingstrasse 26, Germany.

yellow in transmitted light and yellow in reflected light while the powder is almost white. The X-ray diffraction powder patterns of these two compounds were very similar indicating that they might be isotypic.

The crystals of $BaCdS_2$ are light yellow in transmitted and reflected light and the powder is also yellow. The crystals grow in columns slightly elongated along [010].

Weissenberg and Buerger precession photographs of these three compounds showed the diffraction symmetry *mmm* with systematic absences $0kl$, $k + l = 2n + 1$, $hk0$, $h = 2n + 1$, consistent with the space groups *Pnma* and $Pn2_1a$. Lattice constants were obtained from single crystal diffraction maxima using a three circle diffractometer, $MoK\alpha_1$ and $MoK\alpha_2$ radiation ($\lambda_1 = 0.70926$ Å, $\lambda_2 = 0.71354$ Å), and the instrument set at a take-off angle of 1° and a 0.05° slit in front of the aperture of the scintillation counter. For Ba_2CdSe_3 38 measurements of 2θ were made and a least squares fit of the data yielded $a = 9.2247(9)$ Å, $b = 4.4823(6)$ Å, $c = 17.8706(11)$ Å. For Ba_2CdS_3, 34 2θ values were measured and a least squares refinement of the data yielded $a = 8.9145(6)$ Å, $b = 4.3356(2)$ Å, and $c = 17.2439(9)$ Å. The lattice parameters and possible space groups are very similar to those observed for Ba_2MnSe_3 and Ba_2MnS_3, respectively (*2*), indicating that all these compounds might have the same structure. For $BaCdS_2$ 44 values of 2θ were used in the least squares refinement and $a = 7.2781(3)$ Å, $b = 4.1670(1)$ Å, $c = 13.9189(6)$ Å.

For Ba_2CdSe_3 and Ba_2CdS_3 three dimensional X-ray diffraction intensity data to $\sin\theta/\lambda = 0.60$ and 0.54, respectively, were collected with $MoK\alpha$ radiation by the stationary crystal–stationary counter technique, using balanced filters, a 5° take-off angle, no slit in front of the counter window, and with the channel width of the pulse height analyzer set to accept 85% of the incident energy. The mosaic spreads of the crystals, evaluated from an ω scan, were 0.7 and 0.9° measured at the base of the peaks. Intensities were counted for 20 sec with a Zr filter and then background was measured for 20 sec with an Y filter. A total of 742 independent reflections were measured for the selenide and 649 of them were considered as observed on the basis that the peak count exceeded the background count by 9 counts. For the sulfide 506 independent reflections were measured and 27 were considered unobserved. The measured intensities were transformed into a set of structure amplitudes after Lorentz, polarization and absorption corrections were applied. The shape of the Ba_2CdSe_3 crystal, $0.04 \times 0.02 \times 0.28$ mm, was approximated by six planes, and the transmission factor varied between 0.433 and 0.550 ($\mu_l = 296 cm^{-1}$, $\rho_x = 5.61$ g/cc). The shape of the sulfide crystal, approximately $0.10 \times 0.10 \times 0.20$ mm, was described by eight planes and the transmission factors ranged between 0.238 and 0.316, ($\mu_l = 159$ cm^{-1}, $\rho_x = 4.82$ g/cc).
The Eq. (6)

$$\sigma(|F|) = \frac{1}{2}\left[K\frac{1 + b}{1 - b}\right]^{1/2}$$

where $b = I_y/I_{Zr}$ is the background to peak ratio and K is the product of the absorption, Lorentz and polarization corrections, was used to estimate the standard deviation of the observed structure factor amplitudes. For unobserved reflections, the standard deviation was set at $|F|/\sqrt{2}$ and $|F|$ was computed by assuming the intensity to be 4.5 counts above background and applying to this the corresponding corrections.

For $BaCdS_2$ three-dimensional intensity data were collected with a linear diffractometer by the stationary counter-moving crystal technique, with $MoK\alpha_1$ radiation monochromatized with a graphite single crystal. The crystal was aligned so that the spindle axis of the machine was parallel to the *b* axis. For each reflection the intensity was integrated by rotating ω at the rate of 1°/min. The interval of integration ranged from 3 to 6° for reflections having $\Upsilon \leqslant 15°$ and from 3 to 4° for those having $\Upsilon \geqslant 15°$. Background intensities were counted at both ends of the interval of integration for 60 sec. When the integrated intensity was less than 10^4 counts, the same ω scan was repeated once more. The intensities were measured using a circular receiving aperture 3° wide in front of the scintillation counter. The channel width of the pulse height analyzer was set to accept 85% of the incident power. Five reciprocal lattice layers were explored, $h0l$ to $h4l$. The maximum Υ angle was set to 58° and 711 independent reflections were measured. The intensities were transformed into structure factor amplitudes through the application of absorption, Lorentz and polarization corrections. For the absorption correction the crystal, approximately $0.06 \times 0.09 \times 0.22$ mm, was described by six planes and the transmission factor varied from 0.260 to 0.416, $\mu_l = 152$ cm^{-1}.

TABLE I

ATOMIC PARAMETERS AND STANDARD DEVIATIONS (IN PARENTHESES) FOR $Ba_2CdSe_3 \times 10^{4a}$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ba1	4225(1)	1/4	7146(1)	22(1)	97(6)	8(0)	0	0(1)	0
Ba2	2605(1)	1/4	4593(1)	29(1)	107(6)	7(0)	0	−1(1)	0
Cd	3756(1)	1/4	1328(1)	21(2)	124(8)	8(1)	0	1(1)	0
Se1	3129(2)	1/4	2766(1)	29(2)	126(11)	6(1)	0	−1(1)	0
Se2	1179(2)	1/4	721(1)	22(2)	130(11)	7(1)	0	−1(1)	0
Se3	9857(2)	1/4	5961(1)	23(2)	64(10)	8(1)	0	−3(1)	0

[a] The temperature factor is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

The basis (*7*) for accepting a reflection as statistically nonzero was $\Delta I/I \leqslant 0.50$ where

$$\frac{\Delta I}{I} = \frac{(T+t^2B)^{1/2}}{(T-tB)}$$

with T = total counts in time t_T for the ω scan, B = total background counts, $t = t_{T/t_1+t_2}$ where t_1 and t_2 are background counting times (in this case, $t_1 = t_2 = 60$ sec). Of the 711 independent reflections, 612 satisfied this criterion. The standard deviations for the structure factor amplitudes were estimated by the formula

$$\sigma(|F|) = \left[\left(\frac{|F|}{2I}\right)^2 \left[I + \frac{Bt}{2} + 0.0004(I)^2\right]\right]^{1/2}$$

and $1/\sigma^2(|F|)$ were used as weights in the least squares calculations.

TABLE II

ATOMIC PARAMETERS AND STANDARD DEVIATIONS (IN PARENTHESES) FOR Ba_2CdS_3

	x	y	z	B(Å^2)
Ba1	4203 (2)	1/4	7151(1)	0.43(4)
Ba2	2649 (2)	1/4	4575(1)	0.45(4)
Cd	3782 (3)	1/4	1307(1)	0.57(5)
S1	3170(10)	1/4	2741(5)	0.3 (1)
S2	1242(10)	1/4	717(5)	0.2 (1)
S3	9838(10)	1/4	5954(5)	0.2 (1)

Structure Determination

The atomic parameters reported for Ba_2MnSe_3 were used as input for a least-squares calculation. A few cycles of refinement of all positional and anisotropic thermal parameters as well as the scale factor gave $R = 0.0300$, $wR = 0.0360$ ($R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$, $wR = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w F_0{}^2]^{1/2}$, $w = 1/\sigma^2$). The 93 unobserved reflections, and the 7 reflections with strongest intensity were excluded from the refinement. The standard deviation of a reflection of unit weight was 1.167. A structure factor calculation using the final atomic parameters gave $R = 0.0462$ for all 742 measured reflections. The scattering factors were those listed in the "International Tables" (*8*) and they were corrected for the real and imaginary part of the dispersion term. The observed and calculated structure amplitudes are available.[1] The final atomic parameters are listed in Table I.

The atomic parameters reported for Ba_2MnS_3 were used as starting parameters for a least squares refinement. Several cycles of refinement on the positional and isotropic thermal parameters gave $R = 0.0607$ and $wR = 0.0690$. Unobserved reflections and 17 reflections with highest intensity values were excluded from the refinement. The standard deviation of a reflection of unit weight was 1.026. A structure factor calculation based on the final parameters gave $R = 0.0751$ for all 506 measured reflections. The

---

[1] A table of observed and calculated structure factors has been deposited as Document No. NAPS-02102 with the ASIS National Auxiliary Publications Service, c/o Michrofiche Publications, 305 E. 46th St., New York, NY 10017. A copy may be secured by citing the document number and by remitting $5.00 for photocopies or $1.50 for microfiche. Advance payment is required. Make check or money order payable to ASIS-NAPS.

TABLE III

ATOMIC PARAMETERS AND STANDARD DEVIATIONS (IN PARENTHESES) FOR $BaCdS_2 \times 10^{4a}$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ba	1343(1)	3/4	3576(0)	32(1)	86(5)	9(0)	0	−0(0)	0
Cd	1226(2)	1/4	1089(1)	119(2)	148(6)	23(1)	0	38(1)	0
S1	3988(4)	1/4	2576(2)	11(5)	87(17)	8(1)	0	−1(2)	0
S2	2387(4)	3/4	250(2)	53(5)	50(15)	7(1)	0	5(2)	0

[a] The temperature factor is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

scattering factors used were those in the International Tables for neutral atoms, uncorrected for dispersion. The observed and calculated structure amplitudes are available.[1] The final atomic parameters are shown in Table II.

The structure of $BaCdS_2$ is isostructural with $BaCdO_2$ (*9*) but this was not initially recognized and the direct method of phase determination was used in the solution of the structure. Atomic parameters were obtained from a three-dimensional E map and refined by least squares. A few cycles of refinement of the positional and anisotropic thermal parameters yielded $R = 0.0481$ and $wR = 0.0577$. The standard deviation of a reflection of unit weight is 0.959. The scattering factors were taken from the "International Tables" (*8*) for neutral atoms. A structure factor calculation using the parameters obtained in the previous refinement gave $R = 0.0685$ for all 711 measured reflections. The final atomic parameters are shown in Table III. The observed and calculated structure factor amplitudes are available.[1]

Discussion of the Structures

Ba_2CdS_3 and Ba_2CdSe_3 are isostructural with Ba_2MnS_3 and Ba_2MnSe_3 (*2*), which in turn were found to be isotypic with K_2AgI_3 (*10*). The most important interatomic distances are tabulated in Tables IV and V.

The structure of $BaCdS_2$ projected on the (010) plane is shown in Fig. 1a. The most significant interatomic distances are presented in Table VI. Ba is in sevenfold coordination with respect to S, with the usual trigonal prismatic configuration in which the seventh S atom is close

TABLE IV

INTERATOMIC DISTANCES AND ANGLES FOR Ba_2CdS_3 (STANDARD DEVIATIONS IN PARENTHESES)

Distances (Å)			
Ba1–2S1	3.19 (1)	Ba2–S1	3.20 (1)
2S1	3.20 (1)	S2	3.24 (1)
2S2	3.31 (1)	2S2	3.09 (1)
S3	3.32 (1)	S3	3.45 (1)
2Ba1	4.336(4)	2S3	3.23 (1)
Ba2	4.629(4)	2Ba2	4.336(4)
2Cd	3.728(5)	Cd	3.767(5)
Cd–S1	2.53 (1)		
S2	2.48 (1)		
2S3	2.57 (1)		
	Angles(°)		
	S1–Cd–S2	101.7(4)	
	2(S1–Cd–S3)	109.6(4)	
	2(S2–Cd–S3)	109.8(4)	
	S3–Cd–S3	115.3(4)	

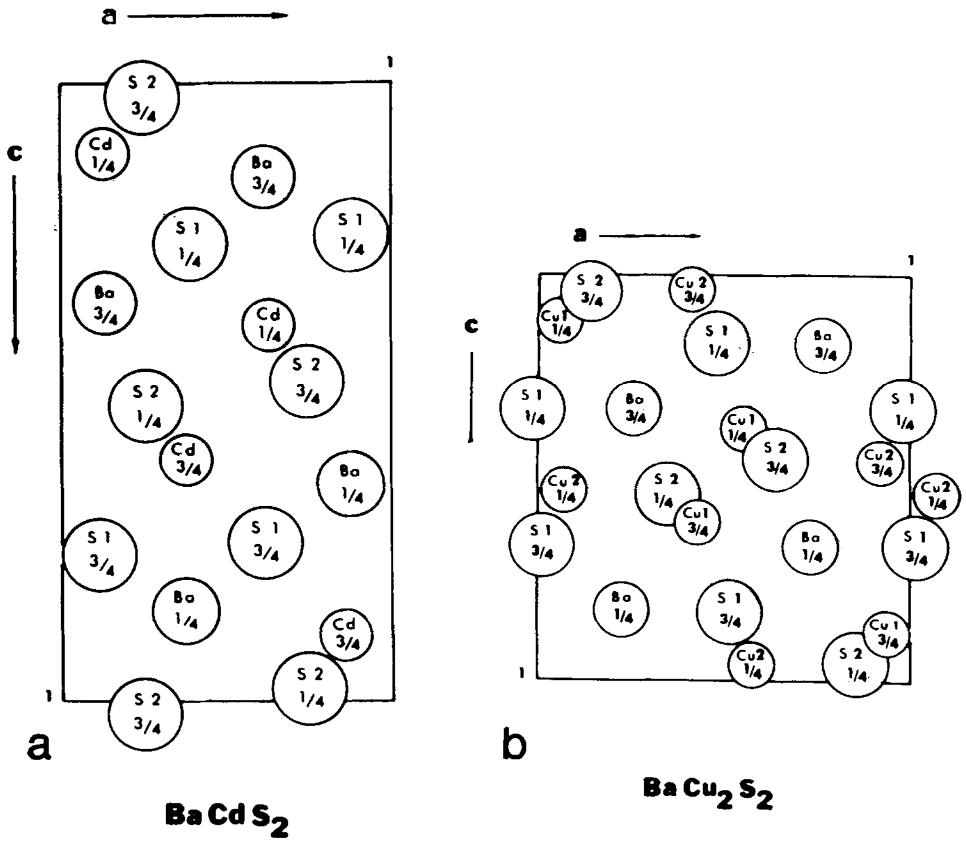

FIG. 1. (a) The projection of the structure of $BaCdS_2$ on (010). (b) The projection of the structure of $BaCu_2S_2$ on (010). The numbers denote the value of the *y* parameter.

TABLE V

INTERATOMIC DISTANCES AND ANGLES FOR Ba_2CdSe_3 (STANDARD DEVIATIONS IN PARENTHESES)

Distances (Å)			
Ba1–2Se1	3.312(3)	Ba2–Se1	3.302(3)
2Se1	3.317(3)	Se2	3.344(3)
2Se2	3.413(3)	2Se2	3.216(3)
Se3	3.433(3)	Se3	3.521(3)
2Ba1	4.482(2)	2Se3	3.341(3)
Ba2	4.801(2)	2Ba2	4.482(2)
2Cd	3.837(3)	Cd	3.914(3)
Cd–Se1	2.634(3)		
Se2	2.613(3)		
2Se3	2.663(3)		

Angles (°)	
Se1–Cd–Se2	101.8(1)
2(Se1–Cd–Se3)	110.2(1)
2(Se2–Cd–Se3)	109.6(1)
Se3–Cd–Se3	114.6(1)

TABLE VI

INTERATOMIC DISTANCES AND ANGLES FOR $BaCdS_2$ (STANDARD DEVIATIONS IN PARENTHESES)

Distances (Å)			
Ba–2S1	3.160(4)	Cd–S1	2.471(4)
2S1	3.138(4)	S1	2.885(4)
2S2	3.259(4)	2S2	2.533(5)
S2	3.311(4)	S2	3.223(5)
Cd	3.920(2)	Cd	4.089(2)
Ba	4.167(1)		

Angles (°)	
S1–Cd–S1	85.4(1)
S1–Cd–S2	84.1(1)
2(S1–Cd–S2)	95.6(1)
2(S2–Cd–S2)	90.3(1)
S2–Cd–S2[a]	110.7(2)
2(S1–Cd–S2)[a]	124.5(1)
S1–Cd–S2	169.5(1)

[a] S–Cd–S angles for the triangular planar configuration.

to one of the rectangular faces of the trigonal prism. The Ba to S distance ranges between 3.14 and 3.31 Å. Cd is close to three S atoms, with Cd–S distances of 2.47 and 2.53 Å (twice) in such a way that the coordination could be described as approximately triangular planar; the sum of the three S–Cd–S angles is 359.7°. There are, however, 2 more S atoms at 2.89 and 3.22 Å which complete a triangular bipyramidal configuration around Cd. The coordination polyhedron around Cd could also be described as a tetrahedron, with the Cd atom located almost at the center of one of the tetrahedral faces, if one decides not to consider the 3.22 Å Cd–S approach as a bonded distance. The thermal vibration of the Cd atom is extremely anisotropic. The long axis of the thermal ellipsoid is perpendicular to the plane defined by the three closest S atoms and has a root mean square deviation of 0.22 Å. This effect could be the result of thermal vibration which is easier in the direction of the axis of the triangular bipyramid, or could perhaps be due to some disorder in the Cd location. A similar effect has been observed for Cu in triangular planar and quasitetrahedral configurations in $BaCu_4S_3$ (*5*).

The BaS_6 trigonal prisms share the triangular faces with other prisms, and the infinite tubes thus formed share two of the prismatic edges in such a way that an infinite sheet of prisms is formed. The sheets are stacked along the *c* axis in such a way that the unshared vertices of the triangular faces of the prisms in one sheet become the caps of the trigonal prisms in the next sheet.

$BaCdS_2$ is isostructural with $BaCdO_2$ and is also related to the structure of $BaMnS_2$ (*11*) which has the $SrZnO_2$ structure type. Both types are very similar to each other in the overall arrangement of the Ba-anion trigonal prisms but in the $SrZnO_2$ structure type the transition metal is clearly tetrahedral which has the effect of keeping the transition metals far away from each other.

$BaCu_2S_2$, $BaCu_2Se_2$

During the preparation of $BaCu_4S_3$ (*5*) a crystal was found in one of the products with lattice parameters different from those of α-$BaCu_4S_3$ or β-$BaCu_4S_3$. A single crystal structure analysis eventually showed the formula to be $BaCu_2S_2$. Several attempts to prepare the sulfide as a single phase proved fruitless. $BaCu_2Se_2$ can be, however, prepared as a single phase material by heating a stoichiometric mixture at 1000° for 3 days and cooling slowly to room temperature. Single crystals of $BaCu_2S_2$ are orange red in transmitted light and metallic black when viewed in reflected light. $BaCu_2Se_2$ crystals are almost opaque and metallic black in reflected light.

Single crystals of both compounds were selected and sets of X-ray diffraction photographs showed for both the symmetry *mmm*, with systematic absences consistent with space groups *Pnma* and $Pn2_1a$. The lattice parameters were obtained by a least squares fit of sets of 2θ measurement taken under the conditions described previously for Ba_2CdSe_3. For $BaCu_2S_2$ 32 measurements were used, $34° \leqslant 2\theta \leqslant 52°$, and the parameters are $a = 9.3081(4)$ Å, $b = 4.0612(3)$ Å, $c = 10.4084(5)$ Å; for $BaCu_2Se_2$ 30 values were used, $38° \leqslant 2\theta \leqslant 54°$, which yielded the parameters $a = 9.5944(6)$ Å, $b = 4.2142(4)$ Å, and $c = 10.7748(8)$ Å.

Three-dimensional X-ray diffraction intensity data were collected for both compounds to $\sin\theta/\lambda = 0.65$ using Mo*Kα* radiation and the experimental conditions described above for Ba_2CdSe_3. Peak widths were about 0.7° for both crystals. A total of 515 independent reflections was measured for $BaCu_2S_2$, and 453 of them were considered as nonzero, ($I > 8$ counts in 20 sec). For $BaCu_2Se_2$, a total of 572 independent reflections was obtained, and 512 were taken as observed on the basis of the above criterion. The intensities were corrected for absorption, and Lorentz and polarization corrections. For the absorption correction the $BaCu_2S_2$ crystal, 0.20 × 0.09 × 0.20 mm, was approximated by six planes and the transmission factor varied between 0.460 and 0.605, $\mu_l = 220$ cm^{-1}. For the needle shaped $BaCu_2Se_2$ crystal, 0.20 × 0.05 × 0.34 mm, the shape was described by six planes and the transmission factor ranged between 0.244 and 0.498, $\mu_l = 369$ cm^{-1}. Standard deviations for the observed structure factor amplitudes were estimated as above for Ba_2CdSe_3.

Structure Determination

a. $BaCu_2S_2$

A Wilson plot indicated that the intensities followed a centric distribution, and correspondingly the space group was chosen as *Pnma.* Iterative application of the symbolic addition method (*12*) produced 233 signed *E*'s in terms of five symbolic phases. The *E* map corresponding to the sign combination producing the minimum number of inconsistencies showed three peaks which could be identified as one Ba and two Cu atoms. An electron density map phased on these three atomic positions showed clearly two more peaks which were interpreted as S atoms. Several cycles of least squares refinement of all positional and anisotropic thermal parameters gave a final $R = 0.0410$ and $wR = 0.0564$ for 439 reflections. The standard deviation of a reflection of unit weight was 1.847. A structure calculation using these final parameters gave $R = 0.0634$ for all 515 reflections. The atomic scattering factors used were those listed in the International Tables (8) for neutral atoms. An electron density difference map showed no peak higher than 0.80 e/Å^3. The final atomic parameters are presented in Table VII. The observed and calculated structure factor amplitudes are available.[1]

b. $BaCu_2Se_2$

Since the lattice parameters and possible space groups were extremely similar to those of $BaCu_2S_2$, the assumption was made that both compounds were isostructural.

The atomic parameters of $BaCu_2S_2$ were used as starting parameters in a least squares refinement. The structure refined in a few cycles to

TABLE VII

ATOMIC PARAMETERS AND STANDARD DEVIATIONS (IN PARENTHESES) FOR $BaCu_2S_2 \times 10^{4\,a}$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ba	2599(1)	$\frac{3}{4}$	3224(1)	20(1)	119(7)	21(1)	0	−2(1)	0
Cu1	564(3)	$\frac{1}{4}$	1108(2)	23(3)	126(15)	22(2)	0	9(2)	0
Cu2	4171(3)	$\frac{3}{4}$	445(2)	14(3)	243(17)	22(2)	0	2(2)	0
S1	4826(5)	$\frac{1}{4}$	1694(5)	16(5)	141(27)	15(4)	0	−5(1)	0
S2	1605(5)	$\frac{3}{4}$	390(5)	3(5)	175(30)	17(4)	0	−1(4)	0

[a] The temperature is $\exp -(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)$.

TABLE VIII

ATOMIC PARAMETERS AND STANDARD DEVIATIONS (IN PARENTHESES) × 10^4 FOR $BaCu_2Se_2$[a]

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ba	2591(1)	3/4	3228(1)	31(1)	120 (5)	19(1)	0	−2(1)	0
Cu1	557(2)	1/4	1098(2)	40(2)	158(11)	29(2)	0	10(1)	0
Cu2	4203(2)	3/4	446(2)	29(2)	210(11)	25(2)	0	3(1)	0
Se1	4805(1)	1/4	1697(1)	25(1)	102 (8)	13(1)	0	−0(1)	0
Se2	1605(1)	3/4	386(1)	22(1)	96 (7)	15(1)	0	−2(1)	0

[a] The temperature factor is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

$R = 0.0226$, $wR = 0.0346$ for 503 observed reflections and with these parameters $R = 0.0373$ for all 572 measured reflections. The standard deviation of a reflection of unit weight is 0.989. The atomic scattering factors were those for neutral atoms listed in the "International Tables" (*8*). The final atomic parameters are presented in Table VIII, and the observed and calculated structure factor amplitudes are available.[1]

Discussion of the Structures

The structure of $BaCu_2S_2$ is shown projected on the (010) plane in Fig. 1b. The most important interatomic distances and angles are presented in Tables IX and X. Ba is in the usual sevenfold coordination with respect to S, with Ba–S distances from 3.09 to 3.29 Å. The corresponding Ba–Se distances are 3.21 to 3.42 Å. The coordination polyhedron is a trigonal prism with one extra anion in front of one of the rectangular faces. There are nine Cu atoms around each Ba, arranged in a trigonal prismatic configuration with all three prismatic faces capped. Ba–Cu distances range between 3.24 and 3.54 Å for $BaCu_2S_2$, and between 3.37 and 3.67 Å for $BaCu_2Se_2$.

Cu1 is tetrahedrally coordinated by the anions, but the tetrahedron is very distorted due to the fact that the Cu atoms are very close to one of the tetrahedral faces, a feature frequently observed in Cu chalcogenides (*5*, *13*). The distances from Cu1 to the three S atoms on the closer tetrahedral face are 2.37 (twice) and 2.39 Å, while the

TABLE IX

INTERATOMIC DISTANCES AND ANGLES FOR $BaCu_2S_2$ (STANDARD DEVIATIONS IN PARENTHESES)

	Distances (Å)		
Ba–2S1	3.310(7)	Cu1–S1	2.389(7)
2S1	3.285(7)	S2	2.551(7)
2S2	3.123(7)	2S2	2.371(7)
S2	3.092(7)	2Cu1	3.247(5)
Cu1	3.454(4)	2Cu2	3.984(5)
2Cu1	3.496(4)		
2Cu1	3.544(4)	Cu2–S1	2.414(7)
Cu2	3.242(4)	2S1	2.487(7)
Cu2	3.479(4)	S2	2.389(7)
2Cu2	3.490(4)	2Cu2	2.714(5)
	Angles (°)		
S2–Cu1–S2	117.8(2)	S1–Cu2–S2	111.4(2)
2(S2–Cu1–S2)	97.5(2)	2(S1–Cu2–S2)	104.9(2)
2(S2–Cu1–S1)	114.8(2)	2(S1–Cu2–S1)	112.8(2)
S1–Cu1–S2	111.0(2)	S1–Cu2–S1	109.5(2)
Cu1–Cu1–Cu1	77.4(2)	Cu2–Cu2–Cu2	96.9(2)

TABLE X

INTERATOMIC DISTANCES AND ANGLES FOR $BaCu_2Se_2$ (STANDARD DEVIATIONS IN PARENTHESES)

Distances (Å)			
Ba–2Se1	3.405(2)	Cu1–Se1	2.483(3)
2Se1	3.416(2)	2Se2	2.458(3)
2Se2	3.231(2)	Se2	2.618(3)
Se2	3.205(2)	2Cu1	3.343(3)
Cu1	3.567(3)	2Cu2	4.144(3)
2Cu1	3.615(3)		
2Cu1	3.676(3)	Cu2–Se1	2.497(3)
Cu2	3.373(3)	Se2	2.494(3)
Cu2	3.551(3)	2Se1	2.567(3)
2Cu2	3.622(3)	2Cu2	2.775(3)
Angles (°)			
Se2–Cu1–Se2	118.1(1)	Se1–Cu2–Se2	110.9(1)
2(Se2–Cu1–Se2)	97.7(1)	2(Se1–Cu2–Se2)	103.8(1)
2(Se2–Cu1–Se1)	114.7(1)	2(Se1–Cu2–Se1)	113.6(1)
Se1–Cu1–Se2	110.7(1)	Se1–Cu2–Se1	110.3(1)
Cu1–Cu1–Cu1	78.1(1)	Cu2–Cu2–Cu2	98.8(1)

distance to the fourth S atom is 2.55 Å. The corresponding distances in the selenide are: 2.46 (twice) and 2.48 Å to the 3 closest Se atoms and 2.62 Å to the fourth one. The shortest Cu1–Cu1 approach is 3.25 Å, and the shortest Cu1–Cu2 distance is 3.98 Å. Cu2 is also tetrahedrally coordinated by S and Se, but the tetrahedral arrangement is not so severely distorted. Cu2–S distances vary between 2.39 and 2.49 Å, while the corresponding range for Cu2–Se distances is 2.49 to 2.57 Å. The closest Cu2–Cu2 approach is 2.76 Å.

As in the previously described structures, trigonal prisms of anions having Ba at the center, form infinite tubes by sharing the basal faces. The tubes in turn make up corrugated sheets roughly parallel to (001) by sharing two edges with neighboring tubes. The stacking of the sheets along the *c* axis occurs by sharing anions in such a way that the vertices of the triangular faces in one sheet become the caps of the trigonal prisms in the next sheet. This arrangement produces tetrahedral holes which are occupied by the Cu atoms. Cu2 atoms constitute a zigzag infinite chain of tetrahedra built by sharing of two adjacent edges of each tetrahedron. The Cu2–Cu2–Cu2 angle is 96.9° in $BaCu_2S_2$ and 98.8° in $BaCu_2Se_2$. A similar chain is built by Cu1, but now the metal atoms are farther away from each other (see Tables IX and X) and the Cu1–Cu1–Cu1 angles are 77.4 and 78.1°, respectively, for the sulfide and selenide. Both tetrahedral chains are linked by corner sharing, thus forming a three-dimensional network of tetrahedra.

References

1. I. E. GRAY AND H. STEINFINK, *J. Amer. Chem. Soc.* **92**, 5093 (1970).
2. I. E. GRAY AND H. STEINFINK, *Inorg. Chem.* **16**, 691 (1971).
3. H. Y. HONG AND H. STEINFINK, *J. Solid State Chem.* **5**, 93 (1972).
4. I. E. GRAY, H. HONG, AND H. STEINFINK, *Inorg. Chem.* **10**, 340 (1971).
5. J. E. IGLESIAS, K. E. PACHALI, AND H. STEINFINK, *Mater. Res. Bull.* **7**, 1247 (1972).
6. H. T. EVANS, *Acta Crystallogr.* **14**, 689 (1961).
7. M. MACK, *Norelco Rep.* **12**, 40 (1965).
8. "International Tables for X-ray Crystallography," Vol. 3. Kynoch Press, Birmingham, England (1962).
9. H. G. SCHNERING, *Z. Anorg. Allg. Chem.* **314**, 144 (1962).
10. C. BRINK AND H. A. KROESE, *Acta Crystallogr.* **5**, 433 (1952).
11. D. SCHMITZ AND W. BRONGER, *Naturwissenschaften* **58**, 322 (1971).
12. F. R. AHMED (Ed.), "Proceedings of the 1969 International Summer School on Crystallographic Computing." Munksgaard, Copenhagen (1970).
13. F. JELLINEK, *in* "Inorganic Sulphur Chemistry" (G. Nickless, Ed.), Chap. 19. Elsevier, Amsterdam (1968).