

## The Crystal Structure of Copper Bromide Triselenide, $\text{CuBrSe}_3$

HELMUT M. HAENDLER AND PHILIP M. CARKNER  
with SHARON MARTIN BOUDREAU AND ROBERT A. BOUDREAU

*Department of Chemistry, University of New Hampshire,  
Durham, New Hampshire 03824*

Received August 10, 1978

The crystal structure of  $\text{CuBrSe}_3$  has been determined. The compound is orthorhombic with unit cell dimensions  $a = 14.363 \text{ \AA}$ ,  $b = 4.488 \text{ \AA}$ ,  $c = 7.696 \text{ \AA}$ ,  $Z = 4$ , and space group  $Pmna$ . Three-dimensional counterdiffraction intensity data ( $\text{MoK}\alpha$ ) were refined with block-diagonal and full-matrix least squares to a conventional unweighted  $R$  of 0.0515. The structure consists of six-membered selenium rings, in a chair-type configuration, separated in one axial direction by rows of bromine atoms and in the other by staggered layers of copper and bromine atoms. The rings are parallel to one another in rows along the  $c$ -direction, but the rows of rings alternate orientation in the  $a$ -direction.

### Introduction

Several chalcogenide halides of copper, gold, mercury, and bismuth have been synthesized and characterized by Rabenau *et al.* (1). There are two homologous series of isotopic tellurium compounds (2), and structures of members of both series have been determined:  $\text{CuBrTe}$  (3),  $\text{CuITe}$  (4), and  $\text{CuClTe}_2$  (5). Three different selenium compounds have been reported (2):  $\text{CuISe}_3$ , rhombohedral;  $\text{CuBrSe}_3$ , orthorhombic; and  $\text{CuClSe}_2$ , monoclinic. The crystal structure of  $\text{CuBrSe}_3$  has been determined.

### Experimental

Single crystals of  $\text{CuBrSe}_3$  were synthesized by chemical transport (6), heating a mixture of  $\text{CuBr}$  and  $\text{Se}$  under vacuum in a Vycor tube in a temperature gradient of 340 to 290°C. The crystals are deep red and prismatic, elongated along the  $a$ -axial direction. Their identity was confirmed by

comparison of the X-ray powder diffraction data<sup>1</sup> (2).

The crystal used for intensity data collection was approximately  $0.06 \times 0.10 \times 0.04 \text{ mm}$ , along  $a$ ,  $b$ , and  $c$ , respectively. Rotation and Weissenberg photographs were taken of the crystal mounted along the  $c$ -axis and of a second crystal mounted along the  $b$ -axis, to confirm the symmetry and unit cell constants (2). The observed systematic absences also confirmed the space group given by Rabenau.

Intensity measurements, to  $2\theta = 60^\circ$ , were made at room temperature on a Syntex P2<sub>1</sub> automatic diffractometer with molybdenum radiation ( $\lambda = 0.71069 \text{ \AA}$ ), in the  $\theta/2\theta$  scanning mode. The background counting time was one-half the peak intensity scan time, and background readings were taken on both sides of the peak. Two reference

<sup>1</sup> The lattice constants listed in Table 3 of Ref. (2) must be read  $c$ ,  $a$ ,  $b$  from left to right to be consistent with the indexing given in Table 4 of that reference.

reflections remained constant during data collection. The crystal data are summarized in Table I.

### Structure Determination and Refinement

Seven hundred and sixty-two unique nonextinct reflections were scanned; 317 of these whose net intensity was greater than three times the standard deviation were classified as observed. The remaining 445 were treated as unobserved but allowable reflections. Reflections with negative intensity were set to zero. The data were corrected for Lorentz and polarization effects. An absorption correction was made, using a  $27 \times 8 \times 15$  grid (3240 sampling points). The value of  $A^*$ , by which the intensity was multiplied, ranged from 3.793 to 10.114. The scattering factors of Cromer and Waber (7) and Hanson *et al.* (8) were used.

Comparisons of  $E$ -statistics indicated a centrosymmetric structure, eliminating temporarily the alternate  $Pnc2(30)$  noncentrosymmetric space group. A triplet search, based on the tangent formula, of 128 reflections with  $|E|$  greater than 1.4 led to two reasonable triplets. The first of these signed about 40 of the 128 reflections; the second signed all of them. An  $E$ -map showed four outstanding peaks, one corresponding to eight equivalent general positions and three to three different sets of four special positions. Because of the similarity in scat-

tering factors of selenium and bromine, assignment of the sets of four was initially arbitrary. Block diagonal refinement with isotropic temperature factors gave  $R = 0.317$  ( $R = \sum |\Delta F| / \sum |F_0|$ ). A change in origin for copper led to an ultimate  $R = 0.076$ , and reversal of copper and bromine improved this to  $R = 0.062$ . At this stage a change was made to anisotropic temperature factors, giving a weighted  $R = 0.053$ .

A series of calculations was made with a full-matrix least-squares refinement program, using unit weights and isotropic temperature factors for all possible combinations of the three sets of four special positions. These results are shown in Table II. An analysis of the significance of these results was made by the method of Hamilton (9). This indicates that the position of the copper atom (4g) can be expressed at a significance level of about 98% relative to its exchange positions with either the bromine or the selenium (that in special positions). It is not possible to differentiate these bromine and selenium atoms on the basis of  $R$ -factors alone, but chemical and structural considerations indicate the appropriate assignments. Three cycles of full-matrix least-squares refinement, using 313 observed reflections, unit weights, and anisotropic temperature factors, converged on the parameters given in Table III, with  $R = 0.0515$ . The function minimized was  $\sum (|F_{0,rel}| - |F_c|/K)^2$ . A list of the observed and calculated structure factors is available from the authors.

TABLE I  
CRYSTAL DATA

Orthorhombic	$Z = 4$
$a = 14.363(15) \text{ \AA}$	$F(000) = 664$
$b = 4.488(4) \text{ \AA}$	$\mu (\text{MoK}\alpha) = 366.2 \text{ cm}^{-1}$
$c = 7.696(6) \text{ \AA}$	Observation conditions
$v = 496.158 \text{ \AA}^3$	$hk0: h = 2n$
$D_m = 5.10 \text{ g cm}^{-3}$ <sup>a</sup>	$h0l: h + l = 2n$
$D_c = 5.09 \text{ g cm}^{-3}$	Space group $Pmna(53)$

<sup>a</sup> Taken from Ref. (2).

TABLE II  
EFFECT OF ATOM LOCATIONS ON R

Copper	Selenium	Bromine	$R$
4g	4h	4f	0.0601
4g	4f	4h	0.0613
4f	4h	4g	0.0719
4f	4g	4h	0.0719
4h	4g	4f	0.0631
4h	4f	4g	0.0644

TABLE III  
FINAL POSITIONAL AND THERMAL PARAMETERS<sup>a,b</sup> FOR CuBrSe<sub>3</sub>

Positional and isotropic thermal parameters						
Atom	x	y	z	B		
Se(8i)	0.1247(2)	0.1057(6)	0.1425(3)	1.06(4)		
Se(4h)	0.0	0.8458(9)	0.2708(5)	1.30(7)		
Cu(4g)	0.25	0.7856(12)	0.25	1.84(11)		
Br(4f)	0.3174(3)	0.5	0.0	1.46(6)		
Anisotropic thermal parameters ( $\times 10^4 \text{ \AA}^2$ )						
Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Se(8i)	97(9)	146(9)	164(10)	-14(6)	-15(5)	-6(5)
Se(4h)	131(17)	209(22)	170(17)	0.0	0.0	8(8)
Cu(4g)	229(25)	238(26)	258(29)	0.0	-22(10)	0.0
Br(4f)	189(16)	204(17)	167(14)	0.0	0.0	-14(8)

<sup>a</sup> The anisotropic thermal parameters are defined as:  $f = f_0 \exp(-2\pi^2(U_{11}h^2a^{*2} + 2U_{12}hka^*b^* + \dots))$ .

<sup>b</sup> Estimated standard deviations are given in parentheses; x, y, and z are fractional coordinates.

Important interatomic distances and angles are summarized in Table IV.

## Discussion

The structure of CuBrSe<sub>3</sub> is illustrated in Figs. 1 and 2. The unique feature of the structure is a six-membered ring of selenium atoms, arranged in chair-type configuration.

TABLE IV  
BOND DISTANCES AND ANGLES IN CuBrSe<sub>3</sub>

Se(8i)-Se(8i) <sup>a</sup>	2.389(3) Å
Se(8i)-Se(8i) <sup>b</sup>	3.582(3)
Se(8i)-Se(4h)	2.354(4)
Se(8i)-Cu(4g)	2.447(4)
Se(8i)-Br(4f)	3.464(4)
Cu(4g)-Br(4f)	2.506(3)
Se(8i)-Se(4h)-Se(8i)	99.06(15)°
Se(4h)-Se(8i)-Se(8i)	100.85(13)
Se(8i)-Cu-Se(8i)	108.11(14)
Cu-Br-Cu	118.48(15)
Br-Cu-Br	134.55(14)

<sup>a</sup> In the selenium ring.

<sup>b</sup> Across the selenium ring.

This can be considered as two diatomic Se<sub>2</sub> units, spaced 3.582 Å apart, each with an Se-Se distance of 2.389 Å. These Se<sub>2</sub> units are connected through two single Se atoms at distances of 2.354 Å. The rings are in layers parallel to the *b*-axis, with the Se<sub>2</sub> units of the rings oriented in the *c*-directions. The "chairs" in alternate rows face in opposite directions. The existence of selenium rings has been observed in Se<sub>8</sub><sup>2+</sup> (10), in which the Se-Se distances range from 2.29 to 2.36 Å. The corresponding bond length in molecular Se<sub>8</sub> is 2.336 Å, with a ring angle of 105.7° (11). The Se-Se distance varies from 2.33 to 2.35 Å in several copper (12) and zirconium (13) selenides.

The rows of Se<sub>6</sub> rings are separated by rows of bromine atoms in the *a*-direction and in the *c*-direction by zigzag chains of alternating copper and bromine atoms, with a Cu-Br distance of 2.506 Å. In CuBr, which has the zinc-blende structure, the corresponding distance is 2.46 Å. There are a few compounds containing copper(I) and bromine with which comparisons can be



arranging use of the  $\text{P2}_1$  Syntex diffractometer located at Boston University. The absorption program was adapted from ABSORB of the X-RAY system (16), and the full-matrix program used was ORXFLS-3 (17). All other computations were made with the National Research Council of Canada Crystallographic Programs (18).

## References

1. A. RABENAU AND H. RAU, in "Inorganic Syntheses," (A. Wold and J. K. Ruff, Eds.), Vol. 14, pp. 160-173, McGraw-Hill, New York (1973).
2. A. RABENAU, H. RAU, AND G. ROSENSTEIN, *Z. Anorg. Allg. Chem.* **374**, 43 (1970).
3. P. M. CARKNER AND H. M. HAENDLER, *J. Solid State Chem.* **18**, 183 (1976).
4. J. FENNER AND A. RABENAU, *Z. Anorg. Allg. Chem.* **426**, 7 (1976).
5. J. FENNER, *Acta Crystallogr. Sect. B* **32**, 3084 (1976).
6. P. M. CARKNER AND H. M. HAENDLER, *J. Cryst. Growth* **33**, 196 (1976).
7. D. T. CROMER AND J. T. WABER, *Acta Crystallogr.* **18**, 104 (1965).
8. H. P. HANSON, F. HERMAN, J. D. LEE, AND S. SKILLMAN, *Acta Crystallogr.* **17**, 1040 (1964).
9. W. C. HAMILTON, *Acta Crystallogr.* **18**, 502 (1965).
10. R. K. MCMULLAN, D. J. PRINCE, AND J. D. CORBETT, *Inorg. Chem.* **10**, 1749 (1971).
11. P. CHERIN AND P. UNGAR, *Inorg. Chem.* **6**, 1589 (1967).
12. R. D. HEYDING AND R. M. MURRAY, *Canad. J. Chem.* **54**, 841 (1976).
13. S. FURUSETH, L. BRATTAS, AND A. KJEKSHUS, *Acta Chem. Scand. A* **29**, 623 (1975).
14. M. MASSAUX AND M-T. LE BIHAN, *Acta Crystallogr. Sect. B* **32**, 1586 (1976).
15. M. R. CHURCHILL AND K. L. KALRA, *Inorg. Chem.* **13**, 1427 (1974); M. R. CHURCHILL, B. G. DE BOER, AND S. J. MENDAK, *Inorg. Chem.* **14**, 2041 (1975).
16. X-RAY SYSTEM, Tech. Rep. TR-192, Computer Science Center, Univ. of Maryland, College Park, Md. (June 1972).
17. W. R. BUSING, K. O. MARTIN, AND H. A. LEVY, ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn. (April 1971).
18. F. R. AHMED, National Research Council Crystallographic Series, National Research Council, Ottawa, Canada.