

The Crystal Structure of Copper Fluorophosphate, $\text{Cu}_2(\text{PO}_4)\text{F}$

BY J. R. REA AND E. KOSTINER

Institute of Materials Science and Department of Chemistry, University of Connecticut, Storrs, Connecticut 06268, U.S.A.

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Copper fluorophosphate, $\text{Cu}_2(\text{PO}_4)\text{F}$, crystallizes in the space group $C2/c$ with cell dimensions $a = 12.737$ (3), $b = 6.182$ (1), $c = 9.962$ (2) Å, $\beta = 119.15$ (2)°, $D_x = 4.674$ g cm⁻³, $Z = 8$. A three-dimensional structural analysis using automatic diffractometer data has been completed and refined by full-matrix least-squares procedures to a residual $R = 0.050$ ($R_w = 0.084$). $\text{Cu}_2(\text{PO}_4)\text{F}$ is isostructural with $\text{Cd}_2(\text{PO}_4)\text{F}$ and $\text{Mn}_2(\text{PO}_4)\text{F}$. However, the copper polyhedra are more distorted than the metal polyhedra in the latter compounds in a manner consistent with the peculiar microsymmetry of the copper ion.

Introduction

As a part of our continuing study of the crystal chemistry of compounds of the composition $\text{M}_2(\text{PO}_4)\text{X}$, where M is a divalent metal and X is a halogen, we have prepared single crystals of copper fluorophosphate, $\text{Cu}_2(\text{PO}_4)\text{F}$, and have carried out a complete structure determination for this compound. It crystallizes in the space group $C2/c$ with cell dimensions similar to those of the compounds $\text{Cd}_2(\text{PO}_4)\text{F}$ (Kostiner & Rea, 1974) and $\text{Mn}_2(\text{PO}_4)\text{F}$ (Rea & Kostiner, 1972) and to the mineral triplite (Waldrop, 1969). This is in contrast to previously published data (Auh & Hummel, 1974) which indicated that $\text{Cu}_2(\text{PO}_4)\text{F}$ has a doubled b axis and crystallizes in the space group $P2_1/c$, and is isostructural with the mineral wagnerite, $\text{Mg}_2(\text{PO}_4)\text{F}$.

$\text{Cu}_2(\text{PO}_4)\text{F}$ is isostructural with $\text{Cd}_2(\text{PO}_4)\text{F}$ and $\text{Mn}_2(\text{PO}_4)\text{F}$. However, the copper ion imposes its own microsymmetry on the already distorted metal polyhedra, making the four short bonds in each polyhedron even shorter than would be expected on the basis of cation size differences, and the two long bonds longer. This behavior is typical of the Cu^{2+} ion in six-coordination (Wells, 1975). These further distortions will be discussed in detail.

Experimental

Single crystals of copper fluorophosphate were grown by standard flux-melt techniques using excess copper fluoride as the flux. A mixture of 25 mol% $\text{Cu}_3(\text{PO}_4)_2$ –75 mol% CuF_2 was placed in a tightly covered platinum crucible and inserted into a resistance-heated furnace which was brought to a temperature of 900°C, soaked for four hours, cooled to 500°C at a rate of 16°C h⁻¹ and then shut off. Irregularly shaped pale pink crystals were separated from the melt.

A crystal was ground to a sphere of radius 0.014 (1) cm; Weissenberg and precession photographs revealed monoclinic symmetry with systematic absences corresponding to the space groups $C2/c$ or Cc . In analogy

with the manganese and cadmium compounds, the space group $C2/c$ was chosen; this was confirmed in the structure refinement.

The lattice parameters were determined in a PICK-II least-squares refinement program, using 48 reflections within the angular range $35^\circ < 2\theta < 56^\circ$; the reflections were automatically centered on a Picker FACS-I four-circle diffractometer using Mo $K\alpha_1$ radiation ($\lambda = 0.70930$ Å). At 22°C the lattice parameters are $a = 12.737$ (3), $b = 6.182$ (2), $c = 9.962$ (2) Å and $\beta = 119.15$ (2)°, where the figures in parentheses represent the standard deviations in the last reported figure. The calculated density, with $Z = 8$, is 4.674 g cm⁻³.

Diffraction intensities were measured using Zr-filtered Mo $K\alpha$ radiation at a take-off angle of 3.0° with the diffractometer operating in the θ – 2θ scan mode. Scans were made at 1° min⁻¹ over 1.3° with allowance for dispersion and with 20 s background counts taken at both ends of the scan. Of the 1572 independent data investigated in the angular range $2\theta < 71^\circ$, 1565 were considered observable according to the criterion $|F_o| > 1.58\sigma_F$, where σ_F is defined as $0.02|F_o| + [C + k^2B]^{1/2}/2|F_o|Lp$; the total scan count is C , k is the ratio of scanning time to the total background time and B is the total background count. Three reflections were systematically monitored and no variations in intensity greater than 4% were observed over the data collection period; the mean variation was very much smaller.

Intensity data were corrected for Lorentz and polarization effects. Absorption corrections (*International Tables for X-ray Crystallography*, 1974) were applied for a spherical crystal with $\mu R = 1.86$. The maximum relative absorption correction applied was 19.6% of $|F_o|$.

Full-matrix least-squares refinement (Busing, Martin & Levy, 1962) using the positional parameters for $\text{Mn}_2(\text{PO}_4)\text{F}$ as a trial structure, a $1/\sigma^2$ weighting scheme, zerovalent scattering factors for Cu, P, F and O (*International Tables For X-ray Crystallography*, 1974), isotropic temperature factor and corrections for secondary extinction and anomalous dispersion,

yielded a residual $R=0.092$ and a weighted residual $R_w=0.143$. The anisotropic refinement, based on a data:parameter ratio of 21 with 74 independently varied parameters, yielded a final $R=0.050$ and $R_w=0.084$ for the observed data.* In the final refinement, the maximum extinction correction (Zachariasen, 1968) was 43% of $|F_o|$ for the 202 reflection.

Discussion

Table 1 gives the final atomic coordinates and anisotropic thermal parameters. The copper atoms lie at the centers of distorted octahedra. Cu(1) is coordinated by three oxygens and one fluorine at an average distance of 1.980 Å and one fluorine and one oxygen at 2.516 and 2.263 Å, respectively. Cu(2) is coordinated by three oxygens and one fluorine at an average distance of 1.965 Å and one fluorine and one oxygen at 2.427 and 2.300 Å, respectively. The fluorines are *cis* in both cases. Table 2 lists angles and distances for the copper polyhedra.

Whereas the phosphate tetrahedron in $Mn_2(PO_4)F$ was quite regular, the phosphate tetrahedron in $Cd_2(PO_4)F$ was somewhat irregular and the one in $Cu_2(PO_4)F$ is even more irregular. The average bond length is 1.536 Å (+0.016, -0.015 Å) and the average angle is 109.5° (+2.6, -3.0°). Table 3 lists the tetrahedral bond angles and distances. The standard deviations for all bond lengths and angles were computed by the function and error program (ORFFE) of Busing, Martin & Levy (1964).

$Cu_2(PO_4)F$ is isostructural with $Mn_2(PO_4)F$, $Cd_2(PO_4)F$ and triplite, the structure of which has been described in detail (Waldrop, 1969). The fluorine atom occupies a single position as opposed to the situation in both wagnerite [$Mg_2(PO_4)F$] (Coda, Giuseppetti & Tadini, 1967) and triploidite [$Mn_{1.5}Fe_{0.5}(PO_4)OH$] (Waldrop, 1970), in which the fluorine atom (or hydroxyl ion) occupies one of two sites in a doubled unit cell. Table 4 lists the metal-anion bond lengths in each structure. The differences in the

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31565 (9 pp.). Copies may be obtained from The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Bond distances, polyhedral edge lengths, and bond angles for copper polyhedra

Numbers in parentheses are estimated standard deviations in the last significant figure.

(i) Interatomic distances (Å)			
Cu(1)—O(2)	1.983 (3)	Cu(2)—O(1)	1.914 (3)
Cu(1)—O(3)	2.263 (4)	Cu(2)—O(1')	2.300 (3)
Cu(1)—O(3')	1.940 (3)	Cu(2)—O(2)	2.033 (3)
Cu(1)—O(4)	2.040 (3)	Cu(2)—O(4)	1.956 (3)
Cu(1)—F	1.956 (3)	Cu(2)—F	1.956 (3)
Cu(1)—F'	2.516 (3)	Cu(2)—F'	2.427 (4)
Cu(1) octahedron		Cu(2) octahedron	
O(2)—O(3)	2.943 (5)	O(1)—O(1')	2.733 (6)
O(2)—O(4)	2.901 (5)	O(1)—O(2)	2.804 (5)
O(2)—F	2.590 (5)	O(1)—F	2.745 (5)
O(2)—F'	3.157 (5)	O(1)—F'	3.435 (5)
O(3)—O(3')	2.598 (6)	O(1')—O(2)	3.595 (5)
O(3)—O(4)	3.872 (5)	O(1')—O(4)	2.886 (5)
O(3)—F	3.004 (5)	O(1')—F	3.268 (5)
O(3')—O(4)	3.073 (5)	O(2)—O(4)	3.174 (5)
O(3')—F	2.844 (5)	O(2)—F'	2.590 (5)
O(3')—F'	3.589 (5)	O(4)—F	2.548 (4)
O(4)—F'	2.548 (4)	O(4)—F'	3.127 (5)
F—F'	2.728 (7)	F—F'	2.785 (7)
(ii) Angles (°)			
O(2)—Cu(1)—O(3)	87.5 (1)	O(1)—Cu(2)—O(1')	80.3 (1)
O(2)—Cu(1)—O(4)	92.3 (1)	O(1)—Cu(2)—O(2)	90.5 (1)
O(2)—Cu(1)—F	82.2 (1)	O(1)—Cu(2)—F	90.3 (1)
O(2)—Cu(1)—F'	88.3 (1)	O(1)—Cu(2)—F'	104.0 (1)
O(3)—Cu(1)—O(3')	75.9 (1)	O(1')—Cu(2)—O(2)	112.0 (1)
O(3)—Cu(1)—O(4)	128.2 (1)	O(1')—Cu(2)—O(4)	85.0 (1)
O(3)—Cu(1)—F	90.5 (1)	O(1')—Cu(2)—F	100.0 (1)
O(3')—Cu(1)—O(4)	101.1 (1)	O(2)—Cu(2)—O(4)	105.4 (1)
O(3')—Cu(1)—F	93.8 (1)	O(2)—Cu(2)—F'	70.4 (1)
O(3')—Cu(1)—F'	106.6 (1)	O(4)—Cu(2)—F	81.3 (1)
O(4)—Cu(1)—F'	67.1 (1)	O(4)—Cu(2)—F'	90.4 (1)
F—Cu(1)—F'	74.0 (1)	F—Cu(2)—F'	78.1 (1)
O(2)—Cu(1)—O(3')	163.0 (2)	O(1)—Cu(2)—O(4)	161.5 (1)
O(3)—Cu(1)—F'	164.3 (1)	O(1')—Cu(2)—F'	175.2 (1)
O(4)—Cu(1)—F	140.8 (1)	O(2)—Cu(2)—F	147.7 (1)

average metal-oxygen bond lengths among the three structures are consistent with differences in the cationic radii (Shannon & Prewitt, 1969). The radii for Cd^{2+} , Mn^{2+} and Cu^{2+} are 0.95, 0.83 and 0.73 Å, respectively; the differences are 0.12, 0.22 and 0.10 Å for $Cd^{2+}-Mn^{2+}$, $Cd^{2+}-Cu^{2+}$ and $Mn^{2+}-Cu^{2+}$, respectively. For the M(1) polyhedra these differences in the average metal-oxygen distances are 0.10, 0.20 and 0.10 Å and for the M(2) polyhedra 0.10, 0.19 and 0.09 Å.

Table 1. Fractional atomic coordinates and anisotropic thermal parameters

Numbers in parentheses are estimated standard deviations in the last significant figure. The B 's are defined by the general temperature factor: $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

	10^4x	10^4y	10^4z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu(1)	615.7 (5)	2621.5 (9)	31.0 (6)	0.67 (2)	1.44 (3)	0.65 (2)	0.37 (1)	0.40 (2)	0.41 (1)
Cu(2)	3465.5 (5)	3840.5 (8)	6481.3 (7)	0.95 (2)	0.50 (2)	0.93 (2)	-0.06 (1)	0.69 (2)	-0.09 (1)
P	1723 (1)	3927 (2)	8024 (1)	0.45 (3)	0.55 (4)	0.36 (3)	-0.01 (2)	0.20 (3)	0.00 (2)
O(1)	3156 (3)	845 (5)	5948 (4)	0.79 (9)	0.49 (8)	0.53 (9)	-0.10 (7)	0.26 (8)	-0.01 (7)
O(2)	2049 (3)	1533 (6)	1895 (4)	0.59 (9)	0.92 (10)	0.58 (9)	0.11 (8)	0.30 (8)	0.05 (8)
O(3)	4225 (3)	684 (6)	3639 (4)	0.87 (10)	0.93 (10)	0.61 (9)	0.08 (8)	0.38 (8)	0.20 (8)
O(4)	3638 (3)	3039 (5)	1329 (4)	0.71 (9)	0.54 (9)	0.73 (10)	-0.10 (7)	0.38 (8)	-0.01 (7)
F	226 (3)	1190 (5)	4016 (4)	1.02 (10)	1.29 (10)	1.58 (11)	-0.02 (7)	1.03 (9)	-0.38 (8)

Table 3. *Bond distances, polyhedral edge lengths, and bond angles for the phosphate tetrahedron*

Numbers in parentheses are estimated standard deviations in the last significant figure.

(i) Interatomic distances (Å)			
P-O(1)	1.525 (3)	O(1)-O(2)	2.518 (5)
P-O(2)	1.553 (3)	O(1)-O(3)	2.526 (5)
P-O(3)	1.521 (3)	O(1)-O(4)	2.461 (5)
P-O(4)	1.547 (3)	O(2)-O(3)	2.507 (5)
		O(2)-O(4)	2.528 (5)
		O(3)-O(4)	2.509 (5)
(ii) Angles (°)			
O(1)-P-O(2)	109.8 (2)	O(2)-P-O(3)	109.3 (2)
O(1)-P-O(3)	112.1 (2)	O(2)-P-O(4)	109.3 (2)
O(1)-P-O(4)	106.5 (2)	O(3)-P-O(4)	109.8 (2)

Table 4. *Metal-anion distances (Å) in $\text{Cd}_2(\text{PO}_4)\text{F}$, $\text{Mn}_2(\text{PO}_4)\text{F}$ and $\text{Cu}_2(\text{PO}_4)\text{F}$*

	Cd	Mn	Cu
M(1)-O(2)	2.258 (4)	2.163 (2)	1.983 (3)
M(1)-O(3)	2.326 (4)	2.205 (2)	2.263 (4)
M(1)-O(3')	2.221 (4)	2.117 (2)	1.940 (3)
M(1)-O(4)	2.236 (4)	2.147 (2)	2.040 (3)
M(1)-F	2.270 (3)	2.113 (2)	1.957 (3)
M(1)-F'	2.468 (3)	2.534 (2)	2.516 (3)
Av. (4 short)	2.246	2.135	1.980
Av. (4 oxygen)	2.260	2.158	2.056
M(2)-O(1)	2.222 (4)	2.131 (2)	1.914 (3)
M(2)-O(1')	2.314 (4)	2.202 (2)	2.300 (3)
M(2)-O(2)	2.222 (4)	2.126 (2)	2.033 (3)
M(2)-O(4)	2.219 (4)	2.121 (2)	1.956 (3)
M(2)-F	2.281 (3)	2.135 (2)	1.956 (3)
M(2)-F'	2.414 (4)	2.372 (2)	2.427 (4)
Av. (4 short)	2.236	2.128	1.965
Av. (4 oxygen)	2.244	2.145	2.051

Since the Cu^{2+} ion in six-coordination is typically distorted to give four short and two long bonds (Wells, 1975), an attempt was made to determine whether the presence of the Cu^{2+} ion causes the distortions in the metal polyhedra in this structure to be significantly different. Although four short and two long bonds are already found in the metal polyhedra in $\text{Mn}_2(\text{PO}_4)\text{F}$ and $\text{Cd}_2(\text{PO}_4)\text{F}$, a detailed comparison of these bonds among the three compounds reveals enhanced distortions in $\text{Cu}_2(\text{PO}_4)\text{F}$. This can be demonstrated as follows. The differences in the averages of the four short bonds (also listed in Table 4) for the M(1) polyhedron are 0.11, 0.27 and 0.16 Å for the Cd-Mn, Cd-Cu and Mn-Cu compounds, respectively. Again, the expected differences are 0.12, 0.22 and 0.10 Å. Thus the difference in the average of the four short metal-anion bonds is consistent with the difference in ionic radii for Cd^{2+} and Mn^{2+} in their respective compounds, but these differences are substantially larger between the cadmium and copper and between the manganese and copper compounds than would be predicted on the basis of cation size differences alone. This indicates a further shortening of the four short bonds in the Cu(1) polyhedron. The same situation obtains when the four short bonds in the M(2) polyhedra are compared. Here the differences in the averages are also 0.11, 0.27 and 0.16 Å.

It can also be seen that the two long bonds in the copper polyhedra are longer than would be expected on the basis of cation size differences. The Cu(1)-O(3), the Cu(2)-O(1') and the Cu(2)-F' distances are actually longer than the corresponding distances in the manganese compound even though Cu^{2+} has a smaller radius than Mn^{2+} . The Cu(1)-F' distance is only 0.02 Å shorter than the Mn(1)-F' distance, whereas a shortening of 0.10 Å would be expected on the basis of cation size differences.

Thus although the three compounds are isostructural, the copper ion imposes its own microsymmetry on the metal polyhedra. This is accomplished by subtle shifts in anion positions. The fluoride ion is a case in point. Table 5 gives the fluoride ion environment for all three structures. The shift of the fluoride within its grossly distorted tetrahedron of metal ions is evident in the 10° increase in the M(1')-F-M(2) angle in the copper compound as compared with the other two. This means that the fluoride has moved closer to the line joining M(1') and M(2). Thus the F-Cu(1') and F-Cu(2) bonds are additionally shortened, and the F-Cu(1) and F-Cu(2') bonds become lengthened compared with the corresponding bonds in $\text{Cd}_2(\text{PO}_4)\text{F}$ and $\text{Mn}_2(\text{PO}_4)\text{F}$. Since Cu(1) and Cu(1') are symmetry related, as are Cu(2) and Cu(2'), there is one very short and one very long Cu-F bond in each Cu polyhedron. Similar shifts can be described for the other anions.

Table 5. *Bond distances and angles for the fluorine environment*

Numbers in parentheses are estimated standard deviations in the last significant figure.

(i) Distances (Å)			
	Cd	Mn	Cu
F-M(1)	2.468 (3)	2.534 (2)	2.516 (4)
F-M(1')	2.270 (3)	2.113 (2)	1.956 (4)
F-M(2)	2.281 (3)	2.135 (2)	1.956 (3)
F-M(2')	2.414 (4)	2.372 (2)	2.427 (4)
(ii) Angles (°)			
	Cd	Mn	Cu
M(1)-F-M(1')	109.0 (1)	109.4 (1)	106.0 (1)
M(1)-F-M(2)	95.4 (1)	93.7 (1)	93.6 (1)
M(1)-F-M(2')	109.9 (1)	110.2 (1)	108.2 (1)
M(1')-F-M(2)	139.1 (1)	140.3 (1)	149.7 (2)
M(1')-F-M(2')	95.5 (1)	95.3 (1)	93.5 (1)
M(2)-F-M(2')	106.6 (1)	106.7 (1)	101.9 (1)

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References

- AUH, K. & HUMMEL, F. A. (1974). *Canad. Miner.* **12**, 346-351.
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305, Oak Ridge, Tennessee.

- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Oak Ridge National Laboratory Report ORNL-TM-306, Oak Ridge, Tennessee.
- CODA, A., GIUSEPPE, C. & TADINI, C. (1967). *Atti Accad. Nazl. Lincei Rend. Classe Sci. Fis. Mat. Nat.* **43**, 212–224.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- KOSTINER, E. & REA, J. R. (1974). *Acta Cryst.* **B30**, 2901–2903.
- REA, J. R. & KOSTINER, E. (1972). *Acta Cryst.* **B28**, 2525–2529.
- SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* **B25**, 925–946.
- WALDROP, L. (1969). *Z. Kristallogr.* **130**, 1–14.
- WALDROP, L. (1970). *Z. Kristallogr.* **131**, 1–20.
- WELLS, A. F. (1975). *Structural Inorganic Chemistry*, 4th ed. Oxford Univ. Press.
- ZACHARIASEN, W. H. (1968). *Acta Cryst.* **A23**, 558–564.

Acta Cryst. (1976). **B32**, 1947

The Crystal Structure of $\text{Bi}(\text{Bi}_2\text{S}_3)_9\text{Br}_3$

BY KONSTANTIN MARIOLACOS

Mineralogisch-Kristallographisches Institut der Universität, D-34 Göttingen, Germany (BRD)

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$\text{Bi}(\text{Bi}_2\text{S}_3)_9\text{Br}_3$ is hexagonal, space group $P6_3$, with $a_0 = 15.545$ (3), $c_0 = 4.019$ (1) Å, $Z = \frac{3}{2}$. The structure investigation was undertaken on synthetic material and refined by full-matrix least-squares methods to a final R of 0.086. The 1332 independent reflexions were collected on a four-circle automatic diffractometer using monochromatized Mo $K\alpha$ radiation. The structure consists of $(\text{Bi}_4\text{S}_6)_\infty$ chains which run parallel to the z direction; these chains are connected to each other by the Br atoms which lie on the threefold axis and the Bi(1) atoms which lie on the 6_3 axis.

Introduction

Krämer (1973) first reported $\text{Bi}_{19}\text{S}_{27}\text{Br}_3$ and gave the lattice constants and powder data. Very few crystal structures of Bi sulphohalogenides have been investigated so far (Lewis & Kupčik, 1974; Ohmasa & Mariolacos, 1974; Mariolacos & Kupčik, 1975). Miehé & Kupčik (1971) have solved the crystal structure of the isotypical $\text{Bi}(\text{Bi}_2\text{S}_3)_9\text{I}_3$, but they could not ascertain whether a centre of inversion exists in this compound. Since by absence of a symmetry centre the Bi-containing sulphohalogenides may be ferroelectric materials, it was interesting to synthesize the Br analog and to investigate its structure in order to answer the question of the existence of a symmetry centre. Furthermore it was of interest to investigate the statistical occupation of the sixfold axis.

Experimental

The crystals were synthesized by chemical transport using the method of Rabenau & Rau (1969) under the following conditions: starting materials were 1 part Bi_2S_3 , 1 part Cu_2S , 2 parts PbS ; transport material: 0.1 $N\text{HBr}$ solution; reaction and crystallization took place in a 140 mm long and 7 mm diameter silica glass tube; $T = 420 \pm 10^\circ\text{C}$; $\Delta T = 15^\circ\text{C}$; filling extent about 15%; time 12 d. After this reaction time the tube was taken away and was slowly cooled in air. Black, metallic, shiny prismatic crystals of $\text{Bi}(\text{Bi}_2\text{S}_3)_9\text{Br}_3$ formed in

the cold part of the tube. Their maximum dimensions were about $0.05 \times 0.08 \times 7$ mm. The chemical composition of the compound was determined by semi-quantitative microprobe analysis and was confirmed after the structure determination. A crystal of size $0.018 \times 0.028 \times 5$ mm was selected for this investigation. The systematic absences $000l$ with $l = 2n + 1$ and the observed Laue group $6/m$ indicated $P6_3$ (No. 173) or $P6_3/m$ (No. 176) as possible space groups; the space group confirmed from the structure analysis is the former. The intensities were collected on an automatic four-circle diffractometer (STADI-4 system of Stoe) using graphite-crystal monochromatized Mo $K\alpha$ radiation and a θ - 2θ scan mode. Two standard reflexions were each monitored 27 times during the data collection and used to calculate the standard deviation of the intensity. Their intensities varied by less than $\pm 3.7\%$ throughout. The lattice constants were determined with the aid of 15 reflexions and refined by least-squares methods.

Crystal data

$\text{Bi}(\text{Bi}_2\text{S}_3)_9\text{Br}_3$, hexagonal, space group $P6_3$; $a_0 = 15.545$ (3), $c_0 = 4.019$ (1) Å; ($\lambda = 0.7114$ Å); $Z = \frac{3}{2}$; $D_{\text{calc}} = 6.69$ g cm $^{-3}$; $\mu = 662$ cm $^{-1}$. For the layers $hk0$ to $hk5$ in the range $\sin \theta / \lambda \leq 0.805$ Å $^{-1}$ 1332 independent reflexions were obtained which were corrected for the Lorentz-polarization effect and for absorption, the prismatic shape being approximated by nine boundary planes in the absorption correction. Individual weights,