given in Tables 2 and 3. Examination of these data suggests that the principal effect on the purine ring of the replacement of the chloride anion with bromide is to lengthen the C(5)–N(7) and C(4)–N(9) bonds while shortening the C(6)–C(5), C(5)–C(4), and C(4)–N(3) bonds. These bond distances are comparable with those found in neutral 8-azaguanine (Sletten, Sletten & Jensen, 1968) and possibly indicate a decreased interaction with the purine ring of the less electronegative bromine (2·96) relative to that of chlorine (3·16) (Allred, 1961) in the corresponding hydrochloride.

The azapurine ring is not quite planar, but comprises a planar five-membered triazole ring [C(4), C(5), N(7), N(8), N(9)] and a planar pyrimidine ring [N(1), C(2), N(3), C(4), C(5), C(6)] which are inclined to each other at an angle of 0·92°; this slight pucker along the C(4)–C(5) bond is commonly found in purine structures (Bugg, 1972) and is very similar to that reported for the similar 8-aza-2,6-diaminopurine cation (Singh, Lewis & Hodgson, 1974; Singh & Hodgson, 1975). The hydrogen bonding is, as expected, quite complex, and the probable intermolecular hydrogen bonds are listed in Table 4; the criterion for inclusion of an interaction in the table was that of Hamilton & Ibers (1968). Replacement of chloride by bromide brings about an increase in the interlayer separation of from 3·11 to 3·35 Å; this difference is presumably partly due to the greater ionic radius of bromide (1·95 Å) than of chloride (1·80 Å, Pauling, 1960), but is also suggestive of a weaker halogen–ring interaction in the bromide. The protonation sites on the azapurine rings are not affected by this change of anion.

Table 4. *Probable A*–H···*B hydrogen bonds*

A	H	*B**	H···*B*	*A*···*B*	*A*–H···*B*
N(1)	H(1)	Br[5]	2·32 (7) Å	3·192 (5) Å	169 (4)°
N(3)	H(3)	O(6)[3]	1·91 (7)	2·818 (6)	165 (5)
N(8)	H(8)	O*W*[6]	2·11 (11)	2·832 (8)	147 (9)
N(8)	H(8)	Br[1]	2·79 (9)	3·389 (6)	132 (8)
N(2)	H(N21)	N(7)[1]	2·14 (7)	3·009 (8)	163 (6)
N(2)	H(N22)	Br[2]	2·81 (7)	3·493 (6)	146 (5)
O*W*	H(O*W*1)	Br[5]	2·82 (16)	3·259 (6)	132 (12)
O*W*	H(O*W*2)	N(9)[4]	2·37 (7)	3·004 (8)	158 (7)

* The digit in brackets represents the symmetry operation applied to atom *B*, where $[1]=(x,y,z)$; $[2]=(-x,-y,-z)$; $[3]=(\frac{1}{2}-x,\frac{1}{2}-y,\frac{1}{2}-z)$; $[4]=(-\frac{1}{2}-x,-\frac{1}{2}+y,\frac{1}{2}-z)$; $[5]=(-\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z)$; $[6]=(\frac{1}{2}+x,\frac{1}{2}-y,-\frac{1}{2}+z)$.

This work was supported by Public Health Service Research Grant No. CA-15171-02 from the National Cancer Institute.

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Refinement of the Crystal Structure of Kröhnkite

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(*Received* 25 *November* 1974; *accepted* 4 *February* 1975)

Abstract. $Na_2Cu(SO_4)_2.2H_2O$, $P2_1/c$, $Z=2$, $D=2{\cdot}913$ g cm^{-3}. Cell constants at 20°C, $a=5{\cdot}807$ (1), $b=12{\cdot}656$ (2), $c=5{\cdot}517$ (1) Å, $\beta=108{\cdot}32$ (1)°, λ(Mo $K\alpha$) = 0·71069 Å. Chains of alternating corner-sharing tetrahedra and octahedra extend along **c** and are linked by Na and hydrogen bonding. The Cu octahedron shows strong Jahn–Teller distortion with four short equatorial and two long axial bonds.

Introduction. The crystals used were from Chuquicamata, Chile. Precession photographs exhibited monoclinic symmetry; reflexions with $l=2n+1$ ($h0l$) and $k=2n+1$ ($0k0$) were absent, consistent with the space group $P2_1/c$ observed by Dahlman (1952) and Rama Rao (1961). A full data set out to a 2θ of 65° and consisting of 1366 non-equivalent reflexions was collected from an irregular equidimensional crystal (volume $\sim 3{\cdot}4\times10^{-3}$

mm^3) with a Syntex $P\bar{1}$ automated diffractometer using graphite monochromated Mo $K\alpha$ radiation; a θ–2θ scan mode was used. Standard data reduction resulted in 1029 observed reflexions (4σ). Structure refinement was carried out on an IBM 370/158 computer with the program *RFINE* (Finger, 1969). Scattering factors were taken from Cromer & Mann (1968) and anomalous dispersion coefficients from Cromer & Liberman (1970). The parameters given by Rama Rao (1961) were used as input to the least-squares routine. Several cycles of full-matrix least-squares refinement resulted in convergence (for isotropic temperature factors) at a conventional R of 4·5% (observed reflexions). Conversion to anisotropic temperature factors of the form $\exp\,(-\sum_{i=1}\sum_{j=1} h_ih_j\beta_{ij})$ and addition of a variable isotropic extinction correction (Zachariasen, 1968) resulted in convergence at an R of 3·3% and R_w of 3·9%. With the universal curves of Brown & Shannon (1973), bond-strength calculations at this stage showed significant bond-strength deficiencies around the O(1) and O(4) anions and an excess around O(W), indicative of hydrogen bonding between these anions. The hydrogen positions were derived by assuming linear O(W)–H···O bonds and distances compatible with the ideal bond-strength sums around each of the three anions. Refinement of the hydrogen positions (using isotropic temperature factors fixed at 0·5 Å^2) together with all other variables resulted in convergence at R and R_w (unit weights) values of 3·1 and 3·6% respectively, a significant reduction at the 0·005 level (Hamilton, 1965). The final parameters are given in Table 1. Interatomic distances and angles were calculated using the program *ERRORS* (L. W. Finger, personal communication) and are given in Tables 2 and 3 respectively.

Table 2. *Selected interatomic distances in kröhnkite*

S tetrahedron		Na polyhedron	
S–O(1)	1·465 (3) Å	Na–O(1)	2·566 (3) Å
S–O(2)	1·475 (2)	Na–O(2)	2·435 (3)
S–O(3)	1·504 (2)	Na–O(2)	2·544 (3)
S–O(4)	1·479 (2)	Na–O(3)	2·504 (3)
Mean	1·481	Na–O(4)	2·458 (3)
		Na–O(4)	2·496 (3)
O(1)–O(2)	2·422 (3)	Na–O(W)	2·386 (3)
O(1)–O(3)	2·431 (3)	Mean	2·484
O(1)–O(4)	2·439 (4)		
O(2)–O(3)	2·445 (3)	Cu octahedron	
O(2)–O(4)	2·414 (3)	Cu–O(2) ×2	2·464 (2)
O(3)–O(4)	2·383 (3)	Cu–O(3) ×2	1·975 (2)
Mean	2·417	Cu–O(W) ×2	1·937 (2)
		Mean	2·125
H-coordination			
H(1)–O(W)	0·82 (5)	O(2)–O(3) ×2	3·154 (3)
H(1)–O(1)	1·87 (5)	O(2)–O(3) ×2	3·162 (4)
H(1)–H(2)	1·49 (6)	O(2)–O(W) ×2	3·236 (3)
H(2)–O(W)	0·93 (5)	O(2)–O(W) ×2	3·133 (3)
H(2)–O(4)	1·82 (5)	O(3)–O(W) ×2	2·843 (3)
		O(3)–O(W) ×2	2·688 (3)
H(1)–Cu	2·37 (5)	Mean	3·036
H(2)–Cu	2·46 (5)		
O(W)–O(1)	2·626 (3)		
O(W)–O(4)	2·696 (3)		

Table 3. *Selected interatomic angles in kröhnkite*

S tetrahedron		Cu octahedron	
O(1)–S–O(2)	110·9 (1)°	O(2)–Cu–O(3)	89·9 (1)°
O(1)–S–O(3)	109·9 (1)	O(2)–Cu–O(3)	90·1 (1)
O(1)–S–O(4)	111·8 (1)	O(2)–Cu–O(W)	93·9 (1)
O(2)–S–O(3)	108·4 (1)	O(2)–Cu–O(W)	86·1 (1)
O(2)–S–O(4)	109·6 (1)	O(3)–Cu–O(W)	93·2 (1)
O(3)–S–O(4)	106·1 (1)	O(3)–Cu–O(W)	86·8 (1)
Mean	109·45	Mean	90·00
H coordination			
H(1)—O(W)–H(2)	115 (4)°		
O(W)–H(1)—O(1)	152 (5)		
O(W)–H(2)—O(4)	156 (4)		
Cu——O(W)–H(1)	112 (3)		
Cu——O(W)–H(2)	113 (3)		

Discussion. The dominant motif of the kröhnkite structure is the chains of S tetrahedra and Cu octahedra extending along the c axis (see Fig. 1); these chains are linked together by Na atoms coordinated by seven anions at distances between 2·39 and 2·57 Å. The Cu octahedron shows typical Jahn–Teller distortion with four short planar bonds and two elongated axial bonds, and the ⟨Cu–O⟩ distance is in good agreement with that forecast by the distortion equation of Shannon & Calvo (1973) (obs. = 2·13, forecast = 2·14 (2) Å). The O(W)–H distances listed in Table 2 are almost certainly too small (Baur, 1972); further indication of this is given in Table 4 where the bond-strength sums are in general too low around the acceptor anions and too high around the donor anion. However, the geometry

Table 1. *Atomic parameters for kröhnkite* ($\beta_{ij}\times 10^5$)

	x	y	z	B equiv.	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0	0	0	0·91 (1)	744 (16)	141 (3)	711 (16)	0	50 (11)	0
Na	0·5714 (3)	0·1247 (1)	0·2099 (3)	1·54 (2)	1377 (46)	248 (9)	1538 (49)	−16 (17)	860 (39)	−27 (17)
S	0·2375 (1)	0·11793 (6)	0·5445 (1)	0·71 (1)	628 (19)	119 (4)	518 (19)	4 (6)	156 (14)	−17 (7)
O(1)	0·0038 (5)	0·1725 (2)	0·4874 (5)	1·22 (3)	869 (61)	207 (12)	1132 (7)	148 (26)	270 (53)	13 (29)
O(2)	0·2911 (4)	0·0573 (2)	0·7844 (4)	1·11 (3)	1003 (65)	194 (13)	765 (63)	48 (24)	250 (54)	128 (25)
O(3)	0·2319 (4)	0·0425 (2)	0·3322 (4)	1·21 (4)	854 (65)	233 (14)	941 (72)	46 (25)	185 (56)	−198 (27)
O(4)	0·4385 (4)	0·1923 (2)	0·5617 (4)	1·19 (4)	1033 (67)	189 (12)	992 (70)	−167 (24)	314 (57)	5 (25)
O(W)	0·8315 (4)	0·1343 (2)	0·9513 (4)	0·99 (3)	831 (62)	148 (12)	842 (66)	−54 (23)	157 (52)	−9 (23)
H(1)	0·927 (9)	0·184 (4)	0·992 (9)	0·5	—	—	—	—	—	—
H(2)	0·712 (9)	0·140 (4)	0·792 (9)	0·5	—	—	—	—	—	—

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30931 (14 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

of the H_2O molecule is compatible with the range of values found by neutron diffraction in many hydrates (Baur, 1970, 1972). The donor–acceptor distances are fairly typical, but it should be noted that these are not necessarily an indication of hydrogen bonding; the O(*W*)–O(3) distance is actually shorter than the donor–acceptor distance O(*W*)–O(4). However, O(*W*)–O(3) is an edge of the Cu octahedron, and inspection of Table 4 shows that the bond strength sum around O(3) approaches ideality without requiring any contribution from hydrogen bonding. The Cu–O(*W*)–H angles are statistically equal (~112°) indicating that the pseudo-mirror plane of the H_2O molecule is parallel to the Cu–O(*W*) bond; these angles are less than the maximum possible Cu–O(*W*)–H value of 127° in this configuration, indicating that the pseudo-twofold axis of the water is skewed with respect to the Cu–O(*W*) bond. This results in a slight decrease in the Cu–H distances compared with their maximum possible values, and indicates that the minimization of repulsive interactions is secondary to the bond strength requirements of the anions.

Table 4. *Bond-strength table for kröhnkite**

	S	Cu	Na	H(1)†	H(2)	Σ
O(1)	1·55		0·14	0·18 (0·31)		1·87 (2·00)
O(2)	1·50	0·14 × 2	0·17			1·95
			0·14			
O(3)	1·38	0·44 × 2	0·15			1·97
O(4)	1·49		0·16		0·20	2·00
			0·15			
O(*W*)		0·49 × 2	0·19	1·11 (0·69)	0·84	2·63 (2·21)
Σ	5·92	2·14	1·10	1·29 (1·00)	1·04	

* Calculated from the curves of Brown & Shannon (1973).

† The values in parentheses are those corresponding to ideal sums around O(1) and H(1), and give *D*–H and H–*A* distances of 1·02 and 1·48 Å respectively. The values around H(2) do not appear to be so much in error.

Intensity data were collected at the Materials Research Institute, McMaster University, Hamilton. Financial assistance was provided by the National Research Council of Canada and the University of Manitoba.

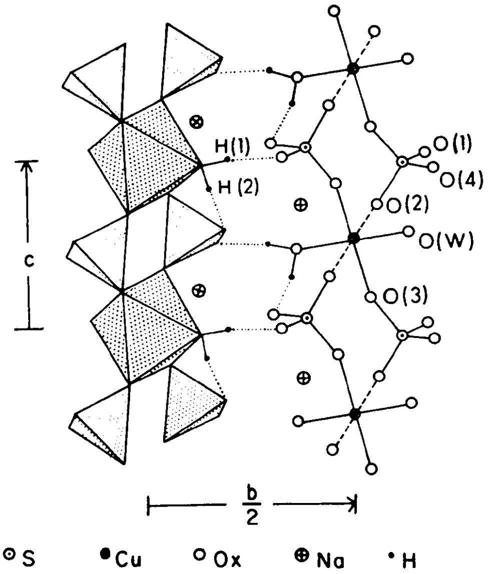

Fig. 1. The structure of kröhnkite projected down the *a* axis. Na–O bonds have been omitted for clarity.

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