SHORT STRUCTURAL PAPERS

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8-Azaguanine Hydrobromide Monohydrate

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Abstract. $C_4H_7O_2N_6Br$, monoclinic, $P2_1/n$, $a=5{\cdot}809$ (3), $b=13{\cdot}073$ (8), $c=10{\cdot}899$ (7) Å, $\beta=84{\cdot}45$ (2)°, $Z=4$, $D_c=2{\cdot}024$, $D_m=2{\cdot}00$ (3) g cm^{-3}. The structure is very similar to that of the corresponding hydrochloride, and consists of sheets of 8-azaguaninium cations which are separated by bromide anions; the interlayer separation is 3·35 Å. The sites of protonation in the cation are N(1), N(3), and N(8).

Introduction. Intensity data were recorded from a crystal of dimensions 0·42 × 0·37 × 0·25 mm. They showed systematic absences of $h+l=2n+1$ for $h0l$ and $k=2n+1$ for $0k0$; the linear absorption coefficient $\mu=74{\cdot}03$ cm^{-1} for Cu $K\alpha$ radiation. All diffraction measurements were made with Cu $K\alpha$ radiation on a four-circle Picker automatic diffractometer with a pulse-height analyzer and scintillation counter; the β radiation was removed by filtering the diffracted beam with 0·5 mil nickel foil. The cell constants were determined by least-squares procedures (Busing & Levy, 1967). The data were corrected for backgrounds, Lorentz–polarization factors and for absorption effects, the latter being calculated with Hamilton's *GONO*9 program. The transmission coefficients were in the range 0·15 (for 601) to 0·42 (for 310). A total of 1274 intensities [$1103>3\sigma(I)$] was obtained out to a limit of $2\theta(\text{Cu } K\alpha)\le 123°$.

The complex is isomorphous with the hydrochloride analog (Kozlowski, Singh & Hodgson, 1974), and the structure was solved by least-squares refinement of the non-hydrogen atom parameters for the hydrochloride with Cl replaced by Br. The hydrogen atoms associated with the azapurine ring and the water molecule were located in a difference Fourier map, using our version of Robinson & Dellacca's *FOURIER* program. The non-hydrogen atoms were refined anisotropically while the hydrogen atoms were refined isotropically, using Ibers's *NUCLS* least-squares program. The function minimized was $\sum w(|F_o|-|F_c|)^2$, and the weights w were taken as $3F_o^2/\sigma^2(F_o^2)$ for data with $2\theta\le 48°$ and as $4F_o^2/\sigma^2(F_o^2)$ for data with $2\theta>48°$; this weighting scheme was necessary to overcome an unacceptable trend in R_2 as a function of $\sin\theta$ in a late stage of refinement. Examination of the data at a late stage of refinement suggested that they were suffering from secondary extinction since for strong low-order data $|F_o|$ was systematically smaller than $|F_c|$. An extinction correction of the form

$$F_o^{\text{corr}}=F_o\{c\beta(\theta)I+[1+c^2\beta^2(\theta)I^2]^{1/2}\}^{1/2},$$

which has been described by Zachariasen (1963, 1968), was applied. The final value of the extinction coefficient c was 3·5 (5) × 10^{-7}.

The final agreement indices $R_1=\sum||F_o|-|F_c||/$

Table 1. *Positional and thermal parameters for* 8-*azaguanine hydrobromide monohydrate*

Non-hydrogen atom positional and thermal parameters have been multiplied by 10^4. Hydrogen positional parameters have been multiplied by 10^3. The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	537 (1)	1477 (1)	82 (1)	246 (4)	36 (1)	81 (1)	2 (1)	50 (1)	0 (1)
O*W*	−4216 (11)	1072 (14)	4537 (6)	331 (20)	43 (3)	184 (8)	23 (7)	105 (10)	−14 (4)
O(6)	1085 (7)	1979 (3)	3249 (3)	322 (16)	22 (2)	74 (4)	−2 (4)	50 (6)	1 (2)
N(1)	247 (9)	3671 (3)	3322 (4)	260 (16)	23 (2)	75 (4)	1 (5)	60 (7)	2 (2)
N(2)	−4156 (10)	351 (4)	1438 (5)	280 (19)	29 (3)	98 (5)	−7 (6)	70 (9)	−2 (3)
N(3)	2578 (8)	4959 (3)	2376 (4)	248 (15)	25 (2)	73 (4)	−9 (5)	43 (6)	4 (2)
N(7)	−4589 (9)	2642 (3)	1594 (4)	302 (18)	32 (3)	78 (4)	4 (6)	30 (7)	−5 (2)
N(8)	−3241 (10)	3351 (4)	1054 (5)	279 (19)	39 (3)	80 (5)	−1 (6)	50 (8)	0 (3)
N(9)	−3962 (8)	4323 (3)	1224 (4)	257 (18)	36 (3)	78 (4)	0 (5)	35 (7)	−1 (3)
C(2)	666 (9)	4682 (4)	3085 (5)	187 (18)	23 (3)	65 (5)	0 (5)	23 (7)	−1 (3)
C(4)	4020 (9)	4208 (4)	1927 (5)	186 (17)	28 (3)	62 (4)	−10 (6)	40 (7)	0 (3)
C(5)	3634 (9)	3184 (4)	2163 (4)	208 (19)	29 (3)	56 (4)	9 (6)	35 (7)	0 (3)
C(6)	1652 (9)	2840 (4)	2936 (4)	236 (19)	24 (3)	57 (4)	−5 (6)	27 (7)	0 (3)

Table 1 (*cont.*)

	x	*y*	*z*	*B*
H(1)	−101 (12)	354 (4)	382 (6)	2·5 (12)
H(3)	304 (10)	563 (5)	232 (5)	2·8 (12)
H(8)	−199 (18)	326 (7)	65 (9)	6·8 (24)
H(N21)	−460 (11)	101 (6)	147 (5)	3·4 (13)
H(N22)	−303 (11)	18 (4)	101 (5)	1·8 (11)
H(O*W*1)	−336 (25)	169 (10)	449 (14)	11·7 (44)
H(O*W*2)	−325 (11)	79 (5)	439 (6)	3·3 (14)

$\sum|F_o|$ and $R_2=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$ were 0·045 and 0·070, respectively. The positional and thermal parameters derived from the last cycle of least-squares refinement, with their associated standard deviations as estimated from the inverse matrix, are given in Table 1.*

Discussion. The structure of 8-azaguanine hydrochloride monohydrate has been shown to consist of base-paired 8-azaguaninium cations arranged in planar parallel sheets with chloride anions in adjacent planes stacked above and below the plane of the purine (Kozlowski, Singh & Hodgson, 1974). In addition to the proton at N(1), the azapurine ring is protonated at N(3) and N(8), which is in contrast to the theoretical prediction that protonation would be at N(7) and N(9) (Pullman & Pullman, 1963). The interactions of the halogen anion with the purine cation were reported to be localized over two bonds of the purine ring instead of delocalized over the entire ring system. While this halogen–purine interaction is similar to that found in one of the two independent molecules of guanosine hydrobromide (Tougard, 1972), it is entirely different from the arrangement found in 9-methylguanine hydrobromide in which the bromide ions stacked one on another to form neighboring pairs of columns throughout the crystal (Sobell & Tomita, 1964). In order to determine the effects of varying the halogen on the structure, intermolecular interactions and sites of protonation, this investigation of the crystal and molecular structure of 8-azaguanine hydrobromide monohydrate was undertaken.

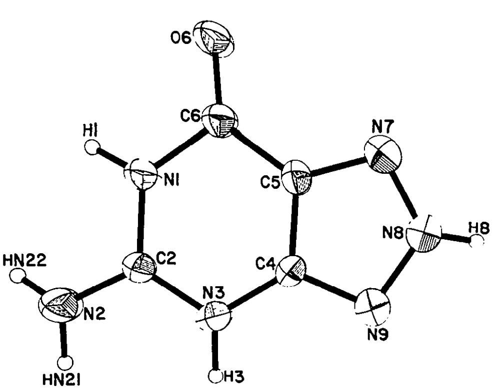

Fig. 1. View of the 8-azaguaninium cation in 8-azaguanine hydrobromide monohydrate. The thermal parameters of the hydrogen atoms have been artificially reduced for clarity.

The structure of 8-azaguanine hydrobromide monohydrate is nearly identical with that of 8-azaguanine hydrochloride monohydrate; a view of the cation is shown in Fig. 1, and a comparison of the bond lengths and angles with those in the hydrochloride analog is

Table 2. *Selected bond lengths* (Å) *in 8-azaguanine hydrobromide monohydrate* (AG.HBr) *and 8-azaguanine hydrochloride monohydrate* (AG.HCl)

	AG.HBr	AG.HCl*
N(1)–C(2)	1·365 (7)	1·365 (3)
C(2)–N(3)	1·339 (7)	1·344 (3)
N(3)–C(4)	1·352 (7)	1·369 (3)
C(4)–C(5)	1·377 (7)	1·391 (3)
C(5)–C(6)	1·432 (7)	1·449 (3)
C(6)–N(1)	1·398 (7)	1·387 (3)
C(5)–N(7)	1·353 (7)	1·334 (3)
N(7)–N(8)	1·315 (7)	1·309 (3)
N(8)–N(9)	1·345 (7)	1·345 (3)
N(9)–C(4)	1·345 (7)	1·326 (3)
C(2)–N(2)	1·310 (7)	1·306 (3)
C(6)–O(6)	1·212 (6)	1·221 (3)
N(1)–H(1)	0·88 (7)	0·89 (4)
N(3)–H(3)	0·92 (7)	0·81 (4)
N(8)–H(8)	0·82 (11)	0·77 (3)
N(2)–H(N21)	0·90 (7)	0·90 (3)
N(2)–H(N22)	0·79 (7)	0·90 (3)

* Kozlowski *et al.* (1974).

Table 3. *Selected bond angles* (°) *in* AG.HBr *and* AG.HCl

	AG.HBr	AG.HCl*
C(6)–N(1)–C(2)	127·4 (5)	127·5 (2)
C(6)–N(1)–H(1)	117 (3)	118 (2)
C(2)–N(1)–H(1)	115 (3)	114 (2)
N(1)–C(2)–N(3)	119·6 (5)	119·8 (2)
N(1)–C(2)–N(2)	118·1 (5)	118·5 (2)
N(2)–C(2)–N(3)	122·3 (5)	121·7 (2)
C(2)–N(2)–H(N21)	122 (4)	122 (2)
C(2)–N(2)–H(N22)	116 (4)	117 (2)
C(2)–N(3)–C(4)	117·6 (4)	117·9 (2)
C(2)–N(3)–H(3)	121 (4)	125 (2)
H(3)–N(3)–C(4)	120 (4)	117 (2)
N(3)–C(4)–C(5)	123·7 (5)	122·9 (2)
N(9)–C(4)–C(5)	109·4 (4)	109·6 (2)
N(3)–C(4)–N(9)	126·9 (5)	127·5 (2)
C(4)–C(5)–C(6)	121·5 (5)	120·8 (2)
N(7)–C(5)–C(6)	129·8 (5)	130·5 (2)
C(4)–C(5)–N(7)	108·7 (4)	108·6 (2)
C(5)–C(6)–N(1)	110·2 (4)	111·1 (2)
C(5)–C(6)–O(6)	129·6 (5)	128·3 (2)
N(1)–C(6)–O(6)	120·1 (5)	120·6 (2)
C(5)–N(7)–N(8)	103·3 (4)	102·9 (2)
N(7)–N(8)–N(9)	116·1 (5)	117·1 (2)
N(7)–N(8)–H(8)	127 (7)	123 (2)
N(9)–N(8)–H(8)	117 (7)	119 (2)
C(4)–N(9)–N(8)	102·5 (4)	101·7 (2)

* Kozlowski *et al.* (1974).

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30929 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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 $[1]=(x,y,z)$; $[2]=(-x,-y,-z)$; $[3]=(\frac{1}{2}-x,\frac{1}{2}-y,\frac{1}{2}-z)$; $[4]=(-\frac{1}{2}-x,-\frac{1}{2}+y,\frac{1}{2}-z)$; $[5]=(-\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z)$; $[6]=(\frac{1}{2}+x,\frac{1}{2}-y,-\frac{1}{2}+z)$.

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Refinement of the Crystal Structure of Kröhnkite

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Abstract. $Na_2Cu(SO_4)_2.2H_2O$, $P2_1/c$, $Z=2$, $D=2\cdot913$ g cm^{-3}. Cell constants at 20°C, $a=5\cdot807$ (1), $b=12\cdot656$ (2), $c=5\cdot517$ (1) Å, $\beta=108\cdot32$ (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 $\sim 3\cdot4\times10^{-3}$