Table 5. *Valence balance for the* CaB_2O_4 *structure*

	O_I	O_{II}	Σ
$\frac{1}{2}$ Ca	$0{\cdot}37+0{\cdot}33+0{\cdot}08$	0·22	1·00
B	1·12	$0{\cdot}95+0{\cdot}92$	2·99
Σ	1·90	2·09	3·99

cannot explain all observed variations in bond lengths nor the observed distortions of the oxygen polyhedra about calcium and boron. For example, the short edge of the BO_3 triangle of 2·319 Å must be ascribed to next nearest neighbor interaction between calcium and boron since this edge is shared between the BO_3 triangle and the CaO_8 polyhedron.

Table 6. *Root mean square thermal displacements along principal axes,* Δ_i, *and direction cosines of principal axes,* $\alpha_1\alpha_2\alpha_3$

Atom	i	Δ_i (Å)	α_1	α_2	α_3
Ca	1	$0{\cdot}087\pm0{\cdot}004$	0·21	0·98	0
	2	$0{\cdot}110\pm0{\cdot}004$	0·98	−0·19	0
	3	$0{\cdot}131\pm0{\cdot}005$	0	0	1·00
B	1	$0{\cdot}071\pm0{\cdot}038$	0·33	0·42	0·85
	2	$0{\cdot}107\pm0{\cdot}016$	0·87	−0·49	−0·09
	3	$0{\cdot}151\pm0{\cdot}021$	0·37	0·76	−0·53
O_I	1	$0{\cdot}101\pm0{\cdot}011$	0·60	0·79	0·16
	2	$0{\cdot}116\pm0{\cdot}012$	0·67	−0·47	−0·47
	3	$0{\cdot}137\pm0{\cdot}012$	0·31	−0·39	0·87
O_{II}	1	$0{\cdot}085\pm0{\cdot}012$	−0·09	1·00	−0·02
	2	$0{\cdot}138\pm0{\cdot}014$	0·05	0·02	1·00
	3	$0{\cdot}170\pm0{\cdot}007$	1·00	0·09	−0·05

In Table 6 the thermal parameters of Table 1 are converted to root mean square displacements along principal axes. Also shown in Table 6 are the orientations of the principal axes expressed in terms of direction cosines, α_1, α_2, α_3, in a cartesian system with X, Y, Z axes along the vectors **a**, **b**, **c**. It is seen that the direction of maximum thermal displacement of the O_{II} atom is approximately normal to the two O_{II}–B bonds.

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The Crystal Structure of Urea Ammonium Bromide

By C. G. C. Catesby*

Research Department, African Explosives and Chemical Industries, Ltd.,
P. O. Northrand, Transvaal, South Africa.

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Crystals of urea ammonium bromide were found to be monoclinic with two molecules in a unit cell of dimensions

$$a=9{\cdot}03\pm0{\cdot}02,\ b=4{\cdot}79\pm0{\cdot}01,\ c=7{\cdot}10\pm0{\cdot}02\ \text{Å with}\ \beta=101{\cdot}3^\circ\pm0{\cdot}1^\circ\ .$$

The space group was found to be $P2_1$. The structure was determined from projections along the b and c axes by using the heavy-atom method. Interatomic distances were obtained which indicated the existence of hydrogen bonds between the ammonium ions and the oxygen atoms of the urea molecules. Examination of the structure also showed the presence of fairly strong electrostatic interactions between the amide groups of the urea molecules and the bromine ions.

Introduction

Little work has been published on the crystallography of the urea inorganic salt complexes, of which a large number exist.

The crystal structure of urea ammonium bromide was examined as part of a series of investigations on these compounds to obtain information on their structures and bonding. In preliminary work carried out in these laboratories it was found that some crystals of urea ammonium bromide appeared to be orthorhombic and others monoclinic. This ambiguity could be accounted for in terms of mimetic twinning (Catesby, 1960), which gave rise to a pseudo-ortho-

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* Present address: Department of Physics, University of Cape Town, Rondebosch, Cape Town, South Africa.

rhombic cell. The true crystal system was found to be monoclinic.

Experimental

Crystals of urea ammonium bromide were prepared by heating 20 g of ammonium bromide and 30·7 g of urea in 10 ml of water and allowing the solution to cool in a desiccator. Crystals of the complex generally appeared after 2–3 hours; they proved to be very hygroscopic. Chemical analysis of the complex showed it to have the formula N_3H_8COBr. The density of the crystals was determined by flotation in toluene and ethylene dibromide.

Some of the crystals were ground and a powder pattern was obtained on a Seifert diffractometer, the specimens being kept in an atmosphere of dry nitrogen.

For a detailed investigation of the structure untwinned crystals were selected. A Unicam camera and a Seifert X-ray generator for Cu $K\alpha$ radiation were used to obtain oscillation and Weissenberg photographs about the axes, the camera being mounted inside a dry box. For measuring the intensities of the *h0l* and *hk0* reflections on the Weissenberg photographs the multiple-film technique was used, 47 *hk0* reflections 111 *h0l* reflections being obtained. The relative intensities of the reflections were measured visually using a standard exposure scale on which one of the reflections from the crystals had been recorded for various times. The intensities were corrected for Lorentz and polarization effects. From the density of the crystals and known mass absorption coefficients, the linear absorption coefficient was found to be 90·5 cm^{-1}; absorption corrections were made by a graphical modification of Albrecht's method (Smith, 1959).

Unit cell and possible space groups

Approximate values of the monoclinic unit-cell parameters were obtained from the Weissenberg and oscillation photographs. These were used to index the powder pattern, which yielded the following values:

$$a=9{\cdot}03\pm0{\cdot}02,\ b=4{\cdot}79\pm0{\cdot}01,\ c=7{\cdot}10\pm0{\cdot}02\ \text{Å}\ ,$$
$$\beta=101{\cdot}3^\circ\pm0{\cdot}1\ .$$

From these the calculated density, with two molecules per unit cell, is 1·74 $g.cm^{-3}$ whilst the density found by flotation is 1·78 $g.cm^{-3}$.

From the Weissenberg photographs the only systematic absences found were for the $0k0$ spectra, when $k=2n+1$. Thus the space group is either $P2_1$ or $P2_1/m$.

Structure analysis

[010] *Projection*

From a Patterson projection the x and z co-ordinates of the bromine ions were obtained. A set of structure factors based on the positions of these ions gave a residual of 35·3%, for an isotropic temperature factor with $B=2{\cdot}3$ Å^2. A Fourier summation was carried out on a Zebra computer for plane group $p2$. The result is shown in Fig. 1.

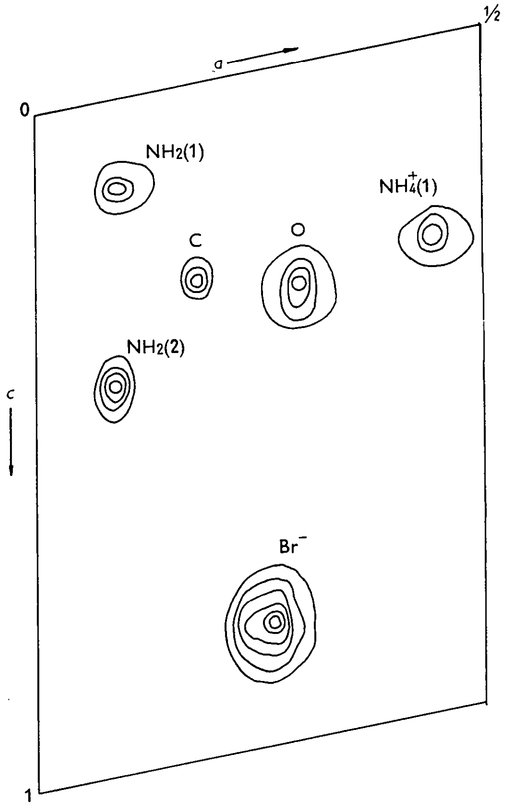

Fig. 1. [010] Electron-density projection. Contours are drawn at arbitrary intervals.

From the projection, the peaks resulting from the urea molecules and bromine ions were identified and a second set of structure factors was calculated incorporating the contribution from these atoms. The residual obtained was 24·4%, for an isotropic temperature factor with $B=3{\cdot}5$ Å^2.

Inspection of the Fourier map showed that the vibrations of some of the atoms were anisotropic. On introducing an average anisotropic temperature factor

$$\exp\,-(B_1\sin^2\varphi+B_2\cos^2\varphi)\sin^2\theta/2$$

with

$$B_1=2{\cdot}5\text{Å}^2\quad\text{and}\quad B_2=4{\cdot}3\ \text{Å}^2$$

(where φ is the angle between the direction of maximum vibration which is parallel to the (104) planes and to the b axis) the residual dropped to 21·1%. On introducing the contribution from the ammonium ions to the structure factors and a modified anisotropic temperature factor the residual dropped to 16·4% for $B_1=2{\cdot}0$ Å^2 and $B_2=5{\cdot}0$ Å^2. Two refinements were carried out using difference projections giving

Table 1. *Observed and calculated structure factors*

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
202	40	55	604	95	85	500	245	−241	$50\bar{7}$	36	−37
302	194	−180	804	60	−57	600	75	−68	303	48	−61
502	145	141	$20\bar{4}$	33	−42	700	105	100	401	193	155
602	60	−79	$30\bar{4}$	165	−184	800	25	24	$50\bar{3}$	125	118
702	67	−68	$40\bar{4}$	59	76	900	92	−88	305	94	94
802	41	53	$50\bar{4}$	113	121	11,0,0	46	66	$60\bar{7}$	35	33
902	63	61	$60\bar{4}$	52	−59	$10\bar{5}$	45	48	$50\bar{1}$	206	−173
10,0,2	40	−50	$70\bar{4}$	24	−18	$10\bar{1}$	141	−138	403	148	−160
$10\bar{2}$	198	−200	$10,0,\bar{4}$	64	−68	$20\bar{5}$	80	−99	$60\bar{5}$	85	−94
$20\bar{2}$	242	232	$10\bar{6}$	40	−61	$10\bar{7}$	29	−38	307	43	−43
$30\bar{2}$	138	131	006	67	74	101	109	132	501	110	94
$40\bar{2}$	218	−228	106	21	22	203	147	181	603	83	82
$60\bar{2}$	138	126	206	58	−60	005	61	67	$60\bar{1}$	28	32
$70\bar{2}$	43	−54	406	38	47	$20\bar{1}$	25	27	503	60	52
$80\bar{2}$	79	−92	606	27	−29	103	75	−78	$70\bar{5}$	24	36
$90\bar{2}$	54	67	$20\bar{6}$	65	−68	$30\bar{3}$	73	−90	601	129	−140
$10,0,\bar{2}$	46	48	$40\bar{6}$	35	40	105	36	−33	$70\bar{3}$	133	−138
$11,0,\bar{2}$	36	−45	$50\bar{6}$	53	−67	$40\bar{7}$	19	−35	505	98	−70
$10\bar{4}$	139	148	$70\bar{6}$	50	46	$30\bar{1}$	304	307	$70\bar{1}$	127	123
004	65	−65	$40\bar{8}$	29	−34	203	130	137	603	128	124
104	175	−171	$20\bar{8}$	36	43	$40\bar{5}$	51	61	$80\bar{5}$	56	60
204	107	93	008	28	−29	107	36	49	$80\bar{3}$	38	−11
304	103	94	308	17	−20	301	225	−190	$80\bar{1}$	82	−102
404	38	−44	300	86	77	$40\bar{3}$	47	−47	703	35	−58
504	21	−18	400	187	151	205	46	−59	801	131	126

a final residual of 11·3%, with $B_1 = 2{\cdot}0$ Å^2 and $B_2 = 5{\cdot}0$ Å^2. The residual was not improved by further adjustments of B_1 and B_2.

No attempt was made to determine the position of the hydrogen atoms. The final set of structure factors for this projection is given in Table 1.

Determination of the space group

At this stage it was still unknown whether the space group was $P2_1$ or $P2_1/m$. Consideration of the equivalent positions of space group $P2_1/m$ with regard to the urea molecules showed that on the grounds of the x and z co-ordinates established from the [010] projection, the only possible twofold equivalent positions that these could occupy would place them on the mirror planes at $y = \frac{1}{4}$ and $\frac{3}{4}$. Since the symmetry of the urea molecule is *mm* it can only take up two possible orientations on the mirror planes. With one of these all the atoms lie in the mirror planes. With the other the carbon and oxygen atoms are in the mirror planes with the amide groups disposed enantiomorphously in the direction of the b axis. The latter disposition is ruled out by the appearance of two amide groups in [010] projection.

Measurement of the interatomic distances between the two amide groups in the [010] projection gave a value of 1·88 Å which is considerably less than the actual separation of 2·30 Å obtained from previous work (Landolt-Börnstein, 1955), indicating that the urea molecules are in fact tilted and do not lie in a plane at right angles to the b axis. This precludes the existence of the mirror planes, and hence space group $P2_1/m$. It was therefore concluded that the space group must be $P2_1$.

[001] *Projection*

In general the [001] projection of space group $P2_1$ is non-centrosymmetrical. The y co-ordinates of the bromine ions were chosen as $y = \frac{1}{4}$ and $y = \frac{3}{4}$ and the phases were allocated to the structure amplitudes as calculated from these co-ordinates and the x co-ordinates obtained from the [010] projection. A centrosymmetrical Fourier summation was then carried out on a Zebra computer. This procedure, of course, results in the superposition of a spurious set of peaks from the urea molecules and ammonium ions on the peaks belonging to the non-centrosymmetrical structure. It is therefore necessary to choose, by trial

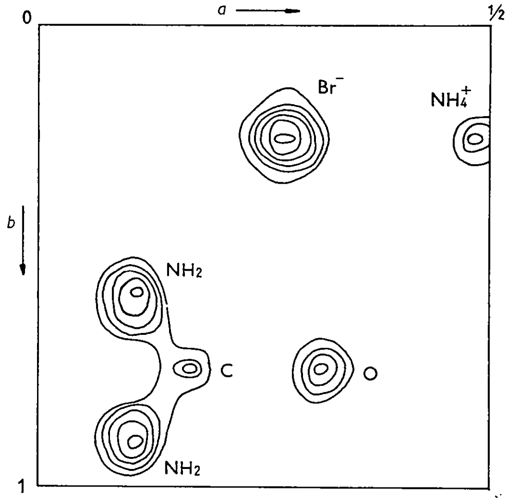

Fig. 2. [001] Electron-density projection. Contours are drawn at arbitrary intervals.

and error, the correct set of peaks. The centrosymmetrical Fourier projection is shown in Fig. 2. Only a single set of peaks is present. Thus the projection is, by chance, centrosymmetrical. This arises because the two amide groups of a urea molecule have the same x co-ordinate and the non-centrosymmetrical nature of the structure results only from a tilt of the amide groups about an axis through the oxygen and carbon atoms. Since this axis in projection is parallel to the x axis of the unit cell, two mirror planes are simulated at $y=\frac{1}{4}$ and $y=\frac{3}{4}$.

A set of structure factors calculated from the positions of the atoms obtained from the Fourier map (Fig. 2) gave a residual of 16·1% for an isotropic temperature factor with $B=3{\cdot}5$ Å^2.

Table 2. *Observed and calculated structure factors*

hkl	F_o	F_c	*hkl*	F_o	F_c
020	293	−316	10,0,0	16	18
120	101	91	060	29	−46
220	213	212	110	166	−154
320	66	−72	210	156	137
420	150	−155	310	232	218
520	115	110	410	68	−72
620	32	24	510	143	−140
720	71	−75	610	98	85
920	75	58	710	55	49
040	76	112	810	81	−72
140	37	−42	910	32	−26
240	62	−95	10,1,0	48	43
340	32	36	130	97	134
440	52	76	330	68	−70
540	38	−43	430	68	70
740	30	39	530	83	80
200	294	−270	630	74	−69
300	55	58	730	50	−50
400	157	145	830	38	30
500	246	−213	150	35	−44
600	68	−65	350	31	38
700	68	87	550	27	−31
800	30	21	650	19	24
900	71	−59			

The atomic co-ordinates were refined by means of a least squares method on a Zebra computer and after 29 cycles the residual was 12·5% for an isotropic temperature factor with $B=4{\cdot}04$ Å^2. The final set of structure factors for this projection is given in Table 2.

Atomic parameters, standard deviations and interatomic distances

The refined atomic parameters obtained from the [010] and [001] projections together with the standard deviations estimated from Cruickshank's formula (Cruickshank, 1949; Ahmed & Cruickshank, 1953) are given in Tables 3 and 4. The intra- and intermolecular distances are listed in Table 5.

Table 3. *Atomic parameters*

	x	y	z
Br^-	0·2754	0·2500	0·8201
$NH_2(1)$	0·098	0·602	0·141
$NH_2(2)$	0·100	0·899	0·406
O	0·314	0·750	0·341
C	0·174	0·750	0·297
NH_4^+	0·490	0·250	0·307

Table 4. *Standard deviations*

	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Br^-	0·003 Å	0·004 Å	0·002 Å
$NH_2(1)$	0·022	0·034	0·014
$NH_2(2)$	0·022	0·034	0·014
O	0·020	0·022	0·021
C	0·036	0·044	0·025
NH_4^+	0·026	0·025	0·030

Table 5

Intramolecular distances and standard deviations

Bond		s.d.
C–O	1·24 Å	0·04 Å
C–NH_2(1)	1·38	0·04
C–NH_2(2)	1·32	0·04

Intermolecular distances and standard deviations

		s.d.
O ··· NH_4^+(1)	2·91 Å	0·03 Å
O ··· NH_4^+(2)	2·76	0·04
Br^- ··· NH_4^+(2) (twice)	3·45	0·02
Br^- ··· NH_4^+ (Br^-, $z=1{\cdot}307$)	3·62	0·02
Br^- ··· NH_2(1)	3·46	0·02
Br^- ··· NH_2(2)	3·49	0·02
Br^- ··· NH_2(1)	3·53	0·02
Br^- ··· NH_2(2)	3·53	0·02

Discussion

Owing to the strong electronegative character of the ammonium ion, this would be expected to enter readily into hydrogen bonding. Although no attempt has been made to locate the position of the hydrogen atoms, the interatomic distances of 2·76 and 2·91 Å between the oxygen and ammonium ions suggest the existence of hydrogen bonding. These values lie within the range 2·76 to 2·98 Å which is generally found for nitrogen to oxygen hydrogen bonds. For example the distance of 2·76 Å is very close to that found for the strong nitrogen-to-oxygen hydrogen bonds found in glycine (Marsh, 1958).

Further evidence for the existence of ammonium-to-oxygen hydrogen bonds is suggested by the shortest bromine-to-ammonium interionic distance, namely 3·45 Å. Reference to the structure of ammonium bromide shows a separation of 3·52 Å for these ions (Smits & Tollenaar, 1942). The shorter distance found in the structure of urea ammonium bromide may be accounted for on the grounds of restricted rotation of the ammonium ion resulting from the hydrogen bonding.

Reference to the atomic co-ordinates obtained for the structure shows that between adjacent unit cells the closest oxygen-to-ammonium separation is 2·91 Å,

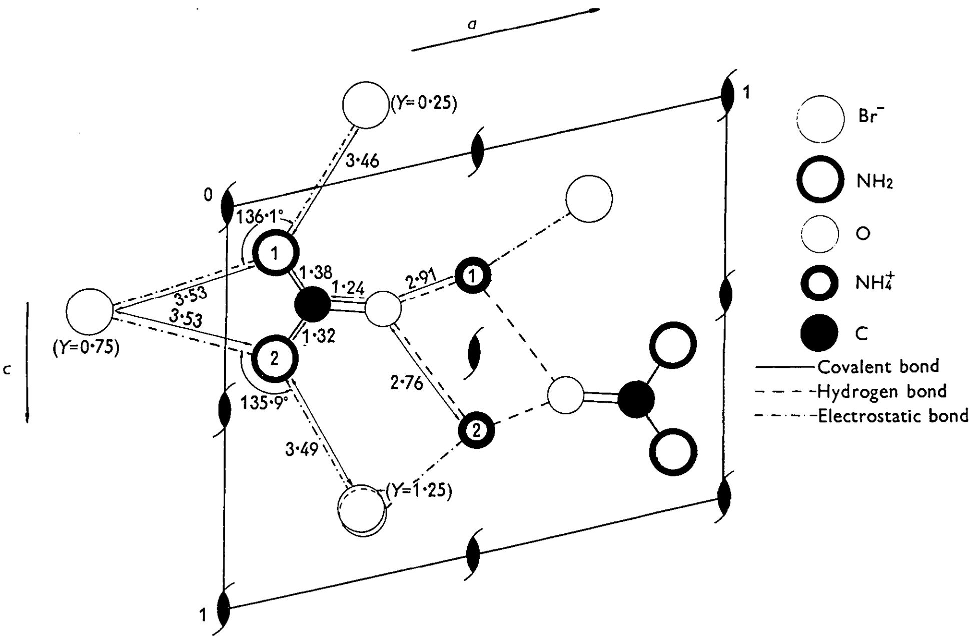

Fig. 3. View of the structure along [010] showing hydrogen and electrostatic bonds.

a value also encountered within the unit cell (Table 5). This implies that a zigzag chain of hydrogen bonds, approximately in the direction of the *b* axis, exists throughout the crystal. An interesting comparison may be drawn between the structure of urea ammonium bromide and the urea hydrocarbon complexes which are clathrate in character. It has been shown, in general, in these hydrocarbon complexes that hydrogen bonds are present between the oxygen and the amide groups of the urea forming a spiral around the hydrocarbon molecule (Schlenk, 1949). In contrast the zigzag chain of hydrogen bonds in urea ammonium bromide involves both constituents of the complex, and this probably accounts for the stoichiometric character.

The four electrostatic bonds between the bromine ions in adjacent unit cells and the amide groups of each urea molecule are of interest since an examination of the structure shows that these are approximately co-planar with the urea molecule.

Calculation of the Br^-–N–Br^- bond angle gives a value of 136·0 ± 0·5° which on comparison with the value of 122° 8′ (Worsham, Levy & Peterson, 1957) for the H–N–H angle in urea itself indicates that the hydrogen atoms of the amide groups are directed towards the bromine ions. The [010] view of the structure and bonds is given in Fig. 3.

The existence of these bonds, together with the close proximity of the positively charged ammonium ions to the carbonyl oxygen atoms, (owing to hydrogen bonding) is clearly of interest from the point of view of the modified charge distribution that would be expected to result in the urea molecule.

The crystal structures of two further urea inorganic salt complexes (Catesby, 1961) are at present being investigated, with a view to determining the general nature of the bonding and to see if similar types of electrostatic interactions occur involving the amide groups of the urea.

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