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Calcium Bromide Hexaurea

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Abstract. $[Ca.6CO(NH_2)_2]Br_2$ is monoclinic, space group $P2_1/c$, a = 10·203 (1), b = 7·881 (1), c = 13·336 (2) Å, β = 94·07 (2)°, Z = 2, D_m = 1·716, D_x = 1·739 g cm^{-3}. Six O atoms of the urea molecules form a nearly regular octahedron around the Ca ion. The Br ions are not included in the first coordination sphere of the cation.

Introduction. Crystals were obtained by slow evaporation of an aqueous solution of calcium bromide and urea with the molar ratio 1:6. A crystal, ground to a sphere of diameter 0·30 mm, was used to collect intensity data on an Enraf–Nonius CAD-4 diffractometer. The cell parameters were obtained from the least-squares fit of the φ, χ, ω, 2θ values for 15 reflexions. They agree with the values previously reported by Durski (1970). The intensities were measured out to θ = 27° with graphite-monochromated Mo $K\alpha$ radiation. A $\theta/2\theta$ scan was used, with scan width varying as 0·80° + 0·42° tan θ. The background was measured at both ends of the reflexions over one quarter of the scan range. Deviations in the intensity of a standard reflexion, monitored after each group of 23 measurements, were less than 2%. Lorentz, polarization and absorption corrections (*International Tables for X-ray Crystallography*, 1968) were applied to the intensity-data set. Of the 1913 measured independent reflexions, 1867 had positive net intensities and were used in further calculations.

The structure was determined by the heavy-atom method and refined by full-matrix least squares, minimizing $\Sigma\, w[F_o - (1/K)F_c]^2$. The weights used were the product of those resulting from counting statistics combined with the Cruickshank (1969) scheme. All H atoms were identified in difference Fourier maps but the refinement of their parameters resulted in unrealistic temperature factors. In the final least-squares cycles, the positions of the H atoms were therefore calculated from the geometry of the urea molecule and kept fixed. Neutral-atom scattering factors (Cromer & Waber,

Table 1. *Atomic positional parameters* ($\times 10^4$) *and their standard deviations for non-hydrogen atoms*

	x	y	z
Ca	0	5000	5000
Br	5102·7 (4)	6418·5 (5)	8558·3 (3)
O(1)	2120 (2)	4180 (4)	4710 (2)
N(1)	4041 (3)	3518 (5)	4083 (3)
N(2)	2389 (3)	4699 (5)	3071 (3)
C(1)	2821 (3)	4121 (5)	3973 (3)
O(2)	722 (2)	7784 (3)	5225 (2)
N(3)	2892 (3)	7914 (5)	5653 (3)
N(4)	1704 (3)	10332 (4)	5436 (3)
C(2)	1730 (4)	8643 (4)	5418 (3)
O(3)	480 (2)	4512 (3)	6711 (2)
N(5)	2647 (3)	4427 (5)	7127 (3)
N(6)	1372 (4)	6201 (6)	7948 (3)
C(3)	1462 (4)	5012 (5)	7250 (3)

Table 2. *Hydrogen-atom parameters* ($\times 10^3$)

The positional parameters calculated from the geometry of the urea molecule and used in the refinement. All hydrogen atoms were assigned an isotropic temperature factor which refined to $U = 0{\cdot}057\,(5)$ Å^2.

	x	y	z
H(1)	437	307	476
H(2)	460	348	350
H(3)	295	465	249
H(4)	149	515	299
H(5)	288	665	564
H(6)	370	859	581
H(7)	256	1101	559
H(8)	88	1088	526
H(9)	273	354	660
H(10)	344	483	755
H(11)	215	660	838
H(12)	48	664	805

1965) were used. Corrections for anomalous scattering were applied to the Br scattering function (Cromer, 1965). Discrepancy indices for all $F_o^2 > 0$ were $R = 0{\cdot}043$, $R_w = 0{\cdot}044$ and $R_g = 0{\cdot}058$, where $R_w = \Sigma w^{1/2}\Delta F/\Sigma w^{1/2}F$ and $R_g = \Sigma w\Delta F^2/\Sigma wF^2$.* The maximum and average shift-to-error ratios were 0·38 and 0·10. The final difference syntheses were featureless except for two peaks of about 1·1 e Å^{-3} near the Br position. Most of the calculations were done with the system of programs written by Sheldrick (1972). The final parameters are listed in Tables 1 and 2.*

Discussion. As far as we know this is the first structure reported in which a non-transition cation has only urea molecules in its first coordination zone. The Ca ion coordinates six O atoms of urea molecules at the vertices of a slightly distorted octahedron of symmetry $\bar{1}$, as shown in Fig. 1. Some of the more important distances are given in Table 3. Of three symmetry-independent urea molecules two are so arranged that the cation lies nearly in the plane of the molecule. Ca–O(1)–C(1) and Ca–O(2)–C(2) angles are 137·0 and 142·2°, respectively; thus only one electron pair of the sp^2-hybridized O atoms is directed towards Ca^{2+}. O(2) is the acceptor in the N(4)–H(8)···O(2) hydrogen bond. The calcium ion is not in the plane of the third urea molecule; the angle between the Ca–O(3) bond and the plane is 50·0°. O(3) is also an acceptor, in the N(2)–H(4)···O(3) intracomplex hydrogen bond.

Table 3. *Distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Urea 1			
C(1)–O(1)	1·256 (4)	N(1)–C(1)–N(2)	117·9 (3)
C(1)–N(1)	1·331 (5)	O(1)–C(1)–N(1)	120·5 (4)
C(1)–N(2)	1·332 (5)	O(1)–C(1)–N(2)	121·6 (3)
Urea 2			
C(2)–O(2)	1·242 (4)	N(3)–C(2)–N(4)	116·4 (3)
C(2)–N(3)	1·335 (5)	O(2)–C(2)–N(3)	121·5 (3)
C(2)–N(4)	1·332 (5)	O(2)–C(2)–N(4)	122·1 (4)
Urea 3			
C(3)–O(3)	1·255 (4)	N(5)–C(3)–N(6)	116·4 (4)
C(3)–N(5)	1·315 (5)	O(3)–C(3)–N(5)	121·5 (4)
C(3)–N(6)	1·329 (5)	O(3)–C(3)–N(6)	122·1 (4)
Calcium shell			
Ca–O(1)	2·316 (2)	O(1)–Ca–O(2)	89·6 (1)
Ca–O(2)	2·327 (2)	O(1)–Ca–O(3)	89·1 (1)
Ca–O(3)	2·331 (2)	O(2)–Ca–O(3)	89·2 (1)
Ca–urea 1 plane	0·046	Ca–O(1)–C(1)	137·0 (2)
Ca–urea 2 plane	0·079	Ca–O(2)–C(2)	142·2 (2)
Ca–urea 3 plane	1·745	Ca–O(3)–C(3)	127·8 (2)

Table 4. *Distances* (Å) *in the hydrogen-bonding system*

D–H···A	Acceptor position	D···A
N(4)–H(8)···O(2)	$-x, 2-y, 1-z$	2·967 (5)
N(2)–H(4)···O(3)	$-x, 1-y, 1-z$	3·026 (4)
N(1)–H(1)···Br	$1-x, -\frac{1}{2}+y, -\frac{3}{2}+z$	3·607 (4)
N(1)–H(2)···Br	$1-x, 1-y, 1-z$	3·689 (4)
N(2)–H(3)···Br	$1-x, 1-y, 1-z$	3·583 (3)
N(3)–H(6)···Br	$1-x, \frac{1}{2}+y, -\frac{3}{2}+z$	3·552 (4)
N(4)–H(7)···Br	$1-x, \frac{1}{2}+y, -\frac{3}{2}+z$	3·539 (4)
N(5)–H(9)···Br	$1-x, -\frac{1}{2}+y, -\frac{3}{2}+z$	3·467 (4)
N(5)–H(10)···Br	x,y,z	3·421 (4)

The complex cations form *bc*-plane layers in an arrangement similar to the two-dimensional close-packing of spheres. Midway between the cation layers there are layers of Br$^-$ ions deviating ±0·11 Å from the plane. The tessellation of Br atoms can be described as deformed hexagons centred on the cation, but there are hydrogen bonds to only four of the six bromide anions forming the mesh, as shown in Fig. 1. Br$^-$ ions are the acceptors of seven hydrogen bonds, six from one of the neighbouring cation layers and one, the shortest, from the other. The distances in the hydrogen-bonding system are given in Table 4.

We are grateful to the X-ray Laboratory of SLAFiBS Kraków for making available the diffractometer.

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* The structure factor table is available from the authors on request and has also been deposited, along with a list of anisotropic thermal parameters, with the British Library Lending Division as Supplementary Publication No. SUP 32675 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

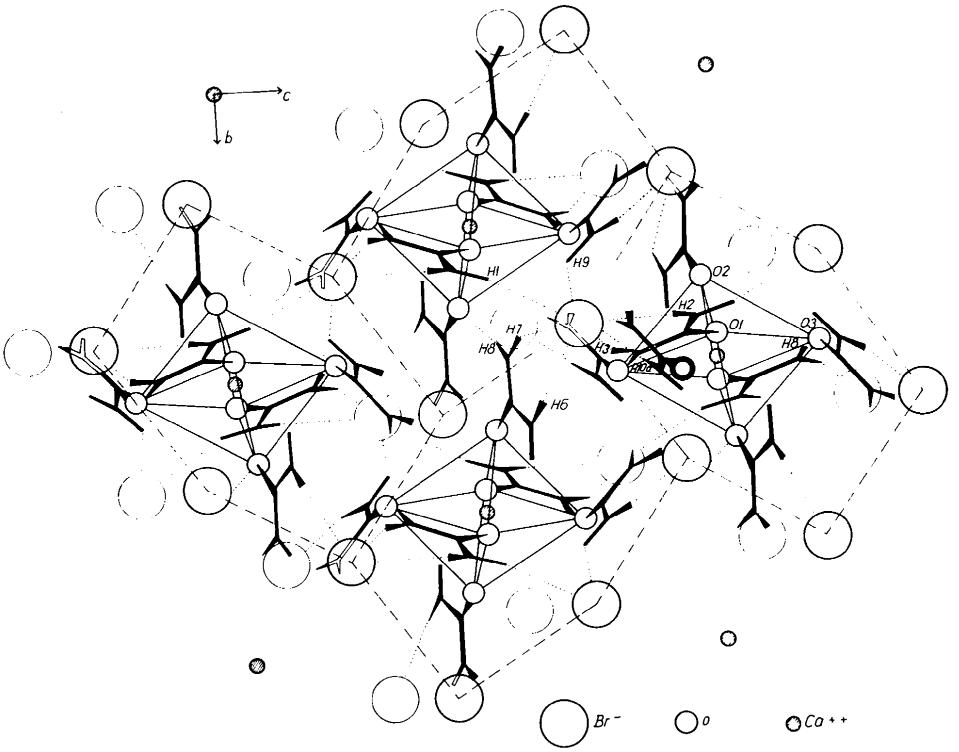

Fig. 1. The layer of $[Ca.6CO(NH_2)_2]^{2+}$ cations, parallel to the *bc* plane, with the adjacent layers of bromide anions. Dot-dashed lines show the tessellation of Br^-, dotted lines denote hydrogen bonds. One urea molecule from the upper layer, drawn in heavier lines, is added to show the complete environment of the Br^- ions.

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Refinement of the Crystal Structure of Brewsterite, $Ba_{0.5}Sr_{1.5}Al_4Si_{12}O_{32}.10H_2O$

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Abstract. Brewsterite, composition derived from electron microprobe analysis: $(K_{0.01}Ba_{0.24}Sr_{0.71})_2$-$Al_{4.1}Si_{11.9}O_{32}.nH_2O$, a = 6·793 (2), b = 17·573 (6), c = 7·759 (2) Å, β = 94·54 (3)°, $P2_1/m$, has a full occupancy of two cation and ten water sites. The Sr,Ba atom is bonded to five water molecules at 2·63–2·83 Å and four framework O atoms at 2·83 and 2·89 Å. Pairs of water molecules at 2·98 or 3·07 Å alternate with Sr,Ba along **a** and **c** to form a two-dimensional system of intersecting chains. Distances between water molecules and framework O atoms range upwards from 2·90 Å. Hydrogen bonding is likely but no unique model is apparent. Tetrahedral distances indicate ~0·3 Al in site $T(A)$, ~0·4 Al in $T(B)$ and $T(C)$, and ~0 Al