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Hexakis(urea)magnesium Bromide–Urea (1/4)

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Abstract. $[Mg\{CO(NH_2)_2\}_6]Br_2.4CO(NH_2)_2$, $C_{10}H_{40}Br_2MgN_{20}O_{10}$, monoclinic, $P2_1/c$, $a = 9{\cdot}723\ (4)$, $b = 7{\cdot}228\ (3)$, $c = 23{\cdot}751\ (9)$ Å, $\beta = 95{\cdot}79\ (4)^\circ$, $D_m = 1{\cdot}550$, $D_x = 1{\cdot}572$ Mg m^{-3}. The Mg^{2+} ions are octahedrally coordinated by the O atoms from six urea molecules. The remaining four urea molecules are hydrogen bonded to the Br^- anions and separate the complex cations.

Introduction. Crystals of the title compound were obtained by slow evaporation of an aqueous solution of magnesium bromide and urea in a molar ratio 1:10. A crystal ground to a sphere of diameter 0·37 mm was used to collect intensity data on an Enraf–Nonius CAD-4 diffractometer. Variable θ–2θ scans in the 2θ range 0–120° and graphite-monochromatized Mo $K\alpha$ radiation were used. The cell parameters were obtained from the least-squares fit of φ, χ, ω, 2θ values for 15 reflections. The space group was determined unambiguously from systematic absences. Lorentz, polarization and absorption corrections were applied. Of the 2960 reflections measured, 2732 independent values with positive intensities were used. The structure was determined by the heavy-atom method and refined by a full-matrix least-squares procedure minimizing $\sum w[|F_o| - (1/K)|F_c|]^2$. The weights were $w^{-1} = \sigma^2(|F_o|)$.

All H atoms were identified in difference Fourier maps and refined using fixed isotropic temperature factors of the atoms to which they were bonded. Neutral-atom scattering factors were used (*International Tables for X-ray Crystallography*, 1974). Discrepancy indices for all $F_o^2 > 0$ were $R = 0{\cdot}049$, $R_w = 0{\cdot}034$ and $R_g = 0{\cdot}031$, where $R = \sum |\Delta F|/\sum |F|$, $R_w = \sum w^{1/2}|\Delta F|/\sum w^{1/2}|F|$ and $R_g = \sum w|\Delta F|^2/\sum w|F|^2$. In the last least-squares cycle the maximum and average shift to e.s.d. ratios for non-hydrogen atoms were 0·27 and 0·05. Most of the calculations were performed with the system of programs written by Sheldrick (1976). Fig. 1 was prepared with the program *PLUTO* (Motherwell, 1972). The final atomic coordinates and their standard deviations are given in Table 1.*

Discussion. The contents of the unit cell are shown in Fig. 1. The Mg^{2+} ion coordinates to six O atoms of the urea molecules at the vertices of a slightly distorted octahedron of symmetry $\bar{1}$. Some of the more important distances and angles are in Table 2. Two urea

Table 1. *Atomic positional coordinates* (×10⁵ *for* Br, ×10⁴ *for* Mg, C, N *and* O *atoms*, ×10³ *for* H *atoms*) *with e.s.d.'s in parentheses*

	x	*y*	*z*
Mg	0	5000	5000
Br	48249 (5)	26885 (8)	29959 (2)
C(1)	1605 (5)	2801 (6)	4173 (2)
N(11)	2576 (7)	2196 (8)	4576 (3)
N(12)	1740 (6)	2287 (7)	3626 (2)
O(1)	623 (3)	3801 (5)	4284 (1)
H(11)	248 (9)	236 (8)	488 (4)
H(12)	324 (7)	121 (9)	446 (3)
H(13)	249 (8)	185 (10)	353 (3)
H(14)	111 (8)	304 (8)	333 (3)
C(2)	657 (6)	2107 (6)	5929 (2)
N(21)	1619 (6)	1476 (10)	6332 (2)
N(22)	−644 (5)	1734 (9)	5992 (3)
O(2)	1003 (4)	3046 (5)	5528 (2)
H(21)	247 (6)	178 (8)	628 (2)
H(22)	138 (6)	70 (9)	664 (3)
H(23)	−86 (7)	92 (10)	626 (3)
H(24)	−133 (10)	210 (11)	575 (4)
C(3)	2612 (5)	7112 (6)	5482 (2)
N(31)	3720 (5)	8133 (8)	5410 (2)
N(32)	2376 (6)	6746 (10)	6014 (2)
O(3)	1824 (3)	6533 (4)	5068 (1)
H(31)	388 (7)	842 (10)	499 (3)
H(32)	430 (6)	853 (7)	567 (3)
H(33)	177 (7)	607 (8)	608 (3)
H(34)	295 (10)	500 (12)	626 (4)
C(4)	4387 (6)	−2585 (6)	−1079 (3)
N(41)	5014 (6)	−2887 (8)	−1536 (2)
N(42)	4129 (7)	−860 (7)	−926 (3)
O(4)	4119 (4)	−3996 (4)	−794 (2)
H(41)	505 (8)	−212 (11)	−179 (4)
H(42)	493 (5)	−387 (7)	−173 (2)
H(43)	383 (9)	−81 (11)	−56 (4)
H(44)	425 (7)	−4 (11)	−118 (3)
C(5)	−1136 (5)	3255 (7)	2544 (2)
N(51)	−1849 (5)	4812 (7)	2605 (2)
N(52)	−1830 (5)	1637 (7)	2521 (2)
O(5)	140 (3)	3284 (5)	2515 (2)
H(51)	−271 (7)	479 (10)	263 (3)
H(52)	−136 (8)	591 (13)	258 (3)
H(53)	−141 (8)	68 (11)	243 (3)
H(54)	−274 (6)	167 (7)	258 (2)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33960 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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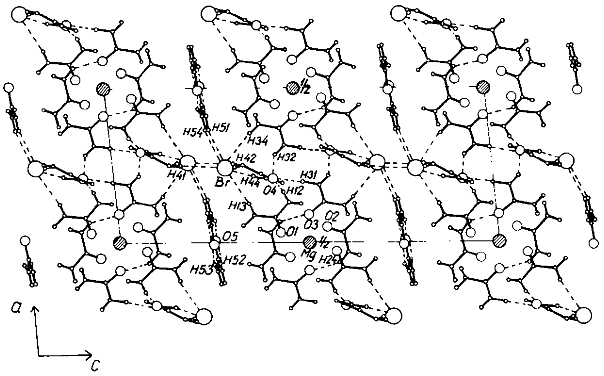

Fig. 1. The structure of $[Mg\{CO(NH_2)_2\}_6]Br_2.4CO(NH_2)_2$ viewed down the *b* axis. Broken lines denote hydrogen bonds.

Table 2. *Some distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

For mean values e.s.d.'s are defined by: $[\sum_n (d - \langle d \rangle)/(n-1)]^{1/2}$.

C(1)–O(1)	1·246 (6)	N(11)–C(1)–N(12)	117·4 (5)
C(1)–N(11)	1·347 (8)	O(1)–C(1)–N(11)	122·3 (5)
C(1)–N(12)	1·370 (8)	O(1)–C(1)–N(12)	120·5 (5)
C(2)–O(2)	1·243 (6)	N(21)–C(2)–N(22)	117·1 (5)
C(2)–N(21)	1·348 (7)	O(2)–C(2)–N(21)	120·5 (5)
C(2)–N(22)	1·317 (8)	O(2)–C(2)–N(22)	122·4 (5)
C(3)–O(3)	1·256 (5)	N(31)–C(3)–N(32)	116·7 (5)
C(3)–N(31)	1·350 (7)	O(3)–C(3)–N(31)	121·5 (5)
C(3)–N(32)	1·333 (7)	O(3)–C(3)–N(32)	121·8 (5)
C(4)–O(4)	1·265 (6)	N(41)–C(4)–N(42)	119·7 (6)
C(4)–N(41)	1·317 (8)	O(4)–C(4)–N(41)	116·4 (5)
C(4)–N(42)	1·329 (7)	O(4)–C(4)–N(42)	123·8 (6)
C(5)–O(5)	1·249 (6)	N(51)–C(5)–N(52)	118·1 (5)
C(5)–N(51)	1·337 (7)	O(5)–C(5)–N(51)	121·3 (5)
C(5)–N(52)	1·348 (7)	O(5)–C(5)–N(52)	120·5 (5)
Mg–O(1)	2·054 (3)	O(1)–Mg–O(2)	93·1 (1)
Mg–O(2)	2·066 (3)	O(1)–Mg–O(3)	88·2 (1)
Mg–O(3)	2·084 (3)	O(2)–Mg–O(3)	88·3 (1)
Mg–urea(1) plane	0·061	Mg–O(1)–C(1)	135·8 (3)
Mg–urea(2) plane	0·638	Mg–O(2)–C(2)	133·7 (3)
Mg–urea(3) plane	0·031	Mg–O(3)–C(3)	133·2 (3)
Mean C–O	1·252 (9)	Mean N–C–N	117·8 (12)
Mean C–N	1·338 (12)	Mean O–C–N	121·1 (19)
Mean N–H	0·89 (8)		

molecules, not bonded to Mg^{2+}, separate the complex cations. Urea(5) form ribbons extending along *b*. The molecules related by the screw axis are bonded together by two hydrogen bonds. The Br^- ion is not included in the first coordination zone of the Mg^{2+} ion. It is an acceptor of seven hydrogen bonds from the amine groups of the urea molecules. Hydrogen bonding gives rise to a three-dimensional net in the structure; the distances and angles are given in Table 3. The intermolecular bonding to the carbonyl O atoms, except O(4), reflects their sp^2 hybridization. The O atoms coordinated by Mg^{2+} are directed with one of the two free electron pairs towards the cation, being approximately in the planes of the urea molecules. Hydrogen bonding to O(3) and O(5) agrees well with the electron distribution of the acceptor. O(4) accepts three hydrogen bonds as in biurea (Brown & Russell, 1976), hydroxyurea (Armagan, Richards & Uraz, 1976), and phenylurea (Kashino & Haisa, 1977).

Of the 20 available H atoms only 13 are involved in hydrogen bonding; the rigid urea molecules, attached to the cation, with donors lying in one plane, are unable to form four hydrogen bonds simultaneously.

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Table 3. *Distances* (Å) *and angles* (°) *in the hydrogen-bonding system*

D–H···*A*	Acceptor position	*D*–H	*D*···*A*	H···*A*	∠*D*–H···*A*	∠C=O···H	Urea plane ···H (acceptor)
N(22)–H(24)···O(3)	$-x,\ 1-y,\ 1-z$	0·88 (9)	2·939 (7)	2·18 (10)	144 (4)	127 (3)	0·94
N(11)–H(12)···O(4)	$x,\ -\frac{1}{2}-y,\ \frac{1}{2}+z$	1·02 (7)	2·939 (6)	1·94 (8)	167 (3)	162 (4)	0·54
N(31)–H(31)···O(4)	$x,\ \frac{1}{2}-y,\ \frac{1}{2}+z$	1·04 (8)	2·991 (6)	1·95 (9)	178 (4)	113 (4)	0·66
N(31)–H(32)···O(4)	$1-x,\ \frac{3}{2}+y,\ \frac{1}{2}-z$	0·85 (6)	2·991 (6)	2·36 (8)	137 (3)	121 (4)	1·33
N(51)–H(52)···O(5)	$-x,\ \frac{1}{2}+y,\ \frac{1}{2}-z$	0·93 (9)	3·039 (6)	2·11 (9)	175 (4)	124 (5)	−0·02
N(52)–H(53)···O(5)	$-x,\ -\frac{1}{2}+y,\ \frac{1}{2}-z$	0·84 (8)	2·934 (6)	2·12 (9)	162 (4)	126 (5)	0·19
N(12)–H(13)···Br	$x,\ y,\ z$	0·85 (8)	3·497 (3)	2·77 (9)	144 (3)		
N(32)–H(34)···Br	$1-x,\ 1-y,\ 1-z$	0·79 (9)	3·437 (4)	2·66 (9)	168 (4)		
N(41)–H(41)···Br	$1-x,\ -y,\ -z$	0·83 (8)	3·490 (3)	2·90 (9)	130 (4)		
N(41)–H(42)···Br	$x,\ -\frac{1}{2}-y,\ -\frac{1}{2}+z$	0·85 (5)	3·643 (3)	2·84 (7)	161 (2)		
N(42)–H(44)···Br	$x,\ \frac{1}{2}-y,\ -\frac{1}{2}+z$	0·87 (7)	3·553 (4)	2·69 (9)	175 (3)		
N(51)–H(51)···Br	$-1+x,\ y,\ z$	0·84 (7)	3·780 (3)	3·04 (8)	148 (3)		
N(52)–H(53)···Br	$-1+x,\ y,\ z$	0·84 (8)	3·629 (3)	2·76 (7)	161 (3)		