N1—Cu—O2	84.79 (7)	N1—Cu—O4	101.42 (7)
O1—Cu—N2	89.85 (7)	O2—Cu—O4	86.12 (7)
N1—Cu—N2	166.44 (7)	N2—Cu—O4	91.46 (7)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H41···O5	0.89 (3)	2.04 (3)	2.855 (3)	153 (3)
O4—H42···O5^{i}	0.89 (3)	1.94 (3)	2.821 (3)	167 (3)
O5—H51···O3^{ii}	0.89 (3)	1.85 (3)	2.733 (3)	171 (3)
O5—H52···O1	0.89 (3)	1.89 (3)	2.757 (3)	165 (3)

Symmetry codes: (i) $2 - x, 2 - y, 1 - z$; (ii) $2 - x, \frac{1}{2} + y, \frac{1}{2} - z$.

All H atoms, except water H atoms, were included at calculated positions using *SHELXL*97 (Sheldrick, 1997*a*) and were refined using a riding model. The U_{iso} value for H atoms of CH and CH_2 groups were taken as $1.2U_{eq}$ of the parent atoms. Atoms H41, H42, H51 and H52 were found from difference Fourier syntheses and refined with $U_{iso} = 1.2U_{eq}$ of the water O atom; O—H distances were restrained equal. An analytical absorption correction based on face indexing was carried out with the following faces and distances (mm): $0\bar{1}0$ 0.0385, 010 0.0385, $0\bar{1}1$ 0.3465, $01\bar{1}$ 0.3850, $\bar{1}00$ 0.0192 and 100 0.1540. The fraction of unique reflections measured to the 2θ value of 51° was 99.0%.

Data collection: *EXPOSE* (Stoe, 1997*b*). Cell refinement: *CELL* (Stoe, 1997*a*). Data reduction: *INTEGRATE* (Stoe, 1997*c*). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*). Molecular graphics: *XP* in *SHELXTL* (Siemens, 1996*a*). Software used to prepare material for publication: *SHELXL*97.

We kindly thank the head of the section for X-ray diffraction, Professor Dr W. Massa, for making diffractometer time available and Madame G. Geiseler for performing the measurements.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1309). Services for accessing these data are described at the back of the journal.

References

Sheldrick, G. M. (1997*a*). *SHELXL*97. Release 97-2. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Sheldrick, G. M. (1997*b*). *SHELXS*97. Release 97-1. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Siemens (1996*a*). *XP* in *SHELXTL*. *Molecular Graphics Program*. Version 5.06. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1996*b*). *XPREP* in *SHELXTL*. *Program for Data Preparation and Reciprocal Space Exploration*. Version 5.05. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Spek, A. L. (1994). *PLATON*. *Molecular Geometry Program*. University ot Utrecht, The Netherlands.

Stoe (1997*a*). *CELL*. *Program for Cell Refinement*. Version 2.79. Stoe IPDS, Darmstadt, Germany.

Stoe (1997*b*). *EXPOSE*. *Stoe IPDS Software for Data Collection*. Version 2.79. Stoe IPDS, Darmstadt, Germany.

Stoe (1997*c*). *INTEGRATE*. *Program for Reduction of IPDS Data*. Version 2.79. Stoe IPDS, Darmstadt, Germany.

Ueki, T., Ashida, T., Sasada, Y. & Kakudo, M. (1967). *Acta Cryst.* **22**, 870–878.

Warda, S. A. (1994). In *Bioanorganische Kupfer(II) Komplexe mit dreizähnigen O,N,O-Chelat-Dianionen und additiven einzähnigen Donorliganden*. Aachen: Verlag Shaker.

Warda, S. A. (1997). *Acta Cryst.* C**53**, 1590–1593.

Warda, S. A. (1998). *Acta Cryst.* C**54**, 189–191.

Acta Cryst. (1998). C**54**, 1758–1760

Magnesium Sulfate Hexaurea Hemihydrate

Todor Todorov, Rosica Petrova, Krasimir Kossev, Josef Macíček and Olyana Angelova

Bulgarian Academy of Sciences, CL Mineralogy & Crystallography, Rakovski str. 92, 1000 Sofia, Bulgaria.
E-mail: jmacicek@bgcict.acad.bg

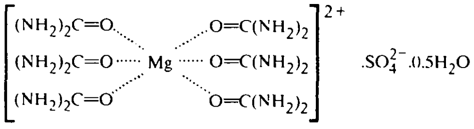
(*Received 15 December 1997; accepted 18 May 1998*)

Abstract

The structure of the title compound, hexakis(urea-*O*)magnesium sulfate hemihydrate, $[Mg(CH_4N_2O)_6]$-$SO_4.0.5H_2O$, consists of a regular arrangement of $[Mg(CH_4N_2O)_6]^{2+}$ cations, SO_4^{2-} anions and water molecules, held together by an extensive network of hydrogen bonds. The Mg atoms are octahedrally coordinated by urea O atoms. The N1—C—O—Mg torsion angles are between −5.1 (5) and −30.5 (5)°.

Comment

Recently, the preparation and crystal structure of a new urea adduct of magnesium sulfate, $MgSO_4.4CH_4N_2O.$-H_2O, were reported by Todorov *et al.* (1998*a*). We have now established an adduct of higher urea content, $MgSO_4.6CH_4N_2O.0.5H_2O$, (I). Formally, these are compounds from the ternary system $MgSO_4$–urea–H_2O. Sulaimankoulov (1971) has studied the solubility diagram of this system and reported only the compound $MgSO_4.CH_4N_2.3H_2O$. Numerous attempts to isolate this latter compound, as well as adducts with other sulfate–urea ratios, have been unsuccessful.



(I)

Our interest in adducts from the $MgSO_4$–urea–H_2O system was prompted by their presence as by-products during the development of a novel method for the

Acta Crystallographica Section C
ISSN 0108-2701 © 1998

synthesis of the well known defoliant $Mg(ClO_3)_2.6$urea, from $MgSO_4$, $NaClO_3$ and urea (Todorov *et al.*, 1998*b*), which improves its purity and activity. This paper reports the crystal structure of the new adduct, $MgSO_4.6CH_4N_2O.0.5H_2O$.

The octahedral coordination of Mg atoms in (I) is provided by the six O atoms from the six different urea molecules. Mg—O distances fall into the typical range of 2.043 (3)–2.098 (3) Å. The type of coordination of the urea molecules can be described with respect to the C═O bond directions. The values for Mg—O—C angles [between 131.7 (2) and 143.8 (2)°] are similar to those cited by Todorov *et al.* (1998*b*) for the orientation of non-bridging urea molecules in other adducts. The N1—C—O—Mg torsion angles, which are a measure of the deviation of Mg—O bonds from the plane of the urea molecule, are between −5.1 (5) and −30.5 (5)°. These torsion angles can be associated into three groups: the values of −5.1 (5) and −8.9 (5)° show almost in-plane coordination for the Urea3 and Urea5 molecules, respectively; moderate deviation in the cases of Urea1, Urea6 and Urea4 is demonstrated by the corresponding torsion angles of −15.7 (5), 20.4 (5) and 24.0 (7)°, respectively; and Urea2 is out-of-plane, with a torsion angle of −30.5 (5)°. In the case of $MgSO_4.4CH_4N_2O.H_2O$, where Mg also has an octahedral coordination, but constituted by one water and one SO_4 O atom in a *cis* arrangement, and four urea O atoms, the N1—C—O—Mg torsion angles fall into a narrower range, between 1.4 (4) and −20.5 (4)°.

The S—O bonds of 1.455 (3)–1.472 (3) Å, and the O—S—O angles in the range 108.6 (2)–111.1 (2)°, describe the ordinary tetrahedral geometry of SO_4 groups. The O atoms from the SO_4 tetrahedra participate as acceptors in weak hydrogen bonds only. This fact explains the shorter S—O_{max} limit, in comparison with the S—O_{max} distance to the coordinated O atom of 1.482 (2) Å in $MgSO_4.4CH_4N_2O.H_2O$.

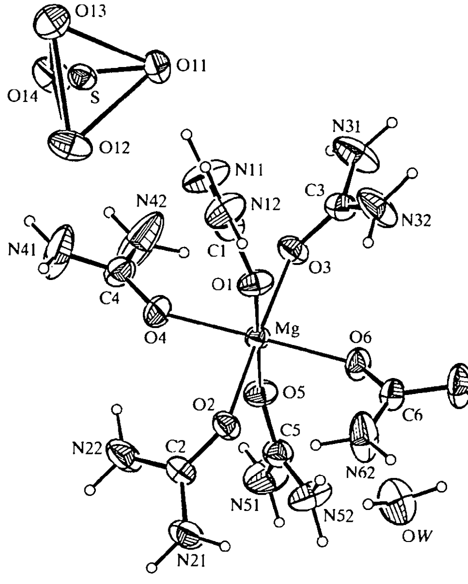


Fig. 1. *ORTEP*II (Johnson, 1976) view of the formula unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are arbitrarily reduced.

The structure of (I) can be described as a regular arrangement of isolated $[Mg(CH_4N_2O)_6]^{2+}$ cations, SO_4^{2-} anions and water molecules. The structural units are held together by an extensive three-dimensional hydrogen-bonding network. All sulfate and only three urea O atoms (O2, O4 and O5) act as acceptors of weak hydrogen bonds of the N—H···O type. The water molecule plays the role of a hydrogen bond donor to two SO_4 tetrahedra, as well as an acceptor in two N—H···O*W* hydrogen bonds. According to the classification of Ferraris & Franchini-Angela (1972), this water molecule belongs to Type E of Class 2.

Experimental

Crystals of the title compound were obtained by slow evaporation at room temperature of an aqueous solution of $MgSO_4.7H_2O$ and urea in the stoichiometric ratio 1:6.

Crystal data

$[Mg(CH_4N_2O)_6]SO_4.0.5H_2O$
$M_r = 489.71$
Orthorhombic
Pccn
$a = 15.316\ (5)$ Å
$b = 19.798\ (5)$ Å
$c = 14.484\ (2)$ Å
$V = 4392\ (3)$ Å^3
$Z = 8$
$D_x = 1.481$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 22 reflections
$\theta = 21.08$–$21.68°$
$\mu = 0.25$ mm^{-1}
$T = 292$ K
Prismatic
0.22 × 0.16 × 0.07 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4304 measured reflections
4304 independent reflections
2867 reflections with $I > 2\sigma(I)$

$\theta_{max} = 26°$
$h = 0 \rightarrow 18$
$k = 0 \rightarrow 24$
$l = 0 \rightarrow 17$
3 standard reflections
frequency: 120 min
intensity decay: −4.7%

Refinement

Refinement on F
$R = 0.050$
$wR = 0.063$
$S = 1.057$
2867 reflections
276 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F) + (0.03F)^2]$
$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 0.404$ e Å^{-3}
$\Delta\rho_{min} = -0.484$ e Å^{-3}
Extinction correction: none
Scattering factors from *SDP*/*PDP* (Enraf–Nonius, 1985)

Table 1. *Selected geometric parameters (Å, °)*

Mg—O1	2.083 (2)	Mg—O6	2.059 (3)
Mg—O2	2.098 (3)	S—O11	1.469 (3)
Mg—O3	2.096 (3)	S—O12	1.455 (3)
Mg—O4	2.043 (3)	S—O13	1.462 (3)
Mg—O5	2.092 (2)	S—O14	1.472 (3)
Mg—O1—C1	135.1 (2)	Mg—O4—C4	143.8 (2)
Mg—O2—C2	131.7 (2)	Mg—O5—C5	135.4 (2)
Mg—O3—C3	131.7 (2)	Mg—O6—C6	138.0 (2)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
O*W*—H*W*1···O13^{i}	2.07	2.987 (3)	160
N12—H121···O11	2.15	3.050 (4)	157
N12—H122···O5^{ii}	2.00	2.945 (4)	175
N21—H211···O12^{iii}	2.00	2.839 (4)	146
N21—H212···O4	2.06	2.901 (4)	147
N22—H221···O14^{iii}	2.02	2.968 (4)	176
N22—H222···O*W*^{iv}	2.16	3.086 (4)	166
N31—H311···O14^{v}	2.10	2.991 (4)	156
N41—H411···O11^{vi}	1.89	2.829 (5)	170
N42—H421···O13^{vi}	2.06	2.990 (5)	167
N61—H611···O12^{vii}	1.90	2.814 (4)	160
N61—H612···O2	2.02	2.871 (4)	147

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $\frac{1}{2}-x, y, \frac{1}{2}+z$; (iii) $-x, 1-y, -z$; (iv) $\frac{1}{2}-x, y, z-\frac{1}{2}$; (v) $\frac{1}{2}-x, \frac{3}{2}-y, z$; (vi) $x, \frac{3}{2}-y, z-\frac{1}{2}$; (vii) $\frac{1}{2}+x, 1-y, \frac{1}{2}-z$.

A decay correction was applied. For calculation of the positions of the water H atoms, the most appropriate acceptor atoms of hydrogen bonds, *A*1 and *A*2, were first determined exploring the geometry surrounding O*W*, as well as the valence sums (Brown & Altermatt, 1985) of the atoms constituting this geometry. H atoms were thus calculated to lie in the O*W*/*A*1/*A*2 plane, with the geometrical constraints O*W*—H = 0.95 Å and H1—O*W*—H2 = 109.5°. Amino H atoms were placed in calculated positions (N—H = 0.95 Å). All H atoms were refined in a riding geometry, with fixed U_{iso} = 0.0506 Å^2.

Data collection: *CAD*-4 *Manual* (Enraf–Nonius, 1988). Data reduction: *SDP*/*PDP* (Enraf–Nonius, 1985). Program(s) used to solve structure: *MULTAN*11/82 (Main *et al.*, 1982). Program(s) used to refine structure: *SDP*/*PDP*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *KAPPA* (Macíček, 1992).

This work has been supported by the Bulgarian Academy of Sciences and the Bulgarian National Science Fund (projects Ch-402 and Ch-651).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1345). Services for accessing these data are described at the back of the journal.

References

Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B**41**, 244–247.

Enraf–Nonius (1985). *Structure Determination Package. SDP/PDP User's Guide*. Version 3.0. Enraf–Nonius, Delft, The Netherlands.

Enraf–Nonius (1988). *CAD*-4 *Manual*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Ferraris, G. & Franchini-Angela, M. (1972). *Acta Cryst.* B**28**, 3572–3583.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Macíček, J. (1992). *KAPPA. Program for the Preparation of Material for Publication from a CIF File.* Bulgarian Academy of Sciences, Sofia, Bulgaria.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Universities of York, England, and Louvain, Belgium.

Sulaimankoulov, K. (1971). *Compounds of Urea with Inorganic Salts*, p. 224. Ilim: Frunze. (In Russian.)

Todorov, T., Petrova, R., Kossev, K., Macíček, J. & Angelova, O. (1998*a*). *Acta Cryst.* C**54**, 456–458.

Todorov, T., Petrova, R., Kossev, K., Macíček, J. & Angelova, O. (1998*b*). *Acta Cryst.* C**54**, 927–929.

Acta Cryst. (1998). C**54**, 1760–1763

Bis(2,2′-bipyridine-*N*,*N*′)(isothiocyanato-*N*)-copper(II) Tricyanomethanide

IVAN POTOČŇÁK,[a] MICHAL DUNAJ-JURČO,[a] DUŠAN MIKLOŠ[a] AND LOTHAR JÄGER[b]

[a]*Department of Inorganic Chemistry, Slovak Technical University, Radlinského 9, 812 37 Bratislava, Slovakia, and* [b]*Institute of Inorganic Chemistry, Martin-Luther-University, Halle-Wittenberg, Weinbergweg 16, 06120 Halle/Saale, Germany. E-mail: potocnak@cvtstu.cvt.stuba.sk*

(*Received 30 January 1998; accepted 5 June 1998*)

Abstract

The crystal structure of $[Cu(NCS)(C_{10}H_8N_2)_2][C(CN)_3]$ is composed of discrete $[Cu(bipy)_2(NCS)]^+$ cations (bipy is 2,2′-bipyridine) and $[C(CN)_3]^-$ anions. The coordination polyhedron of Cu^{II} is a distorted trigonal bipyramid with a $\{CuN_5\}$ chromophore.

Comment

Recently, we published the crystal structures of two $[Cu(bipy)_2X][C(CN)_3]$ compounds [X = $C(CN)_3^-$ and OCN^-; Potočňák, Dunaj-Jurčo, Mikloš & Jäger, 1997; Potočňák *et al.*, 1998]. The coordination polyhedra around the five-coordinated Cu^{II} atoms in these two compounds can be described as trigonal bipyramidal with some degree of distortion towards tetragonal pyramidal. In comparison with these compounds, the coordination polyhedra in related $[Cu(phen)_2X][C(CN)_3]$ compounds [phen is 1,10-phenanthroline; X = CN^-, NCS^- and $N(CN)_2^-$] show a smaller degree of distortion towards the tetragonal-pyramidal arrangement (Potočňák *et al.*, 1996*a*,*b*,*c*). As the pseudohalogenide