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Magnesium Sulfate Tetraurea Monohydrate

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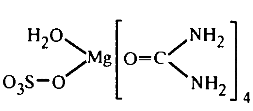
Abstract

In the title adduct, $MgSO_4.4CH_4N_2O.H_2O$ {aqua(sulfato-*O*)tetrakis(urea-*O*)magnesium, [$Mg(SO_4)(CH_4N_2O)_4(H_2O)$]}, the Mg atoms have octahedral coordination, formed by one water and four urea molecules, and one sulfate O atom. The neutral $MgSO_4(urea)_4.H_2O$ clusters are dimerized into centrosymmetric units through two O—H···O hydrogen bonds held together in a network where urea molecules act as both hydrogen-bond donors and acceptors.

Comment

The industrial methods for preparation of the widely used defoliant $Mg(ClO_3)_2$ use mainly $NaClO_3$ and $MgCl_2$ as starting materials (Martinov, 1957; Harvey, 1986). Our investigations (Todorov *et al.*, 1998) on the structure and applicability of $Mg(ClO_3)_2.6CH_4N_2O$, a new defoliating agent with improved purity and biological activity synthesized from $MgSO_4$, $NaClO_3$ and urea, prompted us to investigate the ternary system $MgSO_4$–urea–H_2O. Sulaimankoulov (1971) studied its solubility diagram which revealed only compound $MgSO_4.CH_4N_2O.3H_2O$. Recently, we have recognized a new adduct, $MgSO_4.4CH_4N_2O.H_2O$, (I), and this paper reports its crystal structure.



(I)

The structure of the title compound consists of Mg atoms bonded to four urea O atoms, one water molecule and an SO_4 tetrahedron (Fig. 1). The Mg—O distances are within the typical range 2.064 (2)–2.098 (2) Å, while O—Mg—O angles lie between 84.30 (7) and 94.85 (7)°. The values for C—O—Mg angles are in the relatively narrow range 136.19 (15)–149.89 (15)°. The torsion angles N1—C—O—Mg, used to describe the deviation from the urea in-plane coordination (Macíček *et al.*, 1995), are 1.4 (4), 15.4 (3), −20.5 (4) and 12.3 (4)°, for *U*3 (where *U*3 is urea molecule 3), *U*1, *U*2 and *U*4, respectively. They show a larger, but not significant, deviation around the latter three molecules.

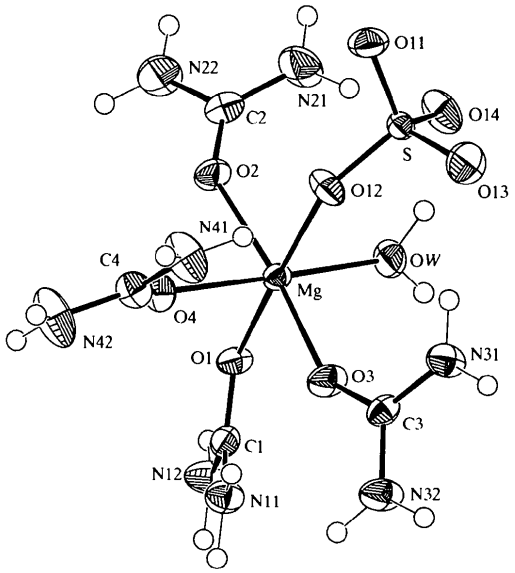


Fig. 1. A view of the title cluster with the atom-numbering scheme. Displacement ellipsoids are plotted at the 50% probability level. H atoms are arbitrarily small.

The SO_4 group has ordinary tetrahedral geometry. The longest S—O distance of 1.482 (2) Å is at the coordinated O atom and the bonds to the terminal O atoms are shorter by more than 7σ. The Mg—O12—S angle of 139.30 (10)° indicates that atom O12 does not coordinate to the Mg atom through either an ion–dipole interaction or through an sp^3 orbital.

The neutral $MgSO_4.4CH_4N_2O.H_2O$ clusters are held together by an extensive network of hydrogen bonds (Fig. 2). Of particular interest is the O*W*—H*W*2···O13(1 − *x*, 1 − *y*, 1 − *z*) bond that relates the cation and anion and could act as a charge-transfer bridge between them. Through two such bonds, the clusters are dimerized into centrosymmetric units. The second hydrogen bond from the water molecule is to the sulfate O14 atom within the cluster. In addition, the water O atom acts as a hydrogen-bond acceptor from the amide H422 atom in an adjacent cluster ($\frac{3}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$). Thus, the water molecule can be classified according to the method of Ferraris & Franchini-Angela (1972) as being of type H, class 2. The urea molecules take part in the hydrogen-bonding scheme as both donors and acceptors.

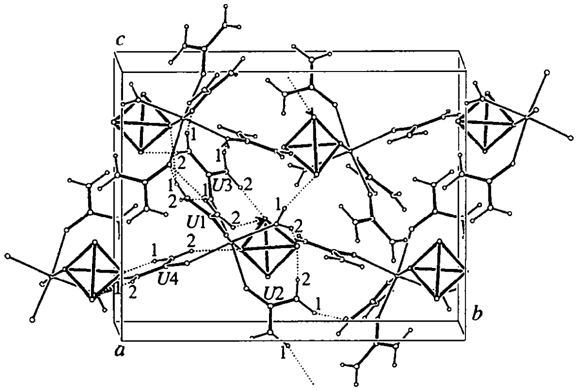


Fig. 2. Projection of the structure down the *a* axis. Dotted lines denote hydrogen bonds.

Experimental

Crystals of the title compound were obtained by slow evaporation of an aqueous solution of $MgSO_4.7H_2O$ and urea in the stoichiometric ratio 1:4 at room temperature.

Crystal data

$[Mg(SO_4)(CH_4N_2O)_4(H_2O)]$
M_r = 378.61
Monoclinic
$P2_1/n$
a = 9.345 (2) Å
b = 14.683 (4) Å
c = 11.244 (3) Å
β = 93.07 (2)°
V = 1540.6 (6) Å^3
Z = 4
D_x = 1.632 Mg m^{-3}
D_m not measured

Mo *Kα* radiation
λ = 0.71073 Å
Cell parameters from 22 reflections
θ = 20.32–21.78°
μ = 0.29 mm^{-1}
T = 292 K
Elongated
0.33 × 0.29 × 0.23 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2*θ* scans
Absorption correction: none
6440 measured reflections
3025 independent reflections
2240 reflections with $I > 3\sigma(I)$
R_{int} = 0.015

θ_{max} = 26.0°
h = 0 → 11
k = −18 → 18
l = −13 → 13
3 standard reflections every 500 reflections
frequency: 120 min
intensity decay: 1.7%

Refinement

Refinement on *F*
R = 0.030
wR = 0.047
S = 0.966
2240 reflections
208 parameters
H atoms constrained
$w = 1/[\sigma^2(F) + (0.04F)^2]$

$(\Delta/\sigma)_{max}$ = 0.092
$\Delta\rho_{max}$ = 0.337 e Å^{-3}
$\Delta\rho_{min}$ = −0.320 e Å^{-3}
Extinction correction: none
Scattering factors from *SDP/PDP* (Enraf–Nonius, 1985)

Table 1. *Selected bond lengths (Å)*

Mg—O12	2.098 (2)	Mg—O4	2.071 (2)
Mg—O*W*	2.091 (2)	S—O11	1.456 (2)
Mg—O1	2.067 (2)	S—O12	1.482 (2)
Mg—O2	2.073 (2)	S—O13	1.463 (2)
Mg—O3	2.064 (2)	S—O14	1.468 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O*W*—H*W*1···O14	0.92	1.95	2.752 (2)	145
O*W*—H*W*2···O13^{i}	0.85	2.13	2.960 (2)	164
N11—H111···O12^{ii}	0.95	2.47	3.194 (3)	133
N11—H111···O2^{ii}	0.95	2.65	3.473 (2)	146
N11—H112···O3	0.95	2.18	2.886 (2)	130
N12—H121···O2^{ii}	0.95	2.27	3.195 (3)	163
N12—H122···O13^{iii}	0.95	2.05	2.951 (3)	159
N21—H211···N11^{iv}	0.95	2.18	3.128 (3)	173
N21—H212···O14	0.95	2.06	2.988 (3)	165
N22—H221···O11^{v}	0.95	2.00	2.907 (3)	158
N31—H311···O4^{vi}	0.95	2.30	3.215 (3)	161
N31—H312···O13	0.95	2.11	3.021 (3)	159
N32—H321···O1^{vi}	0.95	1.99	2.941 (3)	173
N32—H322···O11^{ii}	0.95	1.97	2.897 (3)	166
N41—H411···O14^{vii}	0.95	2.32	3.259 (3)	168
N41—H412···O12	0.95	2.16	2.990 (3)	145
N42—H421···O13^{vii}	0.95	2.30	3.207 (3)	160
N42—H422···O*W*^{viii}	0.95	2.64	3.528 (3)	156

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

H*W* atoms were localized from $\Delta\rho$ maps and amino H atoms were placed in calculated positions (N—H 0.95 Å). All H atoms were refined as riding with fixed isotropic *U* values of 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).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1321). Services for accessing these data are described at the back of the journal.

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[1,2-Bis(2-methoxyethyl-*O*)-η^5-cyclopentadienyl]trichlorozirconium(IV)

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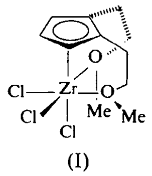
Abstract

The monomeric title compound, [$ZrCl_3(C_{11}H_{17}O_2)$], has a pseudo-octahedral structure. The tridentate ligand contains a cyclopentadienyl ring bearing two 1,2-substituted ether side chains that are forced into a unique facial η^5:η^1:η^1 arrangement. The three Cl atoms occupy the other facial positions. The asymmetric unit contains two independent but almost identical molecules.

Comment

In the last decade, interest in cyclopentadienyl (Cp) ligands bearing functional groups capable of intramolecular coordination has increased enormously (Jutzi *et al.*, 1996). However, only a few examples exist in which two such substituents are attached to the Cp ring (Fryzuk *et al.*, 1993, 1995; Atherton *et al.*, 1995; Mu *et al.*, 1996) and, to the best of our knowledge, only one structure is known in which these substituents are adjacent (1,2) to one another (Barthel-Rosa *et al.*, 1995, 1996). We report here the first structure of a zirconium compound complexed to a 1,2-disubstituted cyclopentadienyl ligand bearing two intramolecular coordinating ether groups, (I).



(I)

The unit cell contains two independent molecules which are identical within error limits and so only one of them will be discussed (Fig. 1).

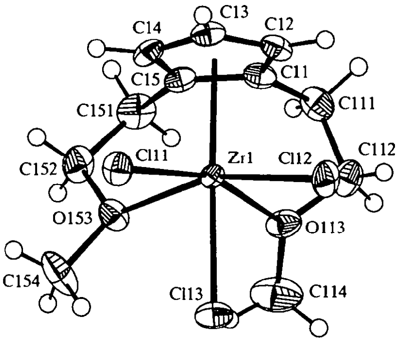


Fig. 1. *DIAMOND* plot (Brandenburg, 1996) (50% probability) of the title compound with the atomic numbering scheme. Only one of the two independent molecules is shown.

The molecule adopts a monomeric pseudo-octahedral structure. The title complex, (I), contains a Cp ring which has two ether side chains substituted in a 1,2-fashion. The tridentate ligand is bonded in a facial η^5:η^1:η^1 arrangement as a result of geometrical constraints. The three Cl atoms occupy the other facial positions. Normally, complexes of type $CpZrCl_3(L)_2$ exhibit a *cis,mer* arrangement of ligands (Erker *et al.*, 1990; Erker, 1990; Wells *et al.*, 1981). Mu and co-workers (Mu *et al.*, 1995) prepared a zirconium trichloride compound bearing a Cp ligand containing one substituent with two donor atoms that is coordinated in a meridional η^5:η^1:η^1-fashion.

There is a slight asymmetry in the η^5-bonding of the Cp unit. The Zr—C bond length progressively increases from C14 and C15 [2.495 (4) and 2.485 (4) Å, respectively] to C13 and C11 [2.535 (4) and 2.537 (4) Å, re-

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