

(Sheldrick, 1997). Molecular graphics: *ZORTEP* (Zsolnai, 1997).

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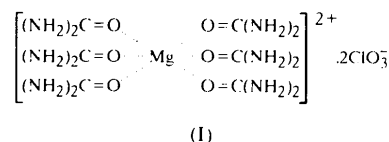
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and 27.3 (4)°, respectively. The structure is built up of $[\text{Mg}(\text{urea})_6]^{2+}$ and ClO_3^- ions held together by hydrogen bonds.

Comment

Magnesium chlorate has been used widely as a defoliant in agrochemistry (Ware, 1983), but it is a highly hygroscopic compound. Under ambient conditions, it exists as a hexahydrate and demands special care and handling upon storage and maintenance. The partial or complete substitution of crystallization water molecules makes this salt more stable and resistant to atmospheric moisture. Moreover, the corresponding adducts possess combined activity as defoliant and fertilizing agents. The adducts known so far are $\text{Mg}(\text{ClO}_3)_2 \cdot 4\text{H}_2\text{O} \cdot 2\text{urea}$, $\text{Mg}(\text{ClO}_3)_2 \cdot 2\text{H}_2\text{O} \cdot 4\text{urea}$ and $\text{Mg}(\text{ClO}_3)_2 \cdot 6\text{urea}$ (Musaev *et al.*, 1984; Suleimankoulov, 1971). This paper reports the crystal structure of $\text{Mg}(\text{ClO}_3)_2 \cdot 6\text{urea}$, (I).



In the title compound, Mg atoms lie on a centre of symmetry and are octahedrally coordinated by the O atoms of six urea molecules. The distances and angles within the urea molecules do not show any unusual values (Table 1). The coordination of the urea molecules can be suitably described with respect to C=O bond direction and N—C—O—Mg torsion angles (Macíček *et al.*, 1995). The values of 136.8 (2), 137.0 (2)

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Hexakis(urea-O)magnesium Dichlorate

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Abstract

In the title compound, $[\text{Mg}\{\text{OC}(\text{NH}_2)_2\}_6](\text{ClO}_3)_2$, Mg atoms are octahedrally coordinated by the O atoms of six urea molecules. Urea1 is in-plane coordinated, while Urea2 and Urea3 are bonded with N21—C2—O2—Mg and N31—C3—O3—Mg torsion angles of 22.2 (4)

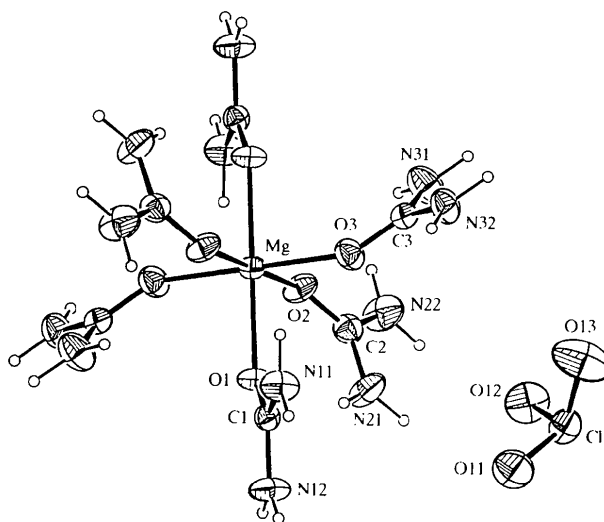


Fig. 1. ORTEP (Johnson, 1976) view of the formula unit of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are arbitrarily reduced.

and 140.1(2)° for the C—O—Mg angles of the three symmetrically non-equivalent urea molecules are similar to those describing the orientation of non-bridging urea molecules in the other adducts cited above. The N11—C1—O1—Mg torsion angle of -4.1(4)° shows that the O1—Mg bond is almost in the plane of the Urea1 molecule. The corresponding torsion angles for Urea2 and Urea3 are 22.2(4) and 27.3(4)°, respectively, revealing a moderate deviation from their planes.

The Cl—O distances and O—Cl—O angles are similar to those reported by Abrahams & Bernstein (1977) for other chlorates. The distance of the Cl atom from the O-atom plane is 0.547(1) Å.

The structure represents a regular arrangement of [Mg(urea)₆]²⁺ and ClO₃⁻ ions held together by a three-dimensional hydrogen-bonding network (Table 2).

Experimental

A mixture of MgSO₄·6H₂O, NaClO₃ and urea (1:2:6) was melted at about 338–343 K and heated in an open crucible at that temperature for 12 h. The crystallized potassium sulfate was filtered off and the adduct was obtained after cooling of the filtrate. Single crystals were prepared by slow evaporation of a water solution.

Crystal data

[Mg(CH₄N₂O)₆](ClO₃)₂

M_r = 551.54

Monoclinic

*P*2₁/*n*

a = 10.435(2) Å

b = 7.312(3) Å

c = 14.596(2) Å

β = 101.29(2)°

V = 1092.2(9) Å³

Z = 2

D_x = 1.677 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 22 reflections

θ = 20.64–21.76°

μ = 0.40 mm⁻¹

T = 292 K

Prismatic

0.29 × 0.13 × 0.10 mm

Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer

ω–2θ scans

Absorption correction: none

5552 measured reflections

2632 independent reflections

1549 reflections with

I > 2σ(*I*)

*R*_{int} = 0.046

θ_{max} = 28.0°

h = 0 → 13

k = -9 → 9

l = -19 → 19

3 standard reflections

frequency: 120 min

intensity decay: -2.0%

Refinement

Refinement on *F*²

R = 0.040

wR = 0.048

S = 0.726

1549 reflections

151 parameters

H atoms constrained

w = 1/[σ²(*F*) + (0.02*F*)²]

(Δ/σ)_{max} = 0.001

Δρ_{max} = 0.318 e Å⁻³

Δρ_{min} = -0.329 e Å⁻³

Extinction correction: none

Scattering factors from *SDP/PDP* (Enraf–Nonius, 1985)

Table 1. Selected geometric parameters (Å, °)

Mg—O1	2.096 (2)	O1—C1	1.259 (3)
Mg—O1 ⁱ	2.096 (2)	C1—N11	1.332 (4)
Mg—O2	2.078 (2)	C1—N12	1.325 (3)
Mg—O2 ⁱ	2.078 (2)	O2—C2	1.243 (3)
Mg—O3	2.067 (2)	C2—N21	1.339 (4)
Mg—O3 ⁱ	2.067 (2)	C2—N22	1.343 (4)
Cl—O11	1.476 (2)	O3—C3	1.248 (3)
Cl—O12	1.463 (2)	C3—N31	1.326 (4)
Cl—O13	1.463 (3)	C3—N32	1.343 (3)
O11—Cl—O12	107.3 (1)	O2—C2—N21	121.7 (3)
O11—Cl—O13	106.8 (2)	O2—C2—N22	121.6 (3)
O12—Cl—O13	106.7 (1)	N21—C2—N22	116.7 (2)
O1—C1—N11	121.3 (2)	O3—C3—N31	122.2 (2)
O1—C1—N12	120.3 (2)	O3—C3—N32	119.5 (3)
N11—C1—N12	118.4 (2)	N31—C3—N32	118.3 (2)

Symmetry code: (i) -*x*, -*y*, -*z*.

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

<i>D</i> —H... <i>A</i>	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N11—H111...O13 ⁱ	2.82	3.575 (4)	136.6
N11—H111...N22 ⁱⁱ	2.86	3.769 (4)	159.4
N11—H112...O11 ⁱⁱⁱ	2.45	2.977 (3)	114.7
N11—H112...O2	2.34	3.037 (3)	129.8
N12—H121...O13 ⁱ	2.06	2.997 (4)	170.5
N12—H122...O1 ^{iv}	2.10	3.021 (3)	163.7
N21—H211...O11	2.31	3.093 (3)	139.1
N21—H212...O1 ^v	2.16	2.988 (3)	144.8
N22—H221...O12	2.29	3.140 (3)	148.0
N22—H222...O13 ^{vi}	2.07	3.008 (4)	171.0
N31—H311...O11 ⁱⁱⁱ	2.12	3.046 (3)	165.1
N31—H312...O12 ^{vii}	2.28	2.939 (4)	125.8
N32—H321...O3 ^{viii}	2.46	3.334 (3)	152.3
N32—H322...O11 ⁱⁱⁱ	2.18	3.103 (4)	162.5

Symmetry codes: (i) *x* - ½, ½ - *y*, *z* - ½; (ii) ½ - *x*, ½ + *y*, - ½ - *z*; (iii) *x* - ½, - ½ - *y*, *z* - ½; (iv) -*x*, 1 - *y*, -*z*; (v) -*x*, -*y*, -*z*; (vi) 1 - *x*, -*y*, -*z*; (vii) -*x*, -1 - *y*, -*z*; (viii) *x* - 1, *y*, *z*; (ix) - ½ - *x*, *y* - ½, - ½ - *z*.

H atoms were geometrically constrained to their neighbouring atoms (N—H 0.95 Å) with *U*_{iso} = 0.0506 Å².

Data collection: *CAD-4 Manual* (Enraf–Nonius, 1988). Data reduction: *SDP/PDP* (Enraf–Nonius, 1985). Program(s) used to solve structure: *MULTAN11/82* (Main *et al.*, 1982). Program(s) used to refine structure: *SDP/PDP*. Molecular graphics: *ORTEPII* (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: SK1132). Services for accessing these data are described at the back of the journal.

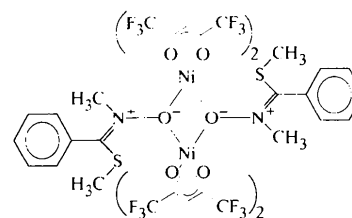
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1989). Magnetic measurements for the latter compound indicated antiferromagnetic coupling between the metal atoms.

In the title compound, (I) (Fig. 1), the thioester nitronone group (O1, N1, C2 and S1) is approximately planar, with an r.m.s. deviation of 0.01 Å. The dihedral angle



(I)

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Bis(μ -{N-[(methylthio)phenylmethylene]-methanamine N-oxide}-O:O)bis[bis-(1,1,1,5,5,5-hexafluoropentane-2,4-dionato-O,O')nickel(II)]

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Abstract

The title compound, $[\text{Ni}_2(\text{C}_5\text{HF}_6\text{O}_2)_4(\text{C}_9\text{H}_{11}\text{NOS})_2]$, crystallizes as a centrosymmetric dimer containing two $\text{Ni}(\text{hfac})_2$ moieties bridged by two nitronone ligands (hfac is the 1,1,1,5,5,5-hexafluoropentane-2,4-dionate anion). The $\text{Ni} \cdots \text{Ni}$ distance is 3.2904 (5) Å, with $\text{Ni}-\text{O}_{\text{nitronone}}$ distances of 2.0776 (12) and 2.0974 (12) Å. The average $\text{Ni}-\text{O}_{\text{hfac}}$ distance is 2.022 (16) Å.

Comment

Although metal adducts of pyridine *N*-oxides are well known, structural reports of complexes of nitronones in which the N atom is not part of an aromatic ring are less common. The present compound was synthesized as part of a study of such complexes. The resulting centrosymmetric dimer contains two $\text{Ni}(\text{hfac})_2$ units (hfac is the 1,1,1,5,5,5-hexafluoropentane-2,4-dionate anion) bridged by two nitronone O atoms. This type of dimeric structure was also found in a series of $M(\text{hfac})_2$ complexes ($M^{2+} = \text{Mn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}$) of 2,5,5-trimethyl-1-pyrroline *N*-oxide (Villamena *et al.*, 1998) and the $\text{Mn}(\text{hfac})_2$ adduct of 2-phenyl-4,4,5,5-tetramethylimidazoline 3-oxide (Carducci & Doedens,

between the phenyl ring and the plane of the thioester nitronone group is 66.00 (4)°. This is comparable to the value of 65.6° found for the uncomplexed nitronone

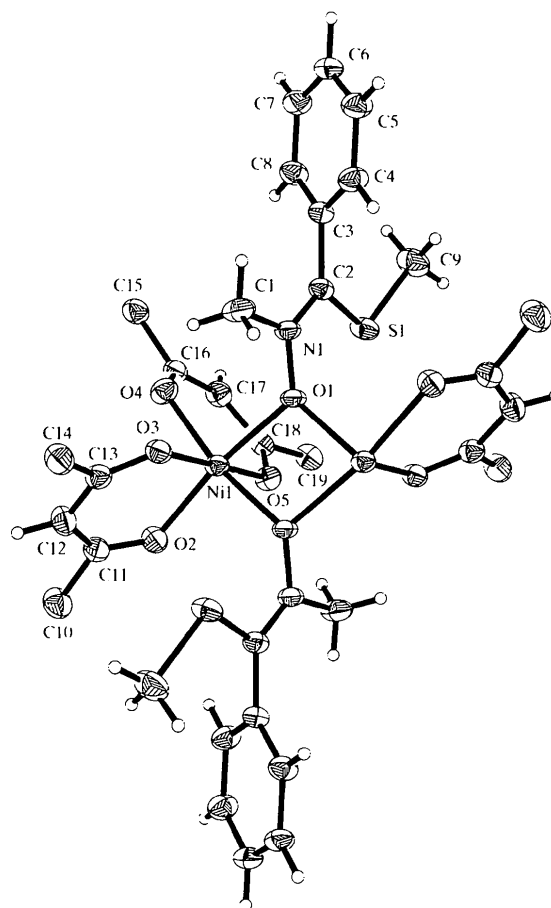


Fig. 1. View of the title compound showing the numbering scheme. Anisotropic displacement ellipsoids are shown at the 50% probability level. F atoms and one hfac ring have been omitted for clarity. H atoms are drawn as circles of arbitrary radii.