Refinement

Refinement on F^2
$R(F) = 0.057$
$wR(F^2) = 0.123$
$S = 1.454$
3848 reflections
241 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0076P)^2 + 21.4166P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.81$ e Å^{-3}
$\Delta\rho_{min} = -0.62$ e Å^{-3}
Extinction correction: none
Scattering factors from
 International Tables for
 Crystallography (Vol. C)

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

Rh1—O1	2.051 (4)	O1—C16	1.325 (6)
Rh1—N1	1.900 (4)	N2—C6	1.288 (7)
Rh1—N2	2.089 (4)	N3—C10	1.291 (8)
Rh1—N3	2.102 (5)		
O1—Rh1—N1	178.02 (16)	N2—Rh1—N3	157.99 (19)
O1—Rh1—N2	100.41 (17)	Rh1—O1—C16	127.6 (3)
O1—Rh1—N3	101.52 (17)	C6—N2—C7	119.2 (4)
N1—Rh1—N2	78.87 (19)	C10—N3—C12	118.4 (5)
N1—Rh1—N3	79.15 (18)		

The structure contains a solvent-accessible void, located on a 4_2 axis, with its centre at $(\frac{1}{4},\frac{3}{4},-0.024)$. Integration of the electron density in this area resulted in a total of zero electrons.

Data collection: *COLLECT* (Nonius, 1998). Cell refinement: *DirAx* (Duisenberg, 1992). Data reduction: *EVAL*14 (Duisenberg, 1998). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *PLATON* (Spek, 1990). Software used to prepare material for publication: *PLATON*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1325). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
Duisenberg, A. J. M. (1992). *J. Appl. Cryst.* **25**, 92–96.
Duisenberg, A. J. M. (1998). PhD thesis, Utrecht University, The Netherlands.
Haarman, H. F., Bregman, F. R., Ernsting, J. M., Veldman, N., Spek, A. L. & Vrieze, K. (1997). *Organometallics*, **16**, 54–67.
Haarman, H. F., Ernsting, J. M., Kranenburg, M., Kooijman, H., Veldman, N., Spek, A. L., van Leeuwen, P. W. N. M. & Vrieze, K. (1997). *Organometallics*, **16**, 887–900.
Haarman, H. F., Kaagman, J. F., Smeets, W. J. J., Spek, A. L. & Vrieze, K. (1997). *Inorg. Chim. Acta*, **270**, 34–45.
Kegley, S. E., Schaverien, C. J., Freudenberger, J. H. & Bergman, R. G. (1987). *J. Am. Chem. Soc.* **109**, 6563–6565.
Nonius (1998). *COLLECT. Program for Data Collection.* Nonius, Delft, The Netherlands.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.
Ziolo, R. F., Shelby, R. M., Stanford, R. H. Jr & Gray, H. B. (1974). *Cryst. Struct. Commun.* **3**, 469–472.

A hydrated diclofenac salt of the hexaaquamagnesium ion

Carlo Castellari,[a] Fabio Comelli[b] and Stefano Ottani[b]

[a]*Dipartimento di Chimica 'G. Ciamician', Università di Bologna, Via Selmi 2, 40126 Bologna, Italy, and* [b]*Centro Studi Fisica Macromolecole, c/o Dipartimento di Chimica 'G. Ciamician', Università di Bologna, Via Selmi 2, 40126 Bologna, Italy. E-mail: stefano@frodo.ciam.unibo.it*
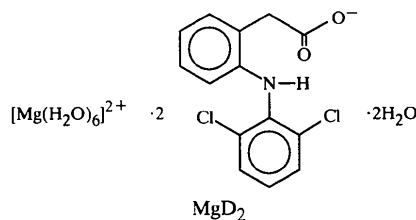
Abstract

In the title compound, hexaaquamagnesium bis{[2-(2,6-dichloroanilino)phenyl]acetate} dihydrate, $[Mg(H_2O)_6]$-$(C_{14}H_{10}Cl_2NO_2)_2 \cdot 2H_2O$, the two centrosymmetric hexaaquamagnesium ions, the two [2-(2,6-dichloroanilino)-phenyl]acetate anions and the two water molecules are tied into an elaborate network of hydrogen bonds.

Comment

In previous work, we investigated the structures of several diclofenac salts (Castellari & Sabatino, 1994, 1996; Castellari & Ottani, 1995, 1996, 1997). We report here the crystal structure of the dihydrated 1:2 salt of $[Mg(OH_2)_6]^{2+}$ with [2-(2,6-dichloroanilino)phenyl]-acetate, hereinafter abbreviated as MgD$_2$.

MgD$_2$

Diclofenac sodium salt (NaD) is an effective drug used in rheumatology and magnesium is an essential cofactor in biology. The asymmetric unit of the MgD$_2$ salt consists of two anions in general positions, two cations located at the inversion centers $\frac{1}{2},0,0$ and $0,\frac{1}{2},0$, and two crystallization water molecules. Each cation is coordinated by six water molecules. The hexahydrated magnesium complex, the carboxylate ions and the water molecules are linked by a network of hydrogen bonds in which, as expected, $[Mg(OH_2)_6]^{2+}$ cations act as proton donors, carboxylate O atoms as proton acceptors and the two water molecules both
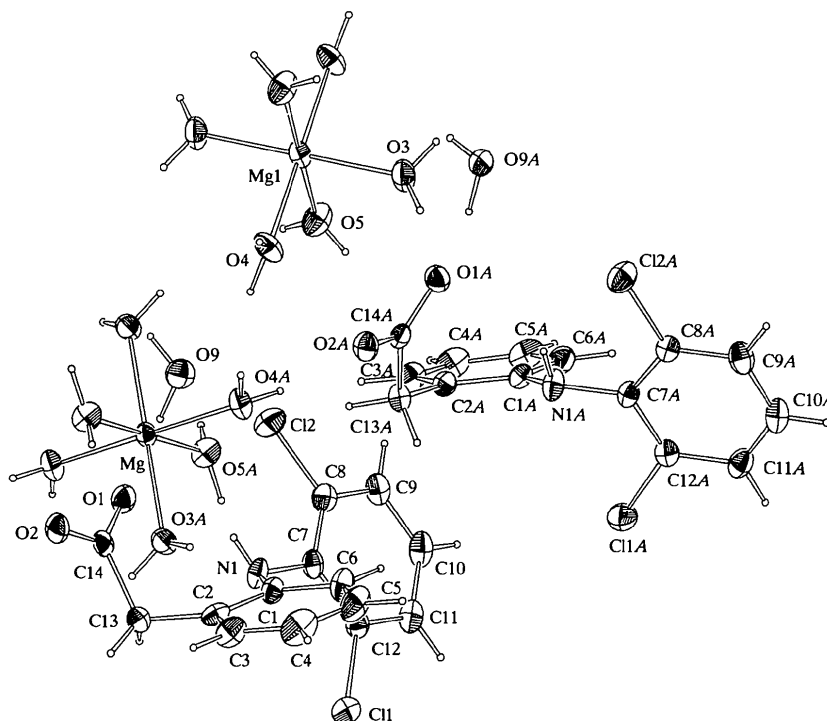
Fig. 1. *ORTEP*II diagram (Johnson, 1976) of MgD₂. Non-H atoms are represented by displacement ellipsoids of 50% probability and H atoms are of arbitrary size.

as proton donors and acceptors (Table 2). The O···O packing contacts around the two hexaaquamagnesium complexes range from 2.673 (4) to 2.902 (4) Å. The crystal engineering leads to an almost complete system of hydrogen bonds; however, the two groups Mg1—O5—H16 and Mg—O5A—H16A point towards the O3 and O3A atoms [O···O distances of 2.940 (4) and 2.906 (4) Å, respectively], but with unfavorable O—H···O angles [82 (4) and 82 (3)°, respectively]. As a consequence of this rather uniform force field, the two independent MgO₆ moieties exhibit only slight deviations (Table 1) from an idealized O_h symmetry, even though only the inversion center is retained in the crystal. Moreover, both the octahedrons appear more regular than in the analogous structure determined by Julian *et al.* (1973).

The molecular conformation of D⁻ is of special interest since it is related to the competitive binding of the drug to the arachidonic acid substrate which is responsible of the anti-inflammatory power of diclofenac. In MgD₂, such structural details of D⁻ are normal. In fact, both the C—O distances (Table 1) and the dihedral angles between the planes of the two aromatic rings [70.6 (1) and 64.3 (1)° for the two independent D⁻ anions] fall in the range found by us in other diclofenac salts (Castellari & Sabatino, 1994, 1996; Castellari & Ottani, 1995, 1996, 1997), *i.e.* the C—O bond lengths are in the range 1.237 (3)–1.263 (3) Å and the dihedral angles are in the range 59.3 (1)–73.6 (1)°.

Experimental

Crystalline MgD₂ was prepared from an aqueous solution containing nearly 2 equivalents of NaD and one of MgCl₂. The precipitate which formed was dried and recrystallized from an ethyl acetate solution.

Crystal data

[Mg(H₂O)₆](C₁₄H₁₀Cl₂-NO₂)₂·2H₂O
$M_r = 758.70$
Monoclinic
$P2_1/c$
$a = 11.670 (3)$ Å
$b = 8.538 (2)$ Å
$c = 34.208 (10)$ Å
$\beta = 92.58 (2)°$
$V = 3405.0 (15)$ Å³
$Z = 4$
$D_x = 1.480$ Mg m⁻³
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 6–14°$
$\mu = 0.429$ mm⁻¹
$T = 293 (2)$ K
Block
$0.20 \times 0.15 \times 0.13$ mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
Profile data from ω scans
Absorption correction: none
8316 measured reflections
8191 independent reflections
3063 reflections with
$I > 2\sigma(I)$

$R_{int} = 0.091$
$\theta_{max} = 27.99°$
$h = -15 \rightarrow 15$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 45$
3 standard reflections
frequency: 160 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.158$
$S = 0.931$
8182 reflections
489 parameters
H atoms treated by a
   mixture of independent
   and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0722P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.004$
$\Delta\rho_{max} = 0.353$ e Å^{-3}
$\Delta\rho_{min} = -0.355$ e Å^{-3}
Extinction correction: none
Scattering factors from
  International Tables for
  Crystallography (Vol. C)

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

Mg1—O4	2.048 (3)	Mg—O4A	2.064 (3)
Mg1—O3	2.050 (3)	C14A—O1A	1.257 (4)
Mg1—O5	2.076 (3)	C14A—O2A	1.262 (4)
Mg—O3A	2.048 (3)	C14—O1	1.255 (4)
Mg—O5A	2.056 (3)	C14—O2	1.260 (4)
O4—Mg1—O3	87.23 (12)	O5A—Mg—O4A	89.34 (12)
O4—Mg1—O5	89.59 (13)	C7A—N1A—C1A	123.3 (4)
O3—Mg1—O5	90.91 (13)	O1A—C14A—O2A	123.5 (4)
O3A—Mg—O5A	90.14 (12)	C7—N1—C1	122.4 (3)
O3A—Mg—O4A	88.91 (12)	O1—C14—O2	124.3 (4)
C1A—N1A—C7A—C12A		−59.1 (6)	
C1—N1—C7—C12		65.2 (5)	

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

D—H···A	H···A	D···A	D—H···A
N1—H1···Cl2	2.54 (4)	2.990 (4)	119 (4)
N1—H1···O1	2.24 (4)	2.898 (4)	143 (5)
N1A—H1A···Cl2A	2.40 (4)	2.969 (4)	130 (4)
N1A—H1A···O1A	2.36 (4)	2.940 (4)	131 (4)
O3—H11···O1A	2.11 (5)	2.902 (4)	160 (5)
O3A—H11A···O1^i	1.99 (5)	2.831 (4)	157 (5)
O3—H12···O2^{ii}	1.87 (4)	2.730 (4)	173 (5)
O3A—H12A···O9A^{iii}	1.95 (5)	2.769 (4)	159 (5)
O4—H13···O9A^{iv}	1.89 (5)	2.713 (4)	167 (5)
O4A—H13A···O2^v	1.92 (4)	2.852 (4)	166 (4)
O4—H14···O9	1.99 (4)	2.879 (4)	159 (4)
O4A—H14A···O2A	1.96 (4)	2.793 (4)	171 (5)
O5—H15···O2A^{vi}	1.87 (5)	2.758 (4)	167 (4)
O5A—H15A···O9	1.94 (5)	2.734 (4)	169 (5)
O9—H23···O1	1.78 (4)	2.834 (4)	172 (4)
O9A—H23A···O1A	1.64 (4)	2.673 (4)	170 (4)
O9—H24···O2^{vii}	1.90 (4)	2.776 (4)	170 (4)
O9A—H24A···O2A^{iv}	2.08 (4)	2.804 (4)	163 (5)

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

The N—H and water H atoms were located from a difference synthesis and were refined isotropically. The remaining H atoms were placed in calculated positions and refined riding on their parent atoms.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEPII* (Johnson, 1976).

We thank Servizio Italiano di Diffusione Dati Cristallografici del CNR (Parma) for access to the Cambridge Structural Database (Allen & Kennard, 1993).

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
Castellari, C. & Ottani, S. (1995). *Acta Cryst.* C**51**, 2612–2615.
Castellari, C. & Ottani, S. (1996). *Acta Cryst.* C**52**, 2619–2622.
Castellari, C. & Ottani, S. (1997). *Acta Cryst.* C**53**, 482–486.
Castellari, C. & Sabatino, P. (1994). *Acta Cryst.* C**50**, 1723–1726.
Castellari, C. & Sabatino, P. (1996). *Acta Cryst.* C**52**, 1708–1712.
Enraf–Nonius (1989). *CAD-4 Software.* Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf–Nonius, Delft, The Netherlands.
Johnson, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Julian, M. O., Day, V. W. & Hoard, J. L. (1973). *Inorg. Chem.* **12**, 1754–1757.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97.* Release 97-1. *Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

trans-Bis(acetato-*O*)bis(2-amino-6-methyl-pyridine-*N*)copper(II)

Nina Lah, Ljubo Golič, Primož Šegedin and Ivan Leban

Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, PO Box 537, SI-1001 Ljubljana, Slovenia. E-mail: nina.lah@uni-lj.si

Abstract

In the title compound, $[Cu(C_2H_3O_2)_2(C_6H_8N_2)_2]$, the Cu atom is surrounded by two O atoms from the two monodentate acetate ligands and by two pyridine N atoms from the two 2-amino-6-methylpyridine ligands in a *trans* square-planar arrangement. The Cu—O and Cu—N distances are 1.952 (2) and 2.046 (2) Å, respectively. The complex has an inversion centre. The remaining carboxylate O atoms are located at 2.764 (3) Å from the Cu atom, above and below this plane. The coordination around the Cu atom can therefore be described as (4+2). The pyridine ring is twisted 73.2 (1)° with respect to the plane formed by the Cu, the N and the more strongly bonded O atoms.

Comment

As part of a continuing study of copper(II) carboxylates, we report here the structure of *trans*-bis(acetato-*O*)bis(2-amino-6-methylpyridine-*N*)copper(II), $[Cu(C_2H_3O_2)_2(C_6H_8N_2)_2]$, (I), which is the first copper complex with 2-amino-6-methylpyridine as a ligand [survey of