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(*Z*)-Bis{μ-[1-(2-naphthylmethyloxy)propan-2-iminato-*O*,*N*:*N*]}bis[bromobis(tetrahydrofuran-*O*)magnesium] ditoluene solvate

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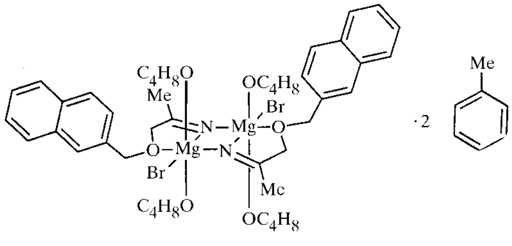
The title compound, $[Mg_2Br_2(C_{14}H_{14}NO)_2(C_4H_8O)_4]\cdot 2C_7H_8$, has been crystallized as a C_2-symmetric dimer and the Mg atom has a distorted octahedral geometry. The metal is chelated by the N atom of the ketiminate and the O atom of the ether moiety, giving a rigid structure.

Comment

Ketiminates are an important class of compounds since they can lead to α-tertiary amines by nucleophilic addition (Charette *et al.*, 1998, and references therein). However, only lithium ketiminates (Barr *et al.*, 1984, 1985, 1986, 1987, 1989; Armstrong *et al.*, 1987; Clegg *et al.*, 1983; Shearer *et al.*, 1979) and their sodium analogues (Clegg *et al.*, 1992) have been crystallized due to the difficulties associated with the preparation of these high energy species. To our knowledge, the corresponding magnesioketiminates and their α-alkoxy analogues have never been characterized. Therefore, we report herein the first crystallographic characterization of an O-protected α-alkoxy magnesioketiminate, (I). We have shown in the past that sequential nucleophilic additions to chiral cyanohydrins lead to α-tertiary amines in high yields and diastereoselectivities (Charette & Mellon, 1998). The induced quaternary stereogenic center has been assigned, and a chelated *N*-magnesioketiminate having the metal *cis* to the alkoxy group has been postulated to explain the stereochemical outcome of the reaction. An enantioselective version involving a chiral Lewis acid has been developed (Charette & Gagnon, 1999), and the level of induction also depends on the structural features of the ketiminate intermediate. The X-ray structure reported in this paper (Fig. 1) confirms the *cis* stereochemistry of the ketiminate obtained under those conditions, thus providing further mechanistic insights into the double nucleophilic addition reaction to cyanohydrins.



(I)

Compound (I) crystallizes as a dimer in space group *C*2/*c* with a twofold axis of symmetry passing through the center of the dimer formed by the N and Mg atoms. The dimeric nature of the molecule is supported by the fact that the Mg—N^{i} distance [symmetry code: (i) $1 - x, y, \frac{1}{2} - z$] is significantly

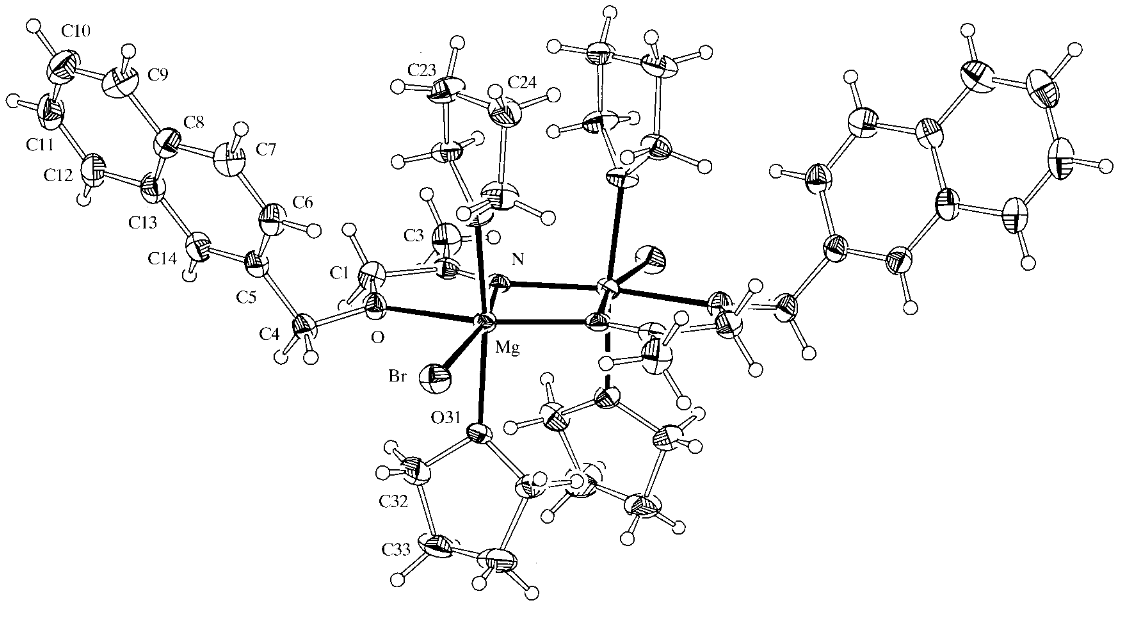


Figure 1
*ORTEP*II (Johnson, 1976) drawing of the title molecule with 40% probability ellipsoids. The disordered solvent is not illustrated.

shorter than the Mg—N bond. Disordered solvent molecules are located in large channels in the *a* direction. The magnesium adopts a distorted octahedral geometry with two coordinated tetrahydrofuran molecules. The Mg—N^i bond length of 2.090 (3) Å and the C2—N—Mg angle of 119.5 (3)° shows that the magnesium is *cis* to the ether moiety. Moreover, the O—Mg bond length of 2.229 (3) Å and the octahedral geometry of the magnesium demonstrates that the metal is chelated by the oxygen of the ether. The difference in the O—Mg bond length with respect to the average of 2.106 (3) Å found in the Cambridge Structural Database (Allen & Kennard, 1993) is probably due to geometry constraints imposed by the sp^2-C2 and sp^3-C1 atoms. The five-membered ring formed by C1—C2—N—Mg—O, together with the C3 atom, lie in a plane with an r.m.s. deviation of 0.02 Å. The C2—N bond length of 1.217 (4) Å corresponds to a C=N double bond, confirming the ketiminate functionality.

Experimental

To a stirred solution of (2-naphthylmethyloxy)acetonitrile (0.036 g, 0.18 mmol) in anhydrous toluene (2 ml) at 273 K was added methyl magnesium bromide (2.96 *M* in ether, 0.065 ml, 0.19 mmol). The solution was warmed slowly to room temperature and stirred until the starting material had disappeared, as indicated by thin-layer chromatography. The white suspension was then solubilized by the addition of anhydrous tetrahydrofuran (5 ml). Complex (I) was crystallized under argon in a glove box at 258 K for one month. Due to the moisture sensitivity of the ketiminate, the crystal was placed under a flow of nitrogen (T = 220 K) during the data collection.

Crystal data

$[Mg_2Br_2(C_{14}H_{14}NO)_2(C_4H_8O)_4]\cdot 2C_7H_8$
M_r = 1105.6
Monoclinic, $C2/c$
a = 23.12 (2) Å
b = 12.566 (9) Å
c = 19.142 (10) Å
β = 93.32 (7)°
V = 5552 (7) Å^3
Z = 4
D_x = 1.3228 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 20–22°
μ = 2.47 mm^{-1}
T = 220 (2) K
Block, clear light yellow
0.27 × 0.15 × 0.14 mm

Data collection

Nonius CAD-4 diffractometer with a gas-stream cryostat
$\omega/2\theta$ scans
Absorption correction: by integration (*ABSORP* in *NRCVAX*; Gabe *et al.*, 1989)
T_{min} = 0.59, T_{max} = 0.77
15 403 measured reflections
5238 independent reflections
2611 reflections with $I > 2\sigma(I)$
R_{int} = 0.096
θ_{max} = 69.85°
$h = -28 \rightarrow 28$
$k = -15 \rightarrow 15$
$l = -23 \rightarrow 23$
5 standard reflections
frequency: 60 min
intensity decay: 20.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.077
S = 0.981
5238 reflections
384 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0212P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.72 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}
Extinction correction: *SHELXL*96 (Sheldrick, 1996)
Extinction coefficient: 2.9 (8) × 10^{-5}

Table 1
Selected geometric parameters (Å, °).

Br—Mg	2.693 (2)	O—C1	1.436 (4)
Mg—N^i	2.090 (3)	O—C4	1.447 (4)
Mg—N	2.129 (3)	N—C2	1.217 (4)
Mg—O21	2.148 (3)	C1—C2	1.526 (5)
Mg—O31	2.180 (3)	C2—C3	1.525 (5)
Mg—O	2.229 (3)	C4—C5	1.504 (5)
N^i—Mg—N	84.11 (14)	O31—Mg—Br	83.86 (8)
N^i—Mg—O21	93.97 (12)	O—Mg—Br	92.46 (10)
N—Mg—O21	94.93 (11)	C1—O—C4	113.4 (3)
N^i—Mg—O31	92.89 (11)	C1—O—Mg	115.3 (2)
N—Mg—O31	92.39 (11)	C4—O—Mg	131.0 (2)
O21—Mg—O31	170.45 (11)	C2—N—Mg^i	144.7 (3)
N^i—Mg—O	158.78 (12)	C2—N—Mg	119.5 (3)
N—Mg—O	74.68 (12)	Mg^i—N—Mg	95.81 (14)
O21—Mg—O	87.37 (11)	O—C1—C2	108.3 (3)
O31—Mg—O	88.65 (11)	N—C2—C3	126.5 (4)
N^i—Mg—Br	108.75 (11)	N—C2—C1	122.1 (3)
N—Mg—Br	166.72 (9)	C3—C2—C1	111.4 (3)
O21—Mg—Br	87.64 (8)		

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

The decay correction was linear. H atoms were constrained to the parent site using a riding model with *SHELXL*96 (Sheldrick, 1996) defaults and C—H = 0.94–0.98 Å. A torsional parameter was refined for the C3 methyl group. The isotropic displacement parameters, U_{iso}, were adjusted to 50% higher than the value of the parent site for methyl H atoms and 20% higher for the others. The toluene solvent was modeled as disordered with two orientations of populations 0.891 (7) and 0.109 (7) related by an in-plane rotation of approximately 120°. The solvent was refined anisotropically using restraints (SAME/ISOR/SIMU/DELU). A final verification of possible voids was performed using the VOID routine of the *PLATON* program (Spek, 1995).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *NRC*-2 and *NRC*-2*A* (Ahmed *et al.*, 1973); program(s) used to solve structure: *SHELXS*96 (Sheldrick, 1990); program(s) used to refine structure: *NRCVAX* (Gabe *et al.*, 1989) and *SHELXL*96 (Sheldrick, 1996); molecular graphics: *ORTEP*II (Johnson, 1976) in *NRCVAX*; software used to prepare material for publication: *NRCVAX* and *SHELXL*96.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1246). Services for accessing these data are described at the back of the journal.

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