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## Dibromo(diethyl ether-*O*)(diisopropylamine-*N*)magnesium(II)

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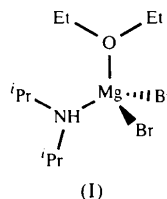
### Abstract

The coordination geometry at the Mg atom in the title complex, [MgBr<sub>2</sub>{(C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>NH}{(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O}], is shown to be distorted tetrahedral. The presence of a secondary amine ligand is unusual in its derivation from an amide. It is also unusual to find both an ether and a simple amine solvating the same magnesium centre [Mg1—N1 2.158 (3) and Mg1—O1 2.041 (3) Å].

### Comment

As part of our continuing investigations of the organometallic complexes present during the course of Mg-mediated enolization reactions (Allan *et al.*, 1997, 1998), we were interested in preparing a range of halomagnesium enolate complexes. This was attempted by the reaction of Hauser bases (R<sub>2</sub>NMgX, where R = alkyl or aryl, and X = halide) with ketones carrying an α-proton. Unless the reaction conditions for this transformation are very tightly controlled, the halomagnesium enolate complexes undergo a dismutation

reaction into the respective dihalides and dienolates. This paper discusses the structure of one such dihalide, [MgBr<sub>2</sub>(OEt<sub>2</sub>)(NH<sup>*i*</sup>Pr<sub>2</sub>)], (I), which is unusual in that the rehydrogenated amine is present as a donor ligand.



The crystal structure consists of monomeric molecular units, with the closest intermolecular interaction being that of N1—H1···Br2<sup>i</sup> [N1···Br2<sup>i</sup> 3.659 (3), H1···Br2<sup>i</sup> 2.78 Å and N1—H1···Br2<sup>i</sup> 163°; symmetry code: (i) 2 - x, 1 - y, -z]. The coordination geometry about the Mg atom is distorted tetrahedral, the largest deviation from ideal geometry being the wide N1—Mg1—Br1 angle of 120.35 (11)° (Table 1). That the angle from N1 to the second bromide ligand is smaller [N1—Mg1—Br2 102.28 (10)°] is a consequence of the molecular conformation adopted by (I). The substituents about the Mg—N bond are eclipsed [O1—Mg1—N1—C4 6.7 (3), Br1—Mg1—N1—C1 -12.9 (3) and Br2—Mg1—N1—H1 4.2°]. Thus, the Br1—Mg1—N1 angle opens to relieve the steric interaction between Br1 and the *syn*-isopropyl group. In contrast, as Br2 lies *syn* to H1, there is little steric repulsion (Br2···H1 3.25 Å). The wider angle at Mg1 from Br2 to O1, as opposed to that from Br1, may similarly be explained by the steric strain imposed by Br2 being *syn* to an ethyl group [Br2—Mg1—O1—C7 -5.4 (3)°].

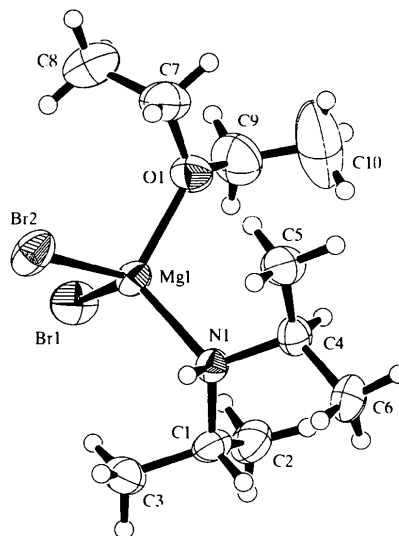


Fig. 1. ORTEP (Johnson, 1976) view of (I). Non-H atoms are shown as 40% probability ellipsoids and H atoms as small spheres of arbitrary radii.

No previous structures of Mg-diisopropylamines, or indeed of any simple Mg-secondary amines, were found in the Cambridge Structural Database (Allen & Kennard, 1993). The Mg—N bond distance does however compare well with those found for coordinated tertiary amines (Kageyama *et al.*, 1983, 1984). The Mg—Br and Mg—OEt<sub>2</sub> distances are also consistent with those found in related complexes (for examples see Allan *et al.*, 1998; Kageyama *et al.*, 1984; Williard & Salvino, 1986; Engelhardt *et al.*, 1988). The geometric parameters involving C10 and C11 are adversely affected by disorder.

## Experimental

All manipulations were carried out under a dry oxygen-free argon atmosphere, using standard Schlenk techniques. Diisopropylamine (10 mmol) was added dropwise to a chilled solution (273 K) of ethylmagnesium bromide (10 mmol of a 3 M solution in diethyl ether) in 10 ml of hexane. 2,4-Dimethyl-3-pentanone (10 mmol) was added over a period of 10 min and the solution stirred for 1 h at 273 K. All solvents were removed under reduced pressure and replaced by 20 ml of toluene. Crystals suitable for diffraction precipitated on standing the solution at 253 K for one week. The crystals were isolated from solution and stored in an argon-filled glove box.

### Crystal data

[MgBr <sub>2</sub> (C <sub>6</sub> H <sub>15</sub> N)(C <sub>4</sub> H <sub>10</sub> O)]	Mo K $\alpha$ radiation
$M_r = 359.44$	$\lambda = 0.71069 \text{ \AA}$
Monoclinic	Cell parameters from 20 reflections
$P2_1/c$	$\theta = 12.25\text{--}13.75^\circ$
$a = 13.9138 (16) \text{ \AA}$	$\mu = 4.972 \text{ mm}^{-1}$
$b = 8.2036 (13) \text{ \AA}$	$T = 295 \text{ K}$
$c = 14.555 (2) \text{ \AA}$	Fragment
$\beta = 99.836 (10)^\circ$	$0.7 \times 0.5 \times 0.3 \text{ mm}$
$V = 1636.9 (4) \text{ \AA}^3$	Colourless
$Z = 4$	
$D_x = 1.459 \text{ Mg m}^{-3}$	
$D_m$ not measured	

### Data collection

Rigaku AFC-7S diffractometer	1747 reflections with $I > 2\sigma(I)$
$\omega/2\theta$ scans	$R_{\text{int}} = 0.033$
Absorption correction: $\psi$ scan (North <i>et al.</i> , 1968)	$\theta_{\text{max}} = 26^\circ$
$T_{\text{min}} = 0.096$ , $T_{\text{max}} = 0.225$	$h = 0 \rightarrow 17$
3346 measured reflections	$k = 0 \rightarrow 10$
3211 independent reflections	$l = -17 \rightarrow 17$
	3 standard reflections every 150 reflections intensity decay: 17.7%

### Refinement

Refinement on $F^2$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.033$	$\Delta\rho_{\text{max}} = 0.623 \text{ e \AA}^{-3}$
$wR(F^2) = 0.096$	$\Delta\rho_{\text{min}} = -0.627 \text{ e \AA}^{-3}$
$S = 0.986$	Extinction correction: none

3211 reflections

147 parameters

H atoms: see below

$$w = 1/[\sigma^2(F_o^2) + (0.0257P)^2 + 1.3936P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

Scattering factors from

*International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Br1—Mg1	2.4541 (14)	O1—C9	1.452 (6)
Br2—Mg1	2.4453 (15)	O1—C7	1.454 (6)
Mg1—O1	2.041 (3)	N1—C4	1.502 (5)
Mg1—N1	2.158 (3)	N1—C1	1.503 (5)
O1—Mg1—N1	112.35 (14)	N1—Mg1—Br1	120.35 (11)
O1—Mg1—Br2	106.64 (11)	Br2—Mg1—Br1	114.68 (6)
N1—Mg1—Br2	102.28 (10)	C9—O1—C7	113.7 (4)
O1—Mg1—Br1	100.18 (10)	C4—N1—C1	114.9 (3)
Br2—Mg1—O1—C9	-161.3 (4)	Br2—Mg1—N1—C4	-107.3 (3)
Br1—Mg1—O1—C9	-41.6 (4)	Br1—Mg1—N1—C4	124.2 (2)
Br2—Mg1—O1—C7	-5.4 (3)	O1—Mg1—N1—C1	-130.4 (3)
Br1—Mg1—O1—C7	114.4 (3)	Br2—Mg1—N1—C1	115.6 (3)
O1—Mg1—N1—C4	6.7 (3)	Br1—Mg1—N1—C1	-12.9 (3)

The sample was mounted in a Lindemann capillary under an argon atmosphere. One methyl group of the OEt<sub>2</sub> ligand was disordered over two sites; the occupancy was refined to 78 (2):22 (2). No H atoms were included for the minor orientation. All other H atoms were included in calculated positions in a riding model. The methyl-group orientations were assigned by refining a rotational parameter about the C—Me bonds.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993). Program(s) used to solve structure: *TEXSAN*. Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1446). Services for accessing these data are described at the back of the journal.

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## Two Conformational (Configurational) Isomers of Diperchlorato[(5*RS*,6*RS*,12*SR*,13*SR*)-5,6,12,13-tetramethyl-1,4,8,11-tetraazacyclotetradecane- $\kappa^4$ N]copper(II)

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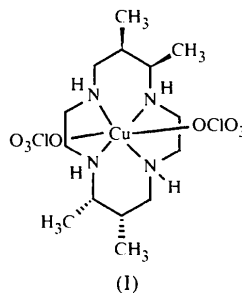
### Abstract

The crystal structure of the title compound, [Cu(ClO<sub>4</sub>)<sub>2</sub>·(C<sub>14</sub>H<sub>32</sub>N<sub>4</sub>)], has been determined by X-ray diffraction. X-ray structure analysis reveals that, owing to disorder, the compound exists in two forms, *A* and *B*. The coordination polyhedron about the Cu<sup>II</sup> ion is centrosymmetric. The Cu<sup>II</sup> ion is six-coordinated in a distorted octahedral geometry, with the four N atoms of the macrocyclic ligand in equatorial positions and the two perchlorate O atoms in axial positions. The four chiral N-atom centres have a 1*RS*,4*RS*,8*SR*,11*SR* configuration and a 1*SR*,4*RS*,8*RS*,11*SR* configuration, respectively, for the two forms, *A* and *B*. However, both have a 5*RS*,6*RS*,12*SR*,13*SR* configuration for the four chiral C-atom centres. Hydrogen bonds help stabilize the crystal structure.

### Comment

Transition metal complexes of 14-membered tetraaza macrocyclic ligands attract extensive study because of their particular stereochemical and biological significance (Boeyens & Dobson, 1987; Bosnich *et al.*, 1965; Cabbiness & Margerum, 1969). Similarly, the extreme kinetic inertness and very high thermodynamic stability of tetraaza macrocyclic ligand complexes are of particular coordination interest, since they greatly

enhance the number of potentially isolable isomers (Liang & Chung, 1980; Lee *et al.*, 1984). To the best of our knowledge, only one structure of the *C*-configuration isomer, *i.e.* the [(5*SR*,6*RS*,12*RS*,13*SR*)-tetramethyl-1,4,8,11-tetraazacyclotetradecane]nickel(II) complex, has been reported (Krajewski *et al.*, 1978). To continue our interest in establishing the coordination geometry around the metal ion and the conformation of the chelate rings, two isomeric structures of diperchlorato[(5*RS*,6*RS*,12*SR*,13*SR*)-5,6,12,13-tetramethyl-1,4,8,11-tetraazacyclotetradecane]copper(II), (*I*), are reported herein.



Owing to disorder, two different conformations (denoted *A* and *B*) of the title compound, (*I*), exist. The complex cation reveals a six-coordinate nature in a distorted octahedral geometry around the Cu<sup>II</sup> ion, with the four N atoms of the macrocyclic ligand being equatorial and the two O atoms of the perchlorate ions being axial. The Cu<sup>II</sup> ion is located at the inversion centre. Both forms are similar to that of (1,4,8,11-tetraazacyclotetradecane)copper(II) (Tasker & Sklar, 1975). Form *A* has a 1*RS*,4*RS*,8*SR*,11*SR* configuration (*trans*-III) (Bosnich *et al.*, 1965) with 75% occupancy, and its tetradentate ligand adopts a stable conformation, with the two six-membered rings in a chair form and the two five-membered rings in a *gauche* form. The *B* form has a 1*SR*,4*RS*,8*RS*,11*SR* configuration (*cis*-IV) with 25% occupancy for the four chiral N-atom centres, and its tetradentate ligand adopts a less stable conformation, with the two six-membered rings in a twisted form and the two five-membered rings in an eclipsed form (Warner & Busch, 1969).

The average Cu—N bond length in form *A* is 2.012(4) Å and that in form *B* is 2.019(7) Å; the Cu—O bond lengths in forms *A* and *B* are 2.535(4) and 2.679(15) Å, respectively (Lu *et al.*, 1991). The axial bond length is longer due to the Jahn–Teller effect (Hitchman & Deeth, 1986). The structure of the perchlorate group is also disordered, with occupancies of 75 and 25%. The geometry of the perchlorate group is slightly distorted tetrahedral, with the Cl—O distances in the range 1.32(1)–1.49(1) Å and O—Cl—O angles in the range 104.7(7)–114.9(14)°. The two methyl groups of C4 and its inversion-related atom (C4') occupy axial