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Key indicators

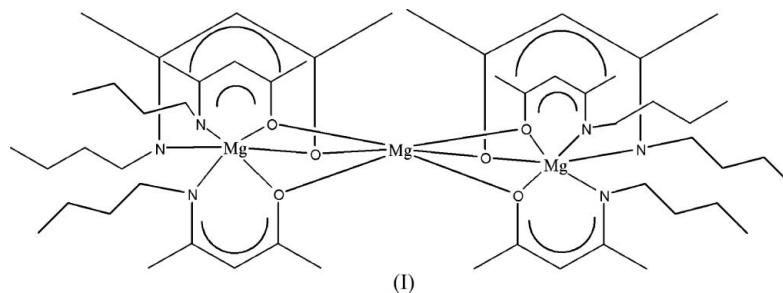
Single-crystal X-ray study
 $T = 103$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
Disorder in main residue
 R factor = 0.068
 wR factor = 0.164
Data-to-parameter ratio = 20.5For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Hexakis[μ_2 -4-(*N*-*n*-butylimino)pentan-2-onato]-
trimagnesium(II)

The title compound, $[\text{Mg}_3(\text{C}_9\text{H}_{16}\text{NO})_6]$, represents a trimeric complex with all Mg atoms having octahedral coordination. The central Mg atom occupies a special position on a crystallographic inversion centre and is coordinated by six O atoms [$\text{Mg}-\text{O} = 2.069$ (2), 2.083 (2) and 2.072 (2) Å], all of which have bridging functions. Each of the peripheral Mg atoms is coordinated by three bridging O atoms [$\text{Mg}-\text{O} = 2.090$ (2), 2.086 (2) and 2.095 (2) Å] and three terminal N atoms of the butylimino groups [$\text{Mg}-\text{N} = 2.206$ (2), 2.202 (2) and 2.196 (2) Å].

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Comment

The synthesis of volatile derivatives of group 2 metals has lately been the focus of several studies (Matthews *et al.*, 2000; Rees *et al.*, 2000) targeted at the development of precursors for the preparation of electronic materials *via* chemical vapour deposition (CVD). Moderately volatile magnesium bis-2,2,6,6-tetramethylheptanedionate has been synthesized previously and is believed to exist as an oligomer in the solid state (Arunasalam *et al.*, 1996). In an attempt to develop a more volatile CVD precursor for magnesium, we have been investigating the utility of the β -ketoimino ligand. This ligand is structurally similar to the well established β -diketonate platform, but has the added advantage of allowing for the incorporation of steric bulk about the metal centre *via* modification of the alkyl group bonded to the N atom. For this purpose, the title compound, (I), was synthesized.



The present single-crystal X-ray diffraction study showed that the compound is trimeric in the solid state (Fig. 1), and all Mg atoms have slightly distorted octahedral coordination. The central Mg atom occupies a special position on a crystallographic inversion centre and is coordinated by six O atoms, which form three bridges with each of the two peripheral Mg atoms. The coordination octahedron of the peripheral Mg atom is made up of the three above-mentioned bridging O atoms and three terminal N atoms of the *N*-*n*-butylimino substituents.

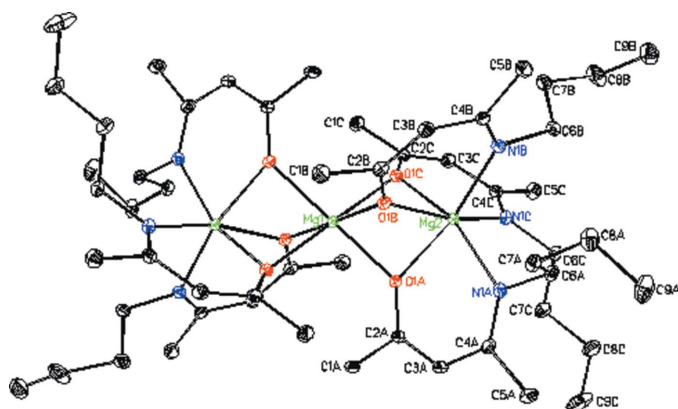


Figure 1

A plot of the structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 20% probability level. H atoms and minor components of the disordered groups have been omitted for clarity. (Symmetry code for unlabelled atoms: $-x, 1-y, 1-z$.)

The Mg–N distances involving terminal Mg atoms [Mg2–N1A 2.206 (2), Mg2–N1B 2.202 (2) and Mg2–N1C 2.196 (2) Å] and the Mg–O distances involving the central Mg atom [Mg1–O1A 2.069 (2), Mg1–O1B 2.083 (2) and Mg1–O1C 2.072 (2) Å] are in good agreement with the corresponding values known for trimeric six-coordinate magnesium β -ketoiminates (Matthews, 1999). These bonds are much longer than those reported for both monomeric tetrahedral (Ouattara *et al.*, 2005) and monomeric octahedral (Matthews *et al.*, 2000) magnesium β -ketoiminates. The Mg–O distances involving the terminal Mg atoms [Mg2–O1A 2.090 (2), Mg2–O1B 2.086 (2) and Mg2–O1C 2.095 (2) Å] are somewhat longer than those for the central Mg atom, due to the influence of the sterically demanding butyl groups on the N atoms. The O–Mg–O angles at the terminal Mg atom [77.54 (8), 77.56 (8) and 78.01 (8)°] are slightly smaller than those at the central Mg atom [78.11 (7), 78.52 (7) and 78.54 (7)°].

Experimental

Under an inert atmosphere of nitrogen, 4-butyliminopent-3-en-2-one (1.282 g, 8.27 mmol) was added to a Schlenk flask containing dry hexane (50 ml) and a magnetic stirrer bar. The mixture was stirred and cooled to 273 K. A solution of 1M dibutylmagnesium in hexane (4.14 ml, 4.14 mmol) was then added *via* a syringe. The mixture was allowed to warm to room temperature with stirring for 1 h. The solvent was removed under reduced pressure to afford a light-yellow solid. The isolated solid was dissolved in dry toluene and held at 268 K for one week, at which time the formation of colourless crystals of (I) was observed. Spectroscopic analysis: ^1H NMR (CDCl_3 , δ , p.p.m.): 0.92 (*s*, 3H, CH_2CH_3), 1.3 (*m*, 4H, CH_2CH_2), 1.90 (*s*, 3H, CH_3CO), 1.965 (*s*, 3H, CH_3CN), 3.21 (*t*, CH_2 , 2H), 4.75 (*s*, CH, 1H); ^{13}C NMR (CDCl_3 , δ , p.p.m.): 13.77 (CH_3), 20.63 (CH_2), 25.38 (CH_2), 31.99 (CH_3CN), 33.14 (CH_3CO), 49.96 (CH_2N), 94.84 (CH), 170.72 (CN), 178.25 (CO).

Crystal data

$[\text{Mg}_3(\text{C}_9\text{H}_{16}\text{NO})_6]$
 $M_r = 998.30$
 Triclinic, $P\bar{1}$
 $a = 10.8426$ (11) Å
 $b = 10.7220$ (11) Å
 $c = 14.7728$ (16) Å
 $\alpha = 100.564$ (2)°
 $\beta = 103.537$ (2)°
 $\gamma = 111.743$ (2)°
 $V = 1479.9$ (3) Å³

$Z = 1$
 $D_x = 1.120$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 4561 reflections
 $\theta = 2.7$ – 28.3 °
 $\mu = 0.10$ mm⁻¹
 $T = 103$ (2) K
 Plate, colourless
 $0.56 \times 0.40 \times 0.15$ mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2002)
 $T_{\min} = 0.713$, $T_{\max} = 0.985$
 10557 measured reflections

6885 independent reflections
 4115 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.050$
 $\theta_{\max} = 28.3$ °
 $h = -14 \rightarrow 14$
 $k = -14 \rightarrow 14$
 $l = -19 \rightarrow 19$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.068$
 $wR(F^2) = 0.164$
 $S = 1.02$
 6885 reflections
 336 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0592P)^2 + 1.0113P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.32$ e Å⁻³
 $\Delta\rho_{\min} = -0.30$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Mg1–O1A	2.0692 (17)	Mg2–O1B	2.086 (2)
Mg1–O1B	2.0825 (19)	Mg2–O1C	2.095 (2)
Mg1–O1C	2.0721 (18)	Mg2–N1A	2.206 (2)
Mg1–Mg2	2.8593 (9)	Mg2–N1B	2.202 (2)
Mg2–O1A	2.090 (2)	Mg2–N1C	2.196 (2)
O1A–Mg1–O1C	78.52 (7)	O1B–Mg2–N1B	85.13 (8)
O1A–Mg1–O1B	78.54 (7)	O1A–Mg2–N1B	162.96 (9)
O1C–Mg1–O1B	78.11 (7)	O1C–Mg2–N1B	101.33 (8)
Mg2–Mg1–Mg2 ⁱ	180	N1C–Mg2–N1B	96.05 (9)
O1B–Mg2–O1A	78.01 (8)	O1B–Mg2–N1A	100.49 (8)
O1B–Mg2–O1C	77.54 (8)	O1A–Mg2–N1A	84.52 (8)
O1A–Mg2–O1C	77.56 (8)	O1C–Mg2–N1A	162.01 (9)
O1B–Mg2–N1C	162.25 (9)	N1C–Mg2–N1A	96.99 (9)
O1A–Mg2–N1C	100.76 (9)	N1B–Mg2–N1A	96.28 (9)
O1C–Mg2–N1C	84.88 (8)		

Symmetry code: (i) $-x, -y + 1, -z + 1$.

The elongated ellipsoids and anomalous values for bond lengths and angles in two of the three *n*-butyl groups prompted the introduction of a disordered model. In the final refinement, one of the *n*-butyl groups has its terminal Me group disordered over two positions, C9C and C9E, with occupancy factors of 0.66 (5) and 0.34 (5), respectively, and another *n*-butyl substituent has its terminal Et group disordered over two positions, C8B–C9B and C8D–C9D, with occupancy factors of 0.855 (6) and 0.145 (6), respectively. The affected C–C bond distances were constrained to be equal. The occupancy factors were refined with their respective sums constrained to unity. The four H atoms in the vicinity of the disordered groups, H71, H72, H81 and H82, were the top four peaks in a difference Fourier map and were constrained to ride on their C atoms without idealization. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C–H distances in

the range 0.95–1.00 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The displacement parameters of C9C/C9E, C8B/C8D and C9B/C9D were constrained to be equal.

Data collection: *SMART-NT* (Bruker, 2001); cell refinement: *SAINT-NT* (Bruker, 2001); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); software used to prepare material for publication: *SHELXTL*.

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