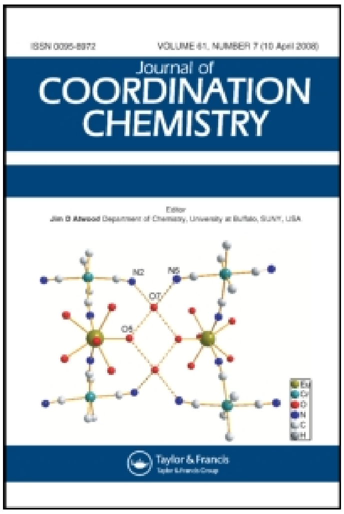

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Synthesis and characterization of bis[4-*N*-(cyclohexylimino)-2-pentanonato]magnesium(II)

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Synthesis and characterization of bis[4-*N*-(cyclohexylimino)-2-pentanonato]magnesium(II)

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A novel β-ketoimine, 4-*N*-(cyclohexylimino)-2-pentanone, was synthesized and reacted with dibutyl magnesium to afford the desired magnesium bis(β-ketoiminate). The complex, bis[4-*N*-(cyclohexylimino)-2-pentanonato]magnesium(II), has been structurally characterized by single-crystal X-ray diffraction methods. Crystallographic analysis shows the four-coordinate complex to be homoleptic and monomeric in the solid state. The geometry around the Mg(II) atom is a distorted tetrahedron. The bulky cyclohexyl groups provide enough steric bulk about magnesium to inhibit intermolecular interactions. The crystal structure of the complex is triclinic, space group $P\bar{1}$, with $a = 8.301(3)$, $b = 11.301(4)$, $c = 12.023(4)$ Å, $\alpha = 75.840(6)$, $\beta = 88.867(6)$, $\gamma = 84.611(6)^\circ$, $Z = 2$. The two normal Mg–O and Mg–N bond lengths are, respectively, 1.9162(11), 1.9265(11) and 2.0699(13), 2.0822(12) Å.

Keywords: Magnesium (II); β-Ketoiminate; Monomeric; Homoleptic; Crystal structure

1. Introduction

Much of the metal–organic chemistry surrounding group 2 metals has been geared toward the preparation of volatile chemical vapor deposition (CVD) precursors [1–3]. The chemistry of these volatile complexes is based primarily on the amide and β-diketonate ligand platforms [4–8]. Both of these ligand types have been used in the preparation of potential metal-oxide and metal-nitride CVD precursors. However, the β-ketoiminate ligand, a hybrid of the β-diketonate and amide systems, has not received much attention in terms of its potential use as a CVD precursor [9–13]. Recently, we have focused our attention on the chemistry of group II β-ketoiminates. The preparation of volatile magnesium oxide precursors has been previously investigated by Drake and coworkers [14]. Their work included the synthesis and characterization of the thermally stable magnesium bis-tetramethylheptanedionate oligomer. The compound exhibited modest volatility under ambient pressure conditions. In an attempt to enhance the volatility of the magnesium oxide precursor, Rees and coworkers made use of a tridentate ligand to prepare the first example of a homoleptic and monomeric six-coordinate

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magnesium β-ketoiminate, and showed that the compound was suitable for growth of MgO [3].

Generally, four-coordinate magnesium complexes exist as dimers and trimers in the solid state [15–20] with only a few existing as monomers [19,21–24]. We report here the synthesis and characterization of a monomeric and homoleptic four-coordinate magnesium β-ketoiminate. The molecular structure consists of a central Mg atom in a distorted tetrahedral geometry coordinating to two bidentate β-ketoiminate ligands through their N and O atoms.

2. Experimental

2.1. *Synthesis*

Under an inert atmosphere of argon, 4-*N*-cyclohexylimino-2-pentanone (1.489 g, 8.22 mmol) was added to a Schlenk flask containing 50 mL of dried hexanes and a magnetic stirring bar. The mixture was cooled to 0°C and dibutylmagnesium (4.22 mL, 1.0 M) was added by syringe. The reaction was allowed to warm to room temperature and stirred for 1 h. The solvent was then removed *in vacuo* and a light yellow solid was isolated. The isolated solid was dissolved in dry toluene and held at −5°C for 1 week at which time the formation of colorless crystals was observed.

2.2. *Physical measurements*

Spectroscopic analysis: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.0–1.8 (m, cyclohexyl); 1.88 (s, CH_3); 1.92 (s, CH_3); 3.27 (s, CH–N); 4.78 (s, CH); ^{13}C NMR (400 MHz, $CDCl_3$): δ 21.33, 25.53, 27.05, 34.24 (cyclohexyl), 58.53 (CH_3), 97.99 (CH), 170.75 (C–N), 179.08 (C–O). Anal. Calcd. for $C_{22}H_{36}N_2O_2Mg$(%): C, 68.66; H, 9.43; N, 7.28. Found: C, 68.60; H, 9.33; N, 7.32.

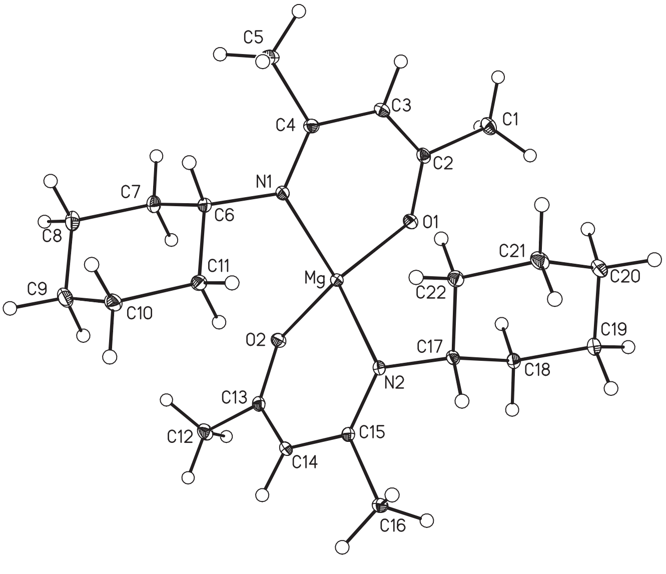

Figure 1. Molecular structure of bis[4-*N*-(cyclohexylimino)-2-pentanonato]magnesium(II).

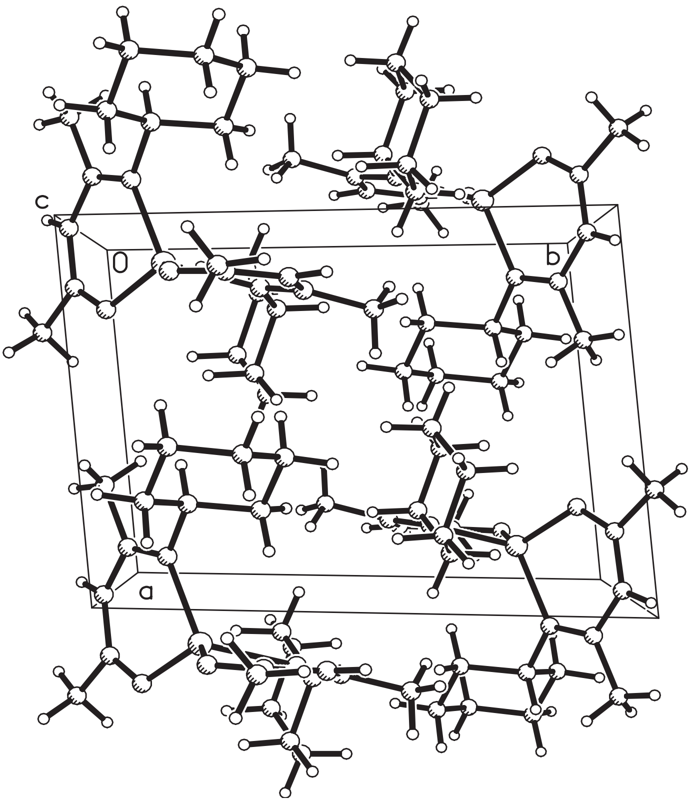

Figure 2. A schematic packing view of bis[4-*N*-(cyclohexylimino)-2-pentanonato]magnesium(II).

2.3. *Crystal structure determination*

X-ray diffraction intensity data were collected on a Brucker SMART CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at -170°C with absorption corrections performed using the SADABS program [25]. Re-collection and analysis of the initial 50 frames showed that no decay correction was needed. The structure was solved by direct methods [26] and refined on F^2 by full-matrix least-squares using the SHELXL97 program package [27].

2.4. *Crystal data*

$[(C_{11}H_{18}NO)_2Mg]$, $M = 384.84$, triclinic, group space $P\bar{1}$, $a = 8.301(3)$, $b = 11.301(4)$, $c = 12.023(4)$ Å, $\alpha = 75.840(6)$, $\beta = 88.867(6)$, $\gamma = 84.611(6)$°, $V = 1088.8(6)$ Å^3, $Z = 2$, $D_x = 1.174\,\mathrm{Mg\,m^{-3}}$, $F(000) = 420$, $\mu(\mathrm{Mo\,K}\alpha) = 0.100\,\mathrm{mm^{-1}}$, $S = 1.040$, $(\Delta_\rho)_{\max} = 0.400$, $(\Delta_\rho)_{\min} = -0.278\,\mathrm{e\,A^{-3}}$.

3. Results and discussion

The molecular structure of the title compound is illustrated in figure 1. The Mg atom is the central atom and the other atoms are numbered except for the hydrogen

Table 1. Selected bond distances (Å) and angles (°) for bis[4-N-(cyclohexylimino)-2-pentanonato] magnesium (II)

Mg–O1	1.9265(11)	O2–C13	1.2902(16)
Mg–O2	1.9162(11)	N2–C15	1.3116(16)
Mg–N1	2.0699(13)	N2–C17	1.4716(15)
Mg–N2	2.0822(12)	C2–C3	1.383(2)
O1–C2	1.2936(16)	C3–C4	1.4424(17)
N1–C4	1.3081(16)	C13–C14	1.3846(18)
N1–C6	1.4791(15)	C14–C15	1.4353(17)
O2–Mg–O1	123.80(5)	C14–C15–C16	114.10(10)
O2–Mg–N1	115.45(4)	C15–N2–C17	120.04(10)
O1–Mg–N1	94.56(5)	C15–N2–Mg	121.63(9)
O2–Mg–N2	93.34(4)	C17–N2–Mg	117.98(7)
O1–Mg–N2	112.45(5)	N2–C17–C22	110.37(10)
N1–Mg–N2	119.40(5)	N2–C17–C18	108.76(10)
C2–O1–Mg	124.65(9)	C18–C17–C22	110.44(10)
C4–N1–C6	119.65(11)	O1–C2–C3	125.98(11)
C4–N1–Mg	121.95(9)	O1–C2–C1	114.94(12)
C6–N1–Mg	118.28(8)	C3–C2–C1	119.08(12)
C13–O2–Mg	125.24(8)	C2–C3–C4	128.04(12)
C13–C14–C15	127.30(11)	C2–C3–H3A	116.0
C13–C14–H14A	116.3	C4–C3–H3A	116.0
C15–C14–H14A	116.3	N1–C4–C3	123.25(12)
O2–C13–C12	115.22(11)	N1–C4–C5	121.72(12)
O2–C13–C14	125.57(11)	C3–C4–C5	115.03(11)
C14–C13–C12	119.17(11)	N1–C6–C7	109.47(10)
N2–C15–C14	123.43(11)	N1–C6–C11	109.58(10)
N2–C15–C16	122.44(11)	C7–C6–C11	110.74(10)

atoms whose numbers have been omitted for clarity. The nitrogen and oxygen atoms are at the corners of the distorted tetrahedron. The N atom is further bonded to a cyclohexyl group that provides enough steric bulk to inhibit intermolecular interactions. The structure exhibits two intramolecular close contacts, H(11A)–Mg (2.68 Å) and H(22A)–Mg (2.71 Å). These distances are shorter than the sum of their respective van der Waals radii, 2.93 Å [28–30]. The two Mg–O and the two Mg–N bond distances are 1.9162(11), 1.9265(11) and 2.0699(13), 2.0822(12) Å, respectively. These bond distances are comparable to the Mg–O and Mg–N bond distances of similar magnesium complexes [19]. The angles about the four-coordinate Mg center deviate from that of an ideal tetrahedron with O1–Mg–N2 and O2–Mg–N2 exhibiting bond angles of 94.56(5) and 93.34(4)°, respectively. The O2–Mg–O1 bond angle is 123.80(5)° while that of N1–Mg–N2 is 119.40(5)°. This deviation is caused by the presence of the two bulky cyclohexyl groups. It has been previously reported that ligand structure can greatly affect the geometry of four-coordinate magnesium complexes [22,31].

Supplementary data

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 232393. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccds.cam.ac.uk); also available from the author Jason S. Matthews.

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