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A magnesium–bis(diaryldiketiminate) complex

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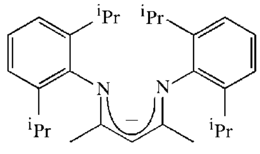
The 1:1 of reaction of dibutylmagnesium with the ligand 2-[(2-isopropylphenyl)amino]-4-[(2-isopropylphenyl)imino]pent-2-ene gives only the 1:2 metal–ligand compound bis[*N*,*N*′-bis(2-isopropylphenyl)pentane-2,4-diiminato]magnesium(II), [Mg($C_{23}H_{29}N_2$)$_2$], as an isolated solid. The coordination geometry about the Mg atom is distorted tetrahedral [N—Mg—N angles range from 90.73 (5) to 136.40 (6)°], with the metal lying out of the ligand plane. The ligands themselves have non-crystallographic C_s geometry. The structure is isotypic with the Zn analogue, and the small differences between these two structures provide evidence for a significant covalent contribution to bonds that are generally described as largely ionic.

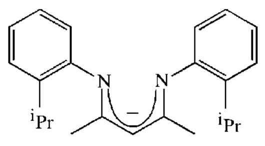
Comment

The bulky 2,6-diaryldiketiminate ligand (I) (Clegg *et al.*, 1998), derived from deprotonation of 2-[(2,6-diisopropylphenyl)amino]-4-[(2,6-diisopropylphenyl)imino]pent-2-ene (Feldman *et al.*, 1997), has enjoyed extensive use in situations where a bidentate mono-anion offering extreme steric protection is required (Bourget-Merle *et al.*, 2002). The 2,6-substituents on each aryl group are particularly effective at stabilizing two- or planar three-coordinate geometries at the ligated metal ion. In contrast, the analogous anion, (II), derived from 2-[(2-isopropylphenyl)amino]-4-[(2-isopropylphenyl)imino]pent-2-ene is found in only two published crystal structures (Cheng *et al.*, 2001; Carey *et al.*, 2003). The additional structural issues raised by the reduction in approximate C_{2v} symmetry of the bulkier (I) to either a C_2 or a C_s ligand symmetry, depending upon conformation, in (II) have yet to be fully investigated. A specific example is that, whereas the full series of group 2 complexes of (I) has been structurally characterized by X-ray crystallography (Harder, 2002), no compounds containing (II) have been reported. We present here the structure of Mg(II)$_2$ (Fig. 1), the first reported group 2 complex containing ligand (II).

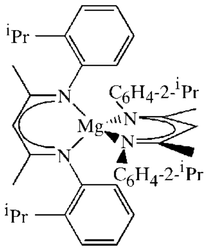
Despite the fact that the stoichiometry employed in the preparation was aimed at isolation of Mg(II)Bu, the Schlenk equilibrium (Schlenk & Schlenk, 1929) was clearly in operation here, and the least soluble component of that equilibrium proved to be Mg(II)$_2$. This behaviour has been seen in other *N*,*N*-bidentate dianion complexes of magnesium (Hao *et al.*, 2002). The structure at the metal centre is distorted tetrahedral. Both ligands adopt a local and approximate C_s symmetry, *i.e.* both isopropyl groups are disposed to the same side of the ligand. In this respect, the structure is the same as the other two known structures containing ligand (II) (Cheng *et al.*, 2001; Carey *et al.*, 2003). On the basis of the limited available solid-state data, it seems that the C_s symmetric disposition, which encourages a distorted tetrahedral geometry at the ligated metal ion, is the preferred geometry of this ligand. In fact, Mg(II)$_2$ is isomorphous, isostructural and isotypic with its zinc analogue (Cheng *et al.*, 2001). A search of the Cambridge Structural Database (Allen, 2002) revealed a small number of other structures in which identical ligand sets for both Mg and Zn atoms generated a pseudo-tetrahedral arrangement of four N atoms around each metal atom (Hao *et al.*, 2002; Gardiner *et al.*, 1994); these pairs were also isotypic. This result underlines the similarity in both size and structural preference of the Zn^{2+} and Mg^{2+} ions. The key structural parameters for Mg(II)$_2$ are shown in Table 1. While consideration of Shannon's ionic radii shows that the radius of the Mg^{2+} ion is expected to be 0.03 Å smaller than that of the Zn^{2+} ion (Shannon & Prewitt, 1969), inspection of the bond lengths shows the opposite to be true. The mean Mg—N distance [2.043 (1) Å] is comparable to the equivalent Zn—N distance [mean 2.007 (2) Å], indicating that the radius of the Mg^{2+} ion is 0.036 Å larger than that of the Zn^{2+} ion in complexes of (II). Shannon later accounted for such discrepancies on the basis of a 'covalency correction' (Shannon, 1976). An alternative in cases where covalency is thought to dominate would be to take the calculated 'atomic radii', where that of Zn^{2+} (1.42 Å) differs from that of Mg^{2+} (1.45 Å) by an appropriate amount (Clementi & Raimondi, 1963). Cases such as this, where ionic radii do not predict the correct trends, could be taken as evidence for the importance of covalency in the bonding. In a



(I)



(II)



Mg(II)$_2$

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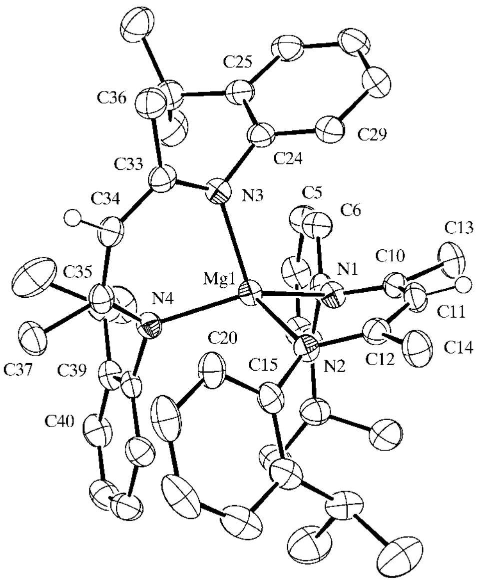

Figure 1
The molecular structure of Mg(II)$_2$, with displacement ellipsoids shown at the 50% probability level. Riding H atoms have been omitted for clarity. Aryl ring C atoms are named cyclically from the atom bound to the N atom.

previously reported case involving two-coordinate Zn and Mg atoms in isotypic molecules, the Mg atom appeared to be 0.08 Å larger (Armstrong *et al.*, 2002), while the three-coordinate metals in isotypic inverse-crown molecules have Mg—N bonds 0.05–0.09 Å longer than their corresponding Zn—N bonds (Forbes *et al.*, 2000). This increased discrepancy can be associated with the expected increased degree of covalency in the Zn—N bonds with a reduction in coordination number. Comparison of other parameters reveals expected trends; for example, the intra-ring N—Zn—N angles are slightly more open than the N—Mg—N angles, a fact that can be directly linked to the aforementioned bond-length differences. Further informative comparisons can be drawn with the recently published structure of Mg(I)$_2$ (Harder, 2002). In that case, the average Mg—N distance was 2.111 (2) Å, an increase of 0.068 Å, which indicates the effect of increased steric crowding. In fact, it has been reported that Zn(I)$_2$ could not be prepared for this reason (Cheng *et al.*, 2001). The slightly greater radius of Mg^{2+} over Zn^{2+} in these circumstances allows for the stability of Mg(I)$_2$. It shares the out-of-NCCCN-plane distortion found for the metal ions in Mg(II)$_2$ and Zn(II)$_2$ [mean 0.884 Å for Mg(II)$_2$, 0.82 Å for Zn(II)$_2$ and 0.91 Å for Mg(I)$_2$]. It is to be expected that further use of ligand (II) will foster distorted-tetrahedral coordination geometries in a wide variety of circumstances, in the same way that (I) has found widespread use in fostering trigonal and bent two-coordinate geometries (Bourget-Merle *et al.*, 2002).

Experimental

A solution of 2-[(2-isopropylphenyl)amino]-4-[(2-isopropylphenyl)imino]pent-2-ene (2.617 g, 7.8 mmol) in dry hexane (5 ml), to which a solution of 'dibutylmagnesium' (8.75 ml of a 0.897 *M* solution in heptanes, Aldrich Chemical Company) had been added under argon, was heated to boiling. Slow cooling of the resulting solution to room temperature afforded a crop of well formed crystals, which were isolated by filtration. A yield of 1.5 g [40% based on the starting pent-2-ene] of Mg(II)$_2$ was obtained. Cooling of the filtrate to 245 K gave a further small crop of Mg(II)$_2$, from which supernatant liquor was removed by syringe prior to transportation to the diffractometer.

Crystal data

$[\mathrm{Mg(C_{23}H_{29}N_2)_2}]$
$M_r = 691.27$
Monoclinic, $P2_1/c$
$a = 16.6252$ (10) Å
$b = 10.6287$ (5) Å
$c = 23.831$ (2) Å
$\beta = 95.484$ (5)°
$V = 4191.8$ (5) Å^3
$Z = 4$
$D_x = 1.095$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9856 reflections
$\theta = 2.9$–27.5°
$\mu = 0.08$ mm^{-1}
$T = 173$ (2) K
Prism, colourless
0.28 × 0.14 × 0.12 mm

Data collection

Nonius KappaCCD diffractometer
ω and φ scans
18 102 measured reflections
9565 independent reflections
5453 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.053$
$\theta_{\rm max} = 27.5°$
$h = -21 \rightarrow 21$
$k = -13 \rightarrow 12$
$l = -30 \rightarrow 30$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.119$
$S = 1.03$
9565 reflections
479 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0545P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.29$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.24$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mg1—N1	2.0374 (13)	Mg1—N2	2.0475 (14)
Mg1—N4	2.0383 (13)	Mg1—N3	2.0499 (13)
N1—Mg1—N4	136.40 (6)	N1—Mg1—N3	110.35 (5)
N1—Mg1—N2	90.73 (5)	N4—Mg1—N3	90.61 (5)
N4—Mg1—N2	111.12 (5)	N2—Mg1—N3	121.02 (6)

All H atoms were placed in calculated positions and treated as riding [methyl C—H = 0.98 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C); methine C—H = 1.00 Å and aryl C—H = 0.95 Å, both with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C)], with the exception of atoms H11*A* and H34*A*, the H atoms of the unsaturated pentene backbone, which were refined isotropically. Methyl-group orientations, apart from that of the C14 group, were obtained by refining a rotation about the C—Me axis. The C14 group was modelled with H atoms disordered over two sites.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1440). Services for accessing these data are described at the back of the journal.

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