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Magnesium−Magnesium Bond Stabilized by a Doubly Reduced α-Diimine: Synthesis and Structure of [K(THF)₃]₂[LMg−MgL]
(L = [(2,6-^{i}Pr₂C₆H₃)NC(Me)]₂²⁻)

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Metal−metal bonding as an important dimension of chemistry has attracted much attention in the past decades. Besides the concept of multiple bonds between transition metals developed by Cotton,[1] a number of metal−metal bonds involving both p- and d-block metals have been reported in recent years, such as the silicon−silicon triple bond[2] and the chromium−chromium quintuple bond.[3] In 2004, the first stable compound containing a Zn−Zn bond, Cp*Zn−ZnCp*, was synthesized by Carmona and co-workers.[4] Consequently, computations were carried out by different research groups not only on the Zn−Zn bond but also on the relevant, then-unknown Mg−Mg bond, leading to the prediction that the latter could also exist.[5−7] In 2007, Green, Jones, and Stasch[8] confirmed this hypothesis by the isolation of two Mg−Mg-bonded compounds, RMgMgR (**1**, R¹ = [(Ar)NC(N^{i}Pr₂)N(Ar)]⁻; **2**, R² = {[(Ar)NC(Me)]₂-CH}⁻; Ar = 2,6-diisopropylphenyl), the first structurally characterized stable molecules with group 2 metal−metal bonds.[9] Very recently, the same group reported a series of Lewis base (THF, dioxane, and pyridines) adducts of **2** (**2a−d**) with longer Mg−Mg bonds as well as two magnesium(II) hydrides, [MgR²(μ-H)]₂ and [MgR²(THF)(μ-H)]₂.[10]

These dimetal species normally contain lower-valence metal ions (+1) stabilized by sterically demanding ligands such as bulky terphenyls, Cp derivatives, and β-diketiminate ligands and can be accessed by reductive coupling of higher-valence metal compounds (precursors) with alkali metals. α-Diimines are well-known N-donor ligands for both main-group and transition metals. We recently used such ligands in the synthesis of two Zn−Zn-bonded compounds, [M(THF)₂]₂[LZn−ZnL] (M = Na, K; L = [(2,6-^{i}Pr₂C₆H₃)NC-(Me)]₂²⁻), by reduction of LZnCl₂ with Na or K in THF.[11,12] In these compounds, the ligand has been reduced to the dianion while the Zn²⁺ center is reduced to Zn⁺. We also examined the effect of the 2,6-substituents of the *N*-phenyl ring on the reduction products and found that the isopropyl groups were essential for the stabilization of the Zn−Zn bond, as the less bulky ligands [(2,6-Et₂C₆H₃)NC(Me)]₂ (L^{Et}) and [(2,6-Me₂C₆H₃)NC(Me)]₂ (L^{Me}) resulted in mononuclear zinc compounds.[12] Indeed, isopropyl substituents can also be found to exist in many of the metal−metal-bonded compounds mentioned above. Therefore we applied the ligand L to magnesium compounds and report herein the synthesis, structure, and results of density functional theory (DFT) computations for a Mg−Mg-bonded compound bearing doubly reduced α-diimine ligands, [K(THF)₃]₂[LMg−MgL]·2THF (**3**), which was obtained by a very convenient and straightforward procedure.

Compound **3** was readily prepared as pink crystals by reduction of a mixture of L and MgCl₂ with excess potassium metal (in a 1:1:3 molar ratio) in THF (Scheme 1).[13] It is air- and moisture-

Scheme 1. Synthesis of **3**
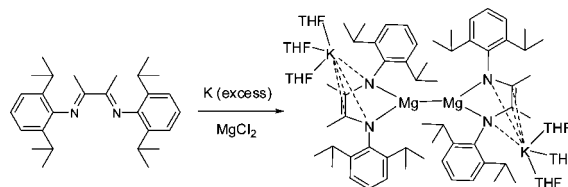
sensitive but thermally stable in solution. Upon removal from the mother liquor, the crystals rapidly lose the solvents with a deepening of the color, and they decompose at 115 °C.

The crystal structure of **3** (Figure 1)[14] shows a centrosymmetric, dimeric structure with a Mg−Mg bond, which is very similar to
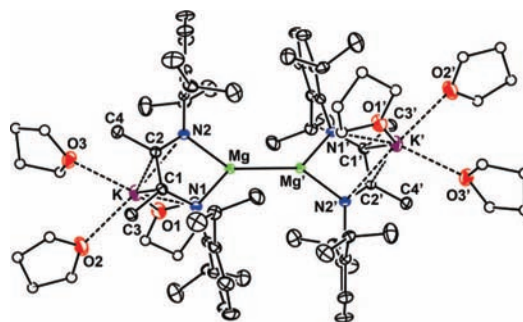
Figure 1. Molecular structure of **3** (thermal ellipsoids are set at the 30% probability level; for clarity, hydrogen atoms have been omitted and C atoms on THF drawn as smaller spheres). Selected bond lengths (Å) and angles (deg): Mg−Mg′, 2.9370(18); Mg−N1, 2.051(2); Mg−N2, 2.043(2); K−N1, 3.134(2); K−N2, 3.192(2); K−C1, 2.889(3); K−C2, 2.925(3); Mg···K, 3.7031(12); N1−Mg−N2, 81.47(9); N1−Mg−Mg′, 138.61(8); N2−Mg−Mg′, 139.30(8). Symmetry code (′): −x, 1 − y, −z.

the structures of the analogous dizinc compounds [M(THF)₂]₂[LZn−ZnL] previously reported by us [Zn−Zn bond lengths: 2.393(1) and 2.399(1) Å].[11,12] Each magnesium center is threefold-coordinated by one chelating ligand and the other Mg atom with a distorted trigonal planar geometry and slightly deviates from the C₂N₂ plane (by 0.155 Å). The dihedral angles of the aryl ring with the C₂N₂Mg metallocycle are 64.52 and 66.22°. As in the Zn−Zn-bonded compound [K(THF)₂]₂[LZn-ZnL], the two MgC₂N₂ metallocycles are nearly coplanar.

The observed Mg−Mg bond distance in **3** [2.9370(18) Å] is slightly longer than those in compounds **1** [2.8508(12) Å] and **2**

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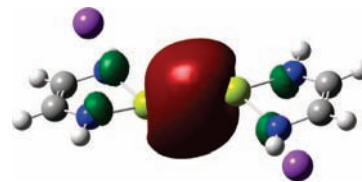§ Graduate School of the Chinese Academy of Sciences.

[2.8457(8) Å] mentioned above[8] but shorter than those in the adducts **2a–d** (3.056–3.196 Å).[10] However, theoretical studies gave a shorter Mg–Mg distance in the range 2.776–2.884 Å.[5,7,15] Similar to **1**, **2**, and **2a–d**, the possibility of the presence of hydride bridges between the two Mg atoms can be ruled out by the following evidence. First, in the ^{1}H NMR spectrum of **3**, there is no signal corresponding to the bridging hydrogen, which was located at 4.03 and 4.21 ppm for the hydride $[MgR^2(\mu\text{-}H)]_2$ and its THF adduct $[MgR^2(THF)(\mu\text{-}H)]_2$, respectively.[10] Second, there is no significant residual electron density between the Mg atoms in the difference map of the refinement. Interestingly, while the Mg heterocycles are close to orthogonal in the β-diketiminate compound **2**, they are nearly coplanar to each other in both the Mg–Mg-bonded adducts **2a–d** and the two magnesium(II) hydrides. This is also the case for compound **3** in this work.

As mentioned above, compound **3** bears a significant resemblance to the Zn analogues. The initial divalent Mg^{2+} ion is reduced to Mg^+ in the product, while the neutral ligand is reduced to the dianion L^{2-}, for whose negative charges a solvated K^+ ion further compensates.[11,12] The two $[K(THF)_3]^+$ units are also located over the five-membered metallocycles, with the K atom being η^4-bonded by the N–C=C–N moiety (Figure 1). The difference between **3** and the dizinc compound $[K(THF)_2]_2[LZn–ZnL]$ is that the K^+ ion is solvated by three THF molecules in **3**. Correspondingly, the K–C (2.907 Å), K–N (3.163 Å), and K–O (mean 2.739 Å) distances in **3** are significantly longer than those in the zinc compound (K–C, 2.902; K–N, 2.945; K–O, mean 2.674 Å) because of the larger steric repulsion in **3**.

Notably, the β-diketiminate compound **2** was found to readily undergo addition with Lewis bases such as THF to yield the adducts **2a–d**.[10] However, the α-diimine-ligated **3** did not show this tendency since it was isolated from THF with six solvent molecules coordinated to the two K^+ ions and two additional THF molecules accommodated in the crystal lattice. We have demonstrated previously that solvent can affect the solid-state aggregation of the product from the reduction of $ZnLCl_2$.[12] The solvent effect was also tested in this work; unfortunately, we have not isolated any product from other solvents to date. Nevertheless, we did obtain a mononuclear Mg(II) compound coordinated by three THF molecules, $MgL^{Mes}(THF)_3$ ($L^{Mes} = [(2,4,6\text{-}Me_3C_6H_2)NC(Me)]_2^{2-}$), in an attempt to construct an Mg–Mg bond by reduction of L^{Mes} with magnesium metal.[16]

DFT studies[17] of a model compound $K_2[(NHCH)_2Mg]_2$ (**3H**) were performed at the B3LYP/DZP level. The optimized structure is very close to that from the results of X-ray diffraction, and the theoretical Mg–Mg bond distance for **3H** (2.906 Å) agrees well with the experimental data for **3** (2.937 Å). The Wiberg bond index gave a Mg–Mg bond order of 0.87 for **3H**, which is comparable to the theoretical Mg–Mg bond order (0.91) for the known compound $\{Mg[(Ar'N)_2C(NMe_2)]\}_2$ (**1'**, $Ar' = 2,6\text{-}Me_2C_6H_3$).[8] The DFT-predicted bond dissociation energy, $E(Mg\text{–}Mg)$, of 41 kcal/mol for **3H** is similar to those calculated for $\{Mg_2[\eta^5\text{-}(BCO)_5]_2\}$,[6] $[HMgMgH]$,[18] and $[MeMgMgF]$[19] (43, 41, and 42 kcal/mol, respectively) but slightly smaller than the value of 45.4 kcal/mol for the Mg–Mg bond in $\{Mg[(HNCH)_2CH]\}_2$ (**2H**).

As shown in Figure 2, the HOMO–2 involves the Mg–Mg σ bond. The HOMO and HOMO–1 for **3H** (Figure S2 in the Supporting Information) are ligand-based orbitals. The LUMO is localized on the ligands with π symmetry, while the LUMO+2 is predominantly the metal–metal π bonding interaction. The Mg–Mg bond is formed mainly by the 2p and 3s orbitals, with 44.8% s, 55% p, and 0.2% d character, as revealed by natural bond orbital

Figure 2. The Mg–Mg bonding orbital (HOMO–2) of the model compound **3H**.

(NBO) analysis. This is different from the composition of the Mg–Mg bond in **1'**, which has mostly s character (93.2%).[8] The natural charges on the Mg and K atoms are +0.58 and +0.86, respectively, while the negative charges are delocalized over the ligand.

We have synthesized the Mg–Mg-bonded compound **3** by a facile one-pot potassium reduction of the α-diimine ligand L and $MgCl_2$. The dimagnesium(I) compound **3** contains dianionic ligands incorporating solvated K^+ ions. The Mg–Mg bonding was further confirmed by DFT studies.

Supporting Information Available: Experimental details, X-ray crystal structure analysis of **3** (CIF), and details concerning the DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Synthesis of **3**: Potassium (0.15 g, 3.91 mmol) was added to a mixture of L (0.50 g, 1.24 mmol) and $MgCl_2$ (0.14 g, 1.26 mmol) in THF, and the suspension was stirred for 3 days. The reaction mixture was filtered, and the filtrate was concentrated to ~30 mL and stored at ca. −20 °C for several days to yield **3** as pink crystals (0.45 g, 48%). ^{1}H NMR (400 MHz, C_6D_6): δ 1.10 (m, 24H, CH(CH_3)$_2$), 1.21 (m, 24H, CH(CH_3)$_2$), 1.40 (THF), 1.84 (s, 12H, CCH_3), 3.56 (THF), 3.90 (m, 8H, CH(CH$_3$)$_2$), 6.63 (m, 4H, *p*-ArH), 6.91 (m, 8 H, *m*-ArH).
(14) Crystal data for **3**: $C_{88}H_{144}N_4K_2O_8Mg_2$; triclinic; space group $P\bar{1}$; $a = 13.138(2)$ Å, $b = 13.301(2)$ Å, $c = 15.464(4)$ Å; $\alpha = 105.160(3)°$, $\beta = 100.332(3)°$, $\gamma = 115.281(2)°$; $V = 2223.4(8)$ Å^3; $D_{calcd} = 1.130$ g cm^{-3}; $Z = 1$; $\mu = 0.174$ mm^{-1}; 15644 reflections measured, 8600 unique ($R_{int} = 0.0365$), 5708 observed [$I > 2\sigma(I)$]; R1 = 0.0633, wR2 = 0.1723.
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