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Magnesium Borohydride Complexed by Tetramethylethylenediamine

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A complex of magnesium borohydride, $Mg(BH_4)_2 \cdot Me_2NC_2H_4NMe_2$, has been synthesized and structurally characterized. This monomer complex has a pseudotetrahedral geometry around the Mg atom with tridentate BH_4 groups and short $Mg \cdots B$ distances.

Magnesium borohydride $Mg(BH_4)_2$, containing 14.6% H, is of interest for hydrogen storage applications. So far, its crystal structure and enthalpy of formation have not been determined experimentally. Theoretical calculations based on first principles and analogy with known structures of $M(M'X_4)_2$ compounds have, so far, given contradictory results.[1,2] It is doubtful that a single crystal of $Mg(BH_4)_2$ can be grown because it decomposes before melting and crystallizes from solutions as a solvate. This means that the structure must be solved on the basis of powder diffraction data, which may not be sufficient to determine the H positions. Therefore, knowledge of crystal chemistry of magnesium borohydride complexes is very important for ultimately solving the crystal structure of the unsolvated product. Only a few crystal structures of $Mg(BH_4)_2$ solvates and complexes have been determined, including complexes with three donor atoms (O or N) bound to the Mg atom, $Mg(BH_4)_2 \cdot 3THF$ (THF = tetrahydrofuran),[3] $Mg(BH_4)_2 \cdot$diglyme,[4] $Mg(BH_4)_2 \cdot 3N^tBuH_2$, and $Mg(BH_4)_2 \cdot 3HNC_5H_2$,[5] and with four donor atoms, $[Mg(BH_4)_2 \cdot 4py] \cdot 2py$ (py = pyridine),[5] and the anionic complex $(PPh_4)_2[Mg(BH_4)_4]$.[6]

We now report the preparation of the first magnesium borohydride complex containing only two donor atoms coordinated to the Mg atom. The addition of tetramethylethylenediamine (TMEDA) to a solution of magnesium borohydride in diethyl ether yields slow precipitation of colorless crystals of the composition $Mg(BH_4)_2 \cdot Me_2NC_2H_4NMe_2$ (**1**; Figure 1). Its structure was studied by single-crystal X-ray diffraction.

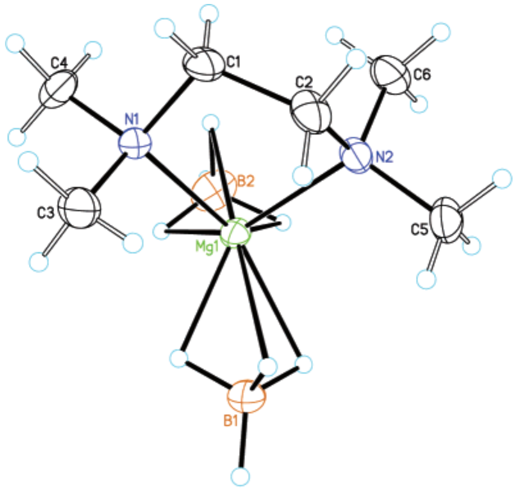

Figure 1. ORTEP plot of the ordered molecule of complex **1** with 40% probability thermal ellipsoids. Selected distances (Å): $Mg1 \cdots B1$ 2.299(2), $Mg1 \cdots B2$ 2.277(3), Mg1−N1 2.190(2), Mg1−N2 2.154(2), average Mg1−H 2.10(1), average $B-H^b$ 1.22(1), average $B-H^t$ 1.10(2). Selected angles (deg): B1−Mg1−B2 123.86(1), N1−Mg1−N2 84.19(6), H^b-B-H^b 112.4(10), H^b-B-H^t 106.1(10).

The Mg atom in **1** has a distorted pseudotetrahedral geometry $[N_2B_2]$. The Cr analogue of **1**, $Cr(BH_4)_2 \cdot Me_2NC_2H_4NMe_2$ (**2**), has a different geometry close to a distorted square plane.[7] The N−M−N angles are very similar in both complexes (84.2° for **1** and 84.3° for **2**) as are other parameters of the TMEDA molecule. However, the B−M−B angles are quite different: 121.1° for **1** and only 96.8° for **2**.[7] This can be explained by the different bonding modes of the BH_4 groups to the metal atom and also by the difference in the geometries of coordination polyhedra (pseudotetrahedral vs pseudo square planar). In **1**, the BH_4 groups are tridentate; i.e., the $Mg-H_3BH$ bonding involves three bridge H atoms from the same B atom M. In contrast, the BH_4 group

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is bidentate in **2** and other known magnesium borohydride solvates $Mg(BH_4)_2 \cdot nL$. In dimeric magnesium borohydride complexes of the general formula $[Mg(BH_4)(\mu\text{-}OR)L]_2$, where R = ^{i}Pr, ^{t}Bu, CH_2CMe_3, CEt_3, $SiMe_3$, Ph and L = OEt_2 and THF, in which the BH_4 group is tridentate and the Mg···B distance is within the range of 2.25−2.29 Å.[8] Increasing the solvation level, L:Mg, in these complexes to 2:1 yields the bidentate BH_4 groups with a typical M···B distance (2.45 Å).[8]

The Mg···B distance in solvates of magnesium borohydride with a tridentate BH_4 group is noticeably shorter (2.25−2.32 Å in **1** and complexes $[Mg(BH_4)(\mu\text{-}OR)L]_2$[8]) than that in solvates with bidentate BH_4 groups (2.4−2.55 Å depending on the ligand).[3−5] Such a strong correlation between the denticity of the BH_4 group and the M···B distance is well-known.[9] The Mg···B distance is slightly shorter in complexes with three O ligands (2.44 Å for the THF complex[3] and 2.40 Å for the diglyme complex[4]) than in complexes with three N ligands (2.52−2.55 Å for complexes with *tert*-butylamine and piperidine[5]). The increase of the number of donor ligands to four in the complex $[Mg(BH_4)_2 \cdot 4py] \cdot 2py$[5] increases the Mg···B distance even more (2.99 Å), but BH_4 groups are still bidentate with a much longer Mg−H distance (2.4 Å) than those in other magnesium borohydride complexes (1.97−2.14 Å). In the more sterically hindered Cr complex $Cr(BH_4)_2 \cdot 4py$ (average M−N distances of 2.13 Å vs 2.21 Å in the Mg analogue) causes transformation of the BH_4 group into a monodentate with Cr···B distances of 3.31 and 3.23 Å.[7] Increasing the basicity and the number of ligands pushes BH_4 groups out of the Mg coordination sphere. Thus, complexation of magnesium borohydride with benzylamine, a stronger base ($pK_a = 9.34$ vs 5.3 for pyridine), yields an ionic salt with $Mg(H_2NCH_2Ph)_6^{2+}$ cations and BH_4^- anions.[5] Similarly, an ionic character was also proposed for complex $Mg(BH_4)_2 \cdot 6NH_3$ (ammonia $pK_a = 9.25$).[10] The crystal structure of the ionic salt $(PPh_4)_2[Mg(BH_4)_4]$ (**3**) consist of PPh_4^+ cations and complex borohydride anions $[Mg(BH_4)_4]^{2-}$.[6] The Mg atom in **3** is located on the 2-fold axis and surrounded by two pairs of equivalent B atoms, which forms an almost regular tetrahedron. Authors suggested that BH_4 groups in **3** are different and have both bi- and tridentate bonding.[6] However, the Mg···B distances are almost equal (2.42 and 2.43 Å), and their lengths are close to the distance in complex $Mg(BH_4)_2 \cdot 3THF$ with bidentate BH_4 groups (2.44 Å). Because the refinement with geometrically defined positions of H atoms in ref 6 is not very reliable, it is concluded that both BH_4 groups in **3** are bidentate.

Three types of magnesium borohydride complexes are known so far: molecular mononuclear solvates $Mg(BH_4)_2 \cdot nL$ where $n = 2-4$, ionic complexes with magnesium MgL_6^{2+} cations, and ionic complexes with complex metal borohydride anions $[Mg(BH_4)_4]^{2-}$. The denticity of the BH_4 group increases from monodentate to bidentate to tridentate as the number of ligands decreases. Theoretical calculation of the $Mg(BH_4)_2$ molecular structure has shown that the tridentate configuration is the most stable in the gas phase.[11]

The principle of maximum coordination saturation and known crystal structures allow us to predict that the Mg atom in unsolvated magnesium borohydride should be coordinated with four BH_4 groups like in the $[Mg(BH_4)_4]^{2-}$ anion and with 8−12 H atoms (10 in structure **3**). Thus, the predicted structures of unsolvated $Mg(BH_4)_2$ with low Mg coordination numbers, like those based on the $Cd(AlCl_4)_2$ structure type with a MgH_6 polyhedron,[1] seem to be unlikely. Based on our analysis of the crystal chemistry of magnesium borohydride complexes, it seems plausible that at least a part of the BH_4 groups in unsolvated magnesium borohydride also should be tridentate (like in **3**) to spatially saturate the coordination sphere of the Mg atom. Magnesium borohydride is more covalent than ionic borohydrides like $NaBH_4$; however, its physical properties (low volatility and high melting point) indicate that it likely has a polymeric structure rather than a molecular structure common to other covalent borohydrides like $Al(BH_4)_3$[12] and $Zr(BH_4)_4$.[13] Therefore, in unsolvated magnesium borohydride, the BH_4 groups should bridge at least two Mg atoms to build a continuous structure like the polymeric structure of $Be(BH_4)_2$.[14] Similar bridging BH_4 groups with the bonding type $\mu{:}\eta^4\text{-}(\mu_3\text{-}H)_2B(\mu_2\text{-}H)_2$ that is tridentate to two Ce atoms were also found in the dimeric complex $[(C_5H_4{}^tBu)_2Ce(BH_4)]_2$.[15] Because of a strong influence of the ligand on the coordination mode of the BH_4 group, it would be very interesting to obtain a $Mg(BH_4)_2$ solvate with the ratio L:Mg < 1 that should contain a bridging BH_4 group. In this case, the information about the BH_4 coordination geometry would be directly transferable to the structure of the unsolvated $Mg(BH_4)_2$.

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Supporting Information Available: Crystallographic data for **1** in CIF format and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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