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Synthesis and Structure of a Magnesium Hydroxide Complex Supported by Tris(pyrazolyl)hydroborato Ligation, $\{[\mathrm{Tp}^{\mathrm{Ar,Me}}]\mathrm{Mg}(\mu\text{-OH})\}_2$ (Ar = p-$\mathrm{Bu^tC_6H_4}$)

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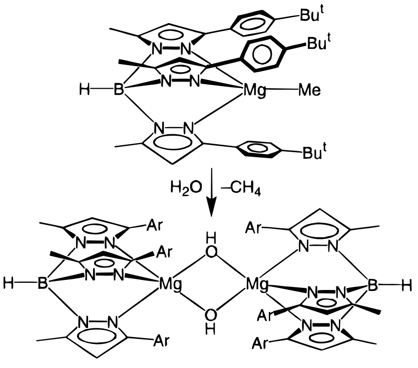
Metal-bound hydroxides participate in some important transformations in biological systems. Although zinc is perhaps the most prevalent metal to utilize the [M−OH] functionality, as exemplified by its role in carbonic anhydrase,[1] other metals also employ hydroxide groups in their mechanisms of action. For example, a [Pb−OH] moiety has been proposed to partake in the Pb(II)-catalyzed cleavage of the sugar−phosphate backbone in yeast $\mathrm{tRNA^{Phe}}$,[2] while the [Mg−OH] moiety has been proposed to be involved in (i) ribozyme cleavage reactions[3] and (ii) the enolase-catalyzed dehydration of 2-phospho-D-glycerate to phosphoenolpyruvate.[4] With regard to the [Zn−OH] functionality, considerable attention has been given to the synthesis of monomeric zinc hydroxide complexes in attempts to model the active sites of zinc enzymes such as carbonic anhydrase. For example, tris(imidazolyl)phosphine and tris(pyrazolyl)hydroborato ligation allows isolation of the cationic and neutral complexes $\{[\mathrm{Pim^{Pr^iBu^t}}]\mathrm{ZnOH}\}(\mathrm{ClO_4})$[5,6] and $[\mathrm{Tp^{RR'}}]\mathrm{ZnOH}$,[7−10] respectively. As an extension of these studies, we chose to investigate the chemistry of the [Mg−OH] moiety in order to compare the reactivities of pre- and post-transition metal hydroxide moieties supported by a common ligand environment. Such comparisons are relevant in view of recent theoretical calculations which suggest that magnesium-substituted carbonic anhydrase may not have substantial activity.[11−13] Accordingly, in order to achieve the above objective, we have explored the use of tris(pyrazolyl)hydroborato ligation to prepare well-defined molecular magnesium hydroxide complexes. In this paper we describe the synthesis and structural characterization of $\{[\mathrm{Tp^{Ar,Me}}]\mathrm{Mg}(\mu\text{-OH})\}_2$ (Ar = p-$\mathrm{Bu^tC_6H_4}$).

Scheme 1



Structurally-characterized magnesium complexes with well-defined [Mg−OH] functionalities are, to our knowledge, unknown. Indeed, even though complexes with magnesium−oxygen bonds are common, the vast majority contain dative covalent[14] $[\mathrm{Mg} \leftarrow \mathrm{O} \leftrightarrow \mathrm{Mg^-}{-}\mathrm{O^+}]$ rather than normal covalent [Mg−O] bonds.[15] In view of the demonstrated ability of tris(pyrazolyl)hydroborato ligation to support the zinc hydroxide complexes $[\mathrm{Tp^{RR'}}]\mathrm{ZnOH}$,[7−10] we rationalized that analogous magnesium complexes should also be isolable. However, although $[\mathrm{Tp^{RR'}}]\mathrm{ZnOH}$ complexes have been prepared by several methods, including (i) the reaction of $[\mathrm{Tp^{RR'}}]\mathrm{ZnX}$ with $\mathrm{OH^-}$ [8,10] and (ii) the reaction of $\mathrm{K[Tp^{RR'}]}$ with $\mathrm{Zn(ClO_4)_2{\cdot}6H_2O}$ in the presence of KOH,[7,9] it is our experience that the magnesium counterparts are not obtained by such procedures. Consequently, we have explored alternative synthetic methods to generate the magnesium hydroxide moiety under milder conditions, and, in particular, a method based on the hydrolytic cleavage of magnesium−alkyl bonds.

Our initial attempts centered on the synthesis of $[\mathrm{Tp^{Bu^t,Me}}]\mathrm{MgOH}$, for which the zinc analogue is known.[7] Unfortunately, although the methyl derivative $[\mathrm{Tp^{Bu^t,Me}}]\mathrm{MgMe}$ did indeed react with $\mathrm{H_2O}$ to eliminate methane, the $[\mathrm{Tp^{Bu^t,Me}}]$ ligand was also cleaved from the magnesium center under such conditions. Therefore, in an effort to stabilize the magnesium hydroxide moiety, we explored the use of different tris(pyrazolyl)hydroborato ligands. Significantly, we found that a stable magnesium hydroxide complex could be obtained by the use of the *p*-*tert*-butylphenyl derivative $[\mathrm{Tp^{Ar,Me}}]$ (Ar = p-$\mathrm{Bu^tC_6H_4}$), a ligand that is related to $[\mathrm{Tp^{Bu^t,Me}}]$ by incorporation of a *p*-phenylene spacer between the pyrazolyl and *tert*-butyl groups.

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(1) Bertini, I.; Luchinat, C. In *Bioinorganic Chemistry*; Bertini, I., Gray, H. B., Lippard, S. J., Valentine, J., Eds.; University Science Books: Mill Valley, CA, 1994.

(2) Brown, R. S.; Hingerty, B. E.; Dewan, J. C.; Klug, A. *Nature* **1983**, *303*, 543−546.

(3) (a) Scott, W. G.; Finch, J. T.; Klug, A. *Cell* **1995**, *81*, 991−1002. (b) Uebayasi, M.; Uchimaru, T.; Koguma, T.; Sawata, S.; Shimayama, T.; Taira, K. *J. Org. Chem.* **1994**, *59*, 7414−7420. (c) Dahm, S. C.; Derrick, W. B.; Uhlenbeck, O. C. *Biochemistry* **1993**, *32*, 13040−13045. (d) Pley, H. W.; Flaherty, K. M.; McKay, D. B. *Nature* **1994**, *372*, 68−74. (e) Pyle, A. M. *Science* **1993**, *261*, 709−714.

(4) (a) Wedekind, J. E.; Reed, G. H.; Rayment, I. *Biochemistry* **1995**, *34*, 4325−4330. (b) Lebioda, L; Stec, B. *Biochemistry* **1991**, *30*, 2817−2822.

(5) Kimblin, C.; Allen, W. E.; Parkin, G. *J. Chem. Soc., Chem. Commun.* **1995**, 1813−1815.

(6) Abbreviations: tris(2-imidazolyl)phosphines are represented by the abbreviation $[\mathrm{Pim^{R,R'}}]$, with the 1- and 4-alkyl substituents listed respectively as superscripts; tris(1-pyrazolyl)hydroborato ligands are represented by the abbreviation $[\mathrm{Tp^{RR'}}]$, with the 3- and 5-alkyl substituents listed respectively as superscripts.

(7) Alsfasser, R.; Trofimenko, S.; Looney, A.; Parkin, G.; Vahrenkamp, H. *Inorg. Chem.* **1991**, *30*, 4098−4100.

(8) Looney, A.; Han, R.; McNeill, K.; Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 4690−4697.

(9) (a) Ruf, M.; Weis, K.; Vahrenkamp, H. *J. Chem. Soc., Chem. Commun.* **1994**, 135−136. (b) Alsfasser, R.; Ruf, M.; Trofimenko, S.; Vahrenkamp, H. *Chem. Ber.* **1993**, *126*, 703−710.

(10) Kitajima, N.; Hikichi, S.; Tananka, M.; Moro-oka, Y. *J. Am. Chem. Soc.* **1993**, *115*, 5496−5508.

(11) Sola, M.; Mestres J.; Duran, M.; Carbó R. *J. Chem. Inf. Comput. Sci.* **1994**, *34*, 1047−1053.

(12) For further theoretical comparisons of $[\mathrm{Mg{-}OH}]^+$ and $[\mathrm{Zn{-}OH}]^+$, see: Sola, M.; Lledos, A.; Duran, M.; Bertrán, J. *Theor. Chim. Acta* **1992**, *81*, 303−318.

(13) In contrast, however, $\mathrm{Mg^{2+}}$ ions have in fact been reported to a have a mild stimulatory effect on the native enzyme,[13a] thereby contradicting an earlier report which proposed that $\mathrm{Mg^{2+}}$ ions inhibit carbonic anhydrase activity.[13b] (a) Porter, M. A.; Grodzinski, B. *Plant Physiol.* **1983**, *72*, 604−605. (b) Bamberger, E. S.; Avron, M. *Plant Physiol.* **1975**, *56*, 481−485.

(14) Haaland, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 992−1007.

(15) (a) Holloway, C. E.; Melnik, M. *J. Organomet. Chem.* **1994**, *465*, 1−63. (b) Bock, C. W.; Kaufman, A.; Glusker, J. P. *Inorg. Chem.* **1994**, *33*, 419−427.

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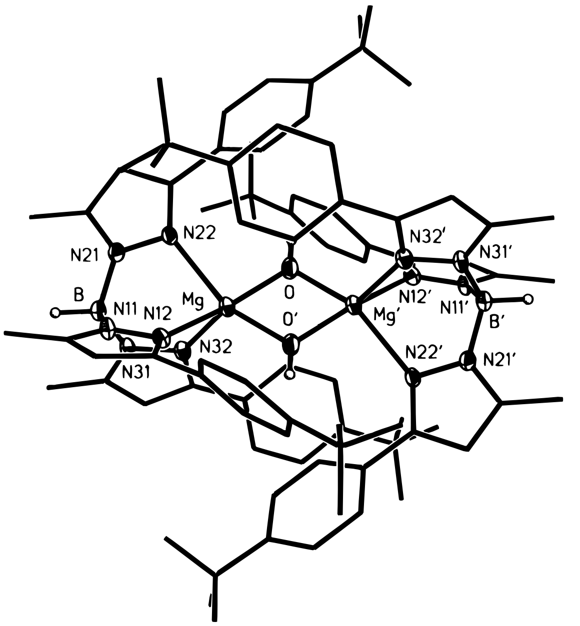

Figure 1. Molecular structure of {[Tp^{Ar,Me}]Mg(μ-OH)}$_2$.

Thus, the magnesium hydroxide complex {[Tp^{Ar,Me}]Mg(μ-OH)}$_2$ may be synthesized by the reaction of the methyl derivative [Tp^{Ar,Me}]MgMe with H_2O in pentane (Scheme 1).[16,17] However, {[Tp^{Ar,Me}]Mg(μ-OH)}$_2$ is unstable in the presence of water, and care must therefore be taken to minimize the presence of excess water in the synthesis. The hydroxide moiety of {[Tp^{Ar,Me}]Mg(μ-OH)}$_2$ is characterized by a ν(^{16}O−H) absorption at 3727 cm^{-1} in the IR spectrum [ν(^{18}O−H) = 3715 cm^{-1}; ν(^{16}O−D) = 2743 cm^{-1}] and signals at δ −0.35 and 23 ppm in the ^{1}H and ^{17}O NMR spectra, respectively.

The molecular structure of {[Tp^{Ar,Me}]Mg(μ-OH)}$_2$ has been determined by X-ray diffraction (Figure 1), demonstrating that the complex exists as a hydroxide-bridged dimer in the solid state. The dimeric nature of {[Tp^{Ar,Me}]Mg(μ-OH)}$_2$ is in marked contrast to the monomeric structure of the related zinc complex [Tp$^{Bu^t,Me}$]ZnOH,[7,18] as discussed below.[19] Although we are unaware of any structurally-characterized simple magnesium hydroxide complexes,[20] the dinuclear [Mg_2O_2] core is precedented for alkoxide and related derivatives.[21,22] The Mg−OH bond lengths [1.955(5) and 1.951(6) Å] in {[Tp^{Ar,Me}]Mg(μ-OH)}$_2$ are considerably shorter than the mean value of 2.061(3) Å observed for the Mg−OH_2 bond in aqua derivatives listed in the Cambridge Structural Database[23] but are comparable to the values in the related alkoxide complexes (1.91−1.96 Å).[21]

It is of some interest to consider the factors responsible for {[Tp^{Ar,Me}]Mg(μ-OH)}$_2$ adopting a hydroxy-bridged dinuclear structure in contrast to the monomeric structures observed for the zinc analogues [Tp$^{RR'}$]ZnOH. In this regard, it is useful to compare the structure of {[Tp^{Ar,Me}]Mg(μ-OH)}$_2$ with those of related zinc hydroxide complexes containing [Zn_2O_2] moieties.[24] On the basis of their difference in covalent radii (Mg = 1.36 Å and Zn = 1.25 Å),[25] a bond to magnesium would be anticipated to be *ca.* 0.11 Å longer than the corresponding bond to zinc. For example, the Mg−C and Zn−C bond lengths in isostructural [Tp$^{Bu^t}$]MgMe [2.118(11) Å][26] and [Tp$^{Bu^t}$]ZnMe [1.971(4) Å][27] differ by *ca.* 0.15 Å. However, the average Mg−O bond length [1.953(2) Å] in {[Tp^{Ar,Me}]Mg(μ-OH)}$_2$ actually falls within the range observed for Zn−O bond lengths in related complexes with [Zn_2O_2] cores[24] and is certainly not significantly longer. It is, therefore, evident that the Mg−O bond lengths in {[Tp^{Ar,Me}]Mg(μ-OH)}$_2$ are shorter than would be anticipated by comparison with related zinc complexes, an observation that is indicative of the ability of magnesium to form particularly strong bonds to oxygen.[28] The adoption of a hydroxy-bridged structure for {[Tp^{Ar,Me}]Mg(μ-OH)}$_2$ is thus in accord with the greater electronegativity and hardness of Mg^{2+} *versus* Zn^{2+},[29] and also the tendency for magnesium to adopt a higher coordination number than that for zinc.[30] Indeed, the fact that {[Tp^{Ar,Me}]Mg(μ-OH)}$_2$ exists as a dimer in spite of the sterically demanding nature of the [Tp^{Ar,Me}] ligand indicates that there is evidently a strong driving force for the magnesium hydroxide moiety to bridge.

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Supporting Information Available: Text giving preparative and X-ray experimental details, elemental analyses, and IR data, tables of NMR data, crystal data, intensity collection parameters, atomic coordinates, bond lengths, bond angles, and thermal parameters, and figures showing two ORTEP views of {[Tp^{Ar,Me}]Mg(μ-OH)}$_2$ (13 pages). Ordering information is given on any current masthead page.

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(16) See Supporting Information.

(17) The related symmetrically disubstituted ligand [Tp^{Ar_2}] (Ar = *p*-Bu^{t}C$_6$H$_4$) has been recently reported. See: Libertini, M.; Yoon, K.; Parkin, G. *Polyhedron* **1993**, *12*, 2539−2542.

(18) Furthermore, although [Tp$^{Pr^i_2}$]ZnOH and [Tp$^{Ar',Me}$]ZnOH (Ar′ = *p*-C$_6$H$_4$Pr^i) have not been structurally-characterized, the complexes have been represented as monomeric species. See refs 9 and 10.

(19) Related dimeric structures have been reported for tris(pyrazolyl)hydroborato derivatives of the transition metals. See ref 10.

(20) Complexes with hydroxide bridges between magnesium and transition metals have been reported: [Mg(μ-OH)$_2$Co(en)$_2$]$^{5+}$ (d_{Mg-O} = 2.07 Å)[20a] and [Mg(μ-OH)$_2$MA$_4$]$^{5+}$, where A$_4$ = (NH$_3$)$_4$, (en)$_2$, or bispictn.[20b] (a) Müller, S.; Thewalt, U. *Z. Naturforsch.* **1989**, *44B*, 257−260. (b) Hodgson, D. J.; Michelsen, K.; Pedersen, E.; Towle, D. K. *J. Chem. Soc., Chem. Commun.* **1988**, 426−428.

(21) (a) Her, T.-Y.; Chang, C.-C.; Lee, G.-H.; Peng, S.-M.; Wang, Y. *Inorg. Chem.* **1994**. *33*, 99−104. (b) Calabrese, J.; Cushing, M. A., Jr.; Ittel, S. D. *Inorg. Chem.* **1988**, *27*, 867−870. (c) Chang C.-C.; Lee, W.-H.; Her, T.-Y.; Lee, G.-H.; Peng, S.-M.; Wang. Y. *J. Chem. Soc., Dalton Trans.* **1994**, 315−322. (d) Williard, P. G.; Salvino, J. M. *J. Chem. Soc., Chem. Commun.* **1986**, 153−154. (e) Bell, N. A.; Moseley, P. T.; Shearer, H. M. M. *Acta Crystallogr.* **1984**, *C40*, 602−604.

(22) Two other complexes with [Mg$_2$O$_2$] cores include [Mg(μ-acen)]$_2$[22a] and Mg$_2$Sb$_4$(OEt)$_{16}$.[22b] (a) Corazza, F.; Floriani, C.; Chiesi-Villa, A.; Guastini, C.; Ciurli, S. *J. Chem. Soc., Dalton Trans.* **1988**, 2341−2345. (b) Bemm, U.; Lashgari, K.; Norrestam, R.; Nygren, M. *J. Solid State Chem.* **1993**, *103*, 366−374.

(23) For examples, see ref 15.

(24) (a) Al-Juaid, S. S.; Buttrus, N. H.; Eaborn, C.; Hitchcock, P. B.; Roberts, A. T. L.; Smith, J. D.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1986**, 908−909. (b) Chaudhuri, P.; Stockheim, C.; Wieghardt, K.; Deck, W.; Gregorzik, R.; Vahrenkamp, H.; Nuber, B.; Wiess, J. *Inorg. Chem.* **1992**, *31*, 1451−1457. (c) Murthy, N. N.; Karlin, K. D. *J. Chem. Soc., Chem. Commun.* **1993**, 1236−1238. (d) Bazzicalupi, C.; Bencini, A.; Bianchi, A.; Fusi, V.; Paoletti, P.; Valtancoli, B. *J. Chem. Soc., Chem. Commun.* **1994**, 881−882. (e) Arif, A. M.; Cowley, A. H.; Jones, R. A.; Koschmieder, S. U. *J. Chem. Soc., Chem. Commun.* **1987**, 1319−1320.

(25) Pauling, L. *The Nature of The Chemical Bond,* 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 256.

(26) Han, R.; Parkin, G. *Organometallics* **1991**, *10*, 1010−1020.

(27) Yoon, K.; Parkin, G. *J. Am. Chem. Soc.* **1991**, *113*, 8414−8418.

(28) For example, the bond energies of the diatomic molecules MgO and ZnO are 86.6 and 38.0 kcal mol^{-1}, respectively. See: *CRC Handbook of Chemistry and Physics*, 76th ed.; Lide, D. R., Editior-in-Chief; CRC Press: New York, 1995−1996.

(29) Pearson, R. G. *Coord. Chem. Rev.* **1990**, *100*, 403−425.

(30) Brown, I. D. *Acta Crystallogr.* **1988**, *B44*, 545−553.