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From Monomers to Solids: Controlled Hydrolysis To Form Novel, Heteroleptic Hydroxide-Containing Complexes

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Four novel alkaline earth metal tetranuclear aryloxide/pyrazolate hydroxides of the general formula $M_4(\text{ligand})_6(OH)_2(\text{donor})_n$ have been prepared by either adding stoichiometric quantities of water to preformed alkaline earth metal aryloxides or in a direct metalation regime combining metal, ligand (alcohol, pyrazole), and donor with stoichiometric amounts of water. The compounds are considered as potential intermediates in the sol–gel process. A nonhydrolyzable magnesium aryloxide has also been obtained using the same reaction scheme. Unexpectedly, a dimeric strontium complex with further association of a second dimer via hydrogen bonding from the solvent of crystallization, ethylenediamine, has been isolated by the treatment of strontium metal with a mixture of alcohol and water. All compounds were characterized using X-ray crystallography, ^1H and ^{13}C NMR, and IR spectroscopy.

Introduction

The hydrolysis of molecular precursors is used extensively to produce technically important oxide- or hydroxide-based materials. Perhaps one of the best-known applications is the controlled hydrolysis of organoaluminum species to produce alkyl-substituted aluminoxanes and methylaluminoxane. These species are key ingredients as catalysts[1] and highly active cocatalysts[2] in polymerization reactions. As a result, extensive studies were aimed toward the further characterization of the active species.[3,4]

The hydrolysis of molecular alkaline earth metal derivatives is a well-established technique for the preparation of oxide materials, central components in the preparation of the ferroelectric ceramics $MTiO_3$ (M = Ca, Sr, Ba),[5] and related solids.[6] While the molecular precursors and the final hydrolysis products are typically well characterized, little information exists as to the details of the intermediate species formed in the process. We here aim to shed light on this topic by adding stoichiometric amounts of water to well-defined molecular compounds with the intention to isolate the intermediate products. Alternatively, the introduction of stoichiometric amounts of ligand and water in direct metalation procedures is also evaluated.

We here report four hydroxide-containing alkaline earth metal tetranuclear species including $[Mg_2(OMes)(\mu\text{-}OMes)_2(OH)(THF)_2]_2\cdot 2THF$ (**1**; MesOH = 2,4,6-trimethylphenol), $[Ca_2(OMes)(\mu\text{-}OMes)_2(OH)(THF)_3]_2\cdot 3THF$ (**2**), $[Ca_2(OMes)(\mu\text{-}OMes)_2(OH)(en)_2]_2\cdot 2PhMe$ (**3**; en = ethylenediamine) and $[Ca_2(\eta^2\text{-}{}^tBu_2Pz)(\mu\text{-}\eta^1{:}\eta^2\text{-}{}^tBu_2Pz)(\mu\text{-}\eta^2{:}\eta^4\text{-}{}^tBu_2Pz)(OH)(THF)]_2$ (**4**; ${}^tBu_2Pz$ = 3,5-di-*tert*-butylpyrazole). All compounds exhibit closely related structural geometry, with four metal centers, six ligands, and two hydroxide functions, suggesting the significant stability of this particular system.

Only a few examples of well-defined alkaline earth metal hydroxides are known, likely a consequence of the high charge/size ratio of the hydroxide moiety, the associated

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tendency toward aggregation, and the subsequent low solubility of the resulting products. Among the few discrete alkaline earth metal hydroxides, the dimeric magnesium species $[(\mathrm{Tp}^{\mathrm{Ar,Me}})\mathrm{Mg}(\mu\text{-OH})]_2$ [Tp = tris(pyrazolyl)hydroborate; Ar = p-${}^t\mathrm{BuC_6H_4}$] stands out. The compound was obtained by treating $(\mathrm{Tp}^{\mathrm{Ar,Me}})\mathrm{MgMe}$ with 1 equiv of water.[7] Clearly, the dimeric formulation of this compound was made possible by the presence of the bulky multidentate ligand. Likewise, almost all other discrete hydroxides contain multidentate ligands, as demonstrated in $[\mathrm{Mg\{HC(MeCNC_6H_3}{}^i\text{-}\mathrm{Pr_2\text{-}2,6)_2\}}(\mu\text{-OH})(\mathrm{THF})]_2\cdot 4\mathrm{THF}$,[8a] $\{[\mathrm{MgOH}][(\mu\text{-S})(\mu\text{-N}{}^t\mathrm{Bu})\mathrm{P}(\mathrm{NH}{}^t\mathrm{Bu})_2]\}_6$,[8b] and the strontium compound $[\{\mathrm{OC_6H_2}{}^t\mathrm{Bu_2\text{-}CHN(CH_2)_2NH_2}\}\mathrm{Sr}(\mu_3\text{-salean}{}^t\mathrm{BuH_2})\mathrm{Sr}(\mu_3\text{-OH})]_2$ [salean-${}^t\mathrm{BuH_4}$ = N,N'-bis(3,5-di-*tert*-butyl-2-hydroxybenzyl)ethylenediamine].[8c] In the absence of multidentate ligands, higher aggregates are often nonhomogeneous and insoluble. Lower aggregates are frequently stabilized by extensive secondary interactions, including hydrogen bonding as seen in $[\mathrm{Li\{Ca_7}(\mu^3\text{-OH})_8\mathrm{I_6(THF)_{12}\}_2}(\mu^2\text{-I})]\cdot 3\mathrm{THF}$, $[\mathrm{Sr_3I_3(OH)_2(THF)_9}]\mathrm{I}$,[9] and $[\mathrm{Ba(OH)I(H_2O)_4}]$.[10] Well-defined heterobimetallic alkoxide hydroxides containing zirconium in addition to a heavy alkaline earth metal of the general formula $[\mathrm{MZr(OH)(O}{}^i\mathrm{Pr)_5(}{}^i\mathrm{PrOH)_3}]_2$ (M = Sr, Ba) display the same tetranuclear core as complexes **1**−**4**.[11]

In addition to compounds **1**−**4**, we also report on a dimeric strontium aqua complex $[\{\mathrm{Sr_2(OMes)_2}(\mu\text{-OMes})_2(\eta^2\text{-en})_3(\eta^1\text{-en})(\mathrm{H_2O})\}_2(\mu\text{-en})]\cdot 3\mathrm{en}$ (**5**), obtained by treating ethylenediamine-activated strontium with an alcohol/water mixture. In here, two strontium dimers are associated via hydrogen bonding between the metal-bound water and the solvent of crystallization ethylenediamine. As a point of reference, we also include the monomeric aryloxide $\mathrm{Mg(PMDTA)(OMes)_2}$ (**6**; PMDTA = N,N,N',N'',N''-pentamethyldiethylenetriamine), where the addition of water, even under reflux conditions, did not result in hydrolysis.

Experimental Section

General Procedures. All reactions were performed under a purified nitrogen atmosphere by using either modified Schlenk techniques and/or a Braun Labmaster 100 drybox. Tetrahydrofuran (THF), toluene, 1,2-dimethoxyethane (DME), and n-hexane were distilled prior to use from a Na/K alloy and freshly degassed using two freeze−pump−thaw cycles. $({}^{n/sec}\mathrm{Bu})_2\mathrm{Mg}$ (1 M solution in heptane) was obtained commercially and used as received. Calcium and strontium metal (+99.9%, distilled ingots) were purchased and stored in the drybox. Commercial ethylenediamine, TMEDA, and N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDTA) were stirred over $\mathrm{CaH_2}$ and distilled prior to use. Ammonia was dried over Na(s) and condensed into the cooled [−78 °C, acetone/$\mathrm{CO_2}$(s)] reaction mixture. HOMes was obtained commercially and used after drying under vacuum. $\mathrm{H}{}^t\mathrm{Bu_2pz}$ was prepared according to literature procedures.[12] $\mathrm{Mg(THF)}_n\mathrm{(OMes)_2}$ was prepared in analogy to the related $\mathrm{Mg(donor)}_n\mathrm{(OMes)_2}$, $\mathrm{Mg(donor)}_n(\mathrm{O\text{-}2,6\text{-}}{}^t\mathrm{Bu_2C_6H_3})_2$, and $\mathrm{Mg(donor)}_n(\mathrm{O\text{-}2,6\text{-}}{}^i\mathrm{Pr_2C_6H_3})_2$.[13,14] The purity of all starting materials and reaction products was determined by ^{1}H NMR spectroscopy, and clean spectra with correct integration were obtained in all cases. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) were recorded on a Bruker DPX-300 spectrometer at 25 °C and referenced to the residual solvent signals. IR spectra were recorded as Nujol mulls between KBr plates on a Perkin-Elmer PE 1600 FT-IR spectrometer. Reliable elemental analyses could not be obtained due to the high oxygen sensitivity of the compounds reported. This is a well-known problem in alkaline earth metal chemistry.[15]

Synthesis of $[\mathrm{Mg_2(OMes)}(\mu\text{-OMes})_2\mathrm{(OH)(THF)_2}]_2\cdot 2\mathrm{THF}$ (1). Compound **1** was obtained using two different synthetic routes. Route *a* involves the treatment of $\mathrm{Mg(THF)}_n\mathrm{(OMes)_2}$ with freshly formed $\mathrm{Mg(THF)}_n\mathrm{(OH)_2}$ in a ratio of 3:1. Route *b* entails the addition of water to preformed $\mathrm{Mg(THF)}_n\mathrm{(OMes)_2}$.

Route a. Preparation of $\mathrm{Mg(OMes)_2}$. A total of 1.36 g (10 mmol) of HOMes was dissolved in 40 mL of THF, and the resulting solution was cooled to −78 °C [acetone/$\mathrm{CO_2}$(s)]. A total of 5 mL of a 1 M $({}^{n/sec}\mathrm{Bu})_2\mathrm{Mg}$ solution (5 mmol, in heptane) was added via syringe. The solution was stirred for 1 h. **Preparation of $\mathrm{Mg(OH)_2}$.** A total of 30 mL of THF was placed in a flask, followed by the addition of 1.7 mL of a 1 M $({}^{n/sec}\mathrm{Bu})_2\mathrm{Mg}$ solution (1.67 mmol, in heptane) and 0.06 g (3.33 mmol) of water (stock solution in THF with a known concentration) at −78 °C [acetone/ $\mathrm{CO_2}$(s)]. Mixture was stirred for 1 h. The $\mathrm{Mg(OMes)_2}$ solution (−78 °C) was combined with the freshly prepared hydroxide solution, and the mixture was slowly warmed to ambient temperature and filtered through a Celite-padded filter frit. The colorless, clear solution was stored at −20 °C. Colorless crystals suitable for X-ray crystallographic studies were obtained within 1 week. Yield: 1.71 g, 0.79 mmol, 79.6%. Introduction of different stoichiometric amounts of water by applying ligand/water ratios of 2:1 and 4:1 [1.36 g (10 mmol) of HOMes, 0.09 g (5 mmol) of water and (1.36 g (10 mmol) of HOMes, 0.045 g (2.5 mmol) of water] all resulted in the formation of **1**.

Route b. A total of 0.68 g (5 mmol) of HOMes was dissolved in 40 mL of hexane, and the resulting solution was cooled to −78 °C [acetone/$\mathrm{CO_2}$(s)]. A total of 3.3 mL of a 1 M $({}^{n/sec}\mathrm{Bu})_2\mathrm{Mg}$ solution (3.33 mmol, in heptane) was added via syringe. A white, cloudy solution formed immediately. The suspension was stirred for 30 min, followed by the addition of 10 mL of THF, upon which most of the solid dissolved. The resulting turbid solution was stirred for 2 h more at −78 °C, followed by the addition of 0.03 g (1.7 mmol) of water by means of a THF stock solution with a known water concentration. The suspension was then stirred for an additional hour more and warmed gradually to room temperature, affording an almost clear solution. After filtration through a Celite-padded filter frit, the colorless solution was stored at −20 °C. Colorless crystals formed within 1 week. Yield: 1.79 g, 0.82 mmol, 82.5%.

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Analytical data for crystals obtained by procedures a and b are identical. Mp: >330 °C (dec).

^{1}H NMR (THF-d_8): δ (ppm) 6.68 (12 H, *m*-H), 3.99 (s, br, 2 H, OH), 2.14 (s, 18 H, *p*-Me), 1.99 (s, 36 H, *o*-Me).

^{13}C NMR (THF-d_8): δ (ppm) 14.69, 19.71, 24.29, 66.38, 128.33.

IR (cm^{-1}): 3521 (br, w), 2924 (s), 2854 (s), 2728 (w), 1466 (s), 1376 (m), 1326 (m), 1308 (m), 1280 (w), 1243 (s), 1194 (w), 1153 (m), 1072 (w), 1030 (m), 955 (w), 881 (w), 851 (m), 832 (w), 800 (m), 751 (w), 722 (w), 681 (w).

Synthesis of $[Ca_2(OMes)(\mu\text{-}OMes)_2(OH)(THF)_3]_2\cdot 3THF$ (2). Compound **2** was prepared by direct metalation using ammonia-activated calcium. Initially obtained inadvertently, the rational synthesis below afforded the pure compound in high yield and purity. The identity and bulk purity of the rationally prepared compound **2** was confirmed by powder X-ray diffraction. The powder pattern matched exactly the calculated peaks from the single-crystal analysis. A total of 0.16 g of calcium (4 mmol), 0.82 g of HOMes (6 mmol), and 30 mL of THF were placed in a flask. After the flask was cooled to −78 °C, about 30 mL of anhydrous ammonia was condensed onto the mixture. The reaction was refluxed for about 2 h (dry ice condenser) followed by dropwise addition of 0.036 g (2 mmol) of water. The reaction was stirred overnight at low temperature. The ammonia was removed upon warming of the mixture to ambient temperature and filtered through a Celite-padded filter frit. Colorless crystals suitable for X-ray crystallographic studies were formed within 1 day at −20 °C. Yield: 1.29 g, 78.4%. Mp: >230 °C (dec).

^{1}H NMR (C_6D_6): δ (ppm) 6.70 (12 H, *m*-H), 4.57 (s, 2 H, OH), 3.56 (m, 72 H, THF), 2.14 (s, 18 H, *p*-Me), 2.05 (s, 36 H, *o*-Me), 1.40 (m, 72 H, THF).

^{13}C NMR (C_6D_6): δ (ppm) 16.68, 21.42, 26.61, 68.68, 123.80, 130.35, 131.66, 138.75.

IR (cm^{-1}): 3625 (br, w), 2950 (s), 2922 (s), 2851 (s), 2728 (w), 2684 (w), 1462 (m), 1457 (m), 1377 (m), 1327 (w), 1307 (w), 1259 (w), 1193 (w), 1154 (w), 1092 (w), 1075 (w), 1054 (w), 955 (w), 916 (w), 874 (w), 855 (w), 798 (w), 763 (w), 748 (w), 723 (w), 673 (w).

Synthesis of $[Ca_2(OMes)(\mu\text{-}OMes)_2(OH)(en)_2]_2\cdot 2PhMe$ (3). Compound **3** was prepared by direct metalation from ethylenediamine (en)-activated calcium. A total of 5 mL of dry ethylenediamine was added to 0.16 g (4 mmol) of calcium, and the resulting solution was stirred for 2 h. A total of 0.82 g (6 mmol) of HOMes was dissolved in 40 mL of toluene containing 0.036 g (2 mmol) of water (addition of a stock solution of toluene with a known concentration). The alcohol/water mixture was combined with the solution containing the activated calcium. The resulting solution was refluxed for 24 h until the metal was consumed, followed by filtration through a Celite-padded filter frit. Crystals suitable for X-ray crystallographic studies were obtained within 1 day at 10 °C. Yield: 1.31 g, 0.92 mmol, 91.6%, based on HOMes. Mp: >295 °C (dec).

^{1}H NMR (C_6D_6): δ (ppm) 6.92 (s, 17 H, *m*-H and Me-Toluene), 2.41, 2.25 (d, 120 H, CH_2-en), 2.32 (s, 3 H, Me-Toluene), 2.25 (s, 18 H, *p*-Me), 1.91 (s, 36 H, *o*-Me), 1.32 (s, br, 2 H, OH), 0.77 (s, 120 H, NH).

^{13}C NMR (C_6D_6): δ (ppm) 17.64, 21.09, 43.16, 124.38, 126.04, 129.68, 129.97.

IR (cm^{-1}): 3850 (w), 3747 (w), 3666 (w), 2918 (s), 2724 (m), 1942 (w), 1732 (w), 1699 (w), 1683 (w), 1652 (w), 1605 (m), 1558 (w), 1454 (s), 1375 (s), 1298 (s), 1198 (m), 1067 (m), 985 (s), 852 (m).

Synthesis of $[Ca_2(\eta^2\text{-}{}^tBu_2Pz)(\mu\text{-}\eta^1{:}\eta^2\text{-}{}^tBu_2Pz)(\mu\text{-}\eta^2{:}\eta^4\text{-}{}^tBu_2Pz)(OH)(THF)]_2$ (4). Compound **4** was obtained by direct metalation with ammonia-activated calcium by inadvertent introduction of water. A total of 0.08 g of calcium (2 mmol), 0.72 g of 3,5-di-*tert*-butylpyrazole (4 mmol), and 30 mL of THF were placed in a Schlenk tube. After the flask was cooled to −78 °C, about 30 mL of anhydrous ammonia was condensed onto the metal and ligand. The reaction mixture was refluxed for several hours with the aid of a dry ice condenser. The ammonia was boiled off upon warming of the mixture to room temperature. Removal of the THF solvent and recrystallization from 20 mL of hexane yielded X-ray-quality crystals upon cooling to −20 °C. Yield: 0.20 g, 14.4%, based on ${}^tBu_2pzH$. Mp: >350 °C (dec).

^{1}H NMR (C_6D_6): δ (ppm) 6.06 (bs, 6 H, H4-pz), 2.98 (bs, 8 H, THF), 2.77 (s, 1.4 H, OH), 1.38−1.16 (m, 122 H, ^{t}Bu and THF).

^{13}C NMR (C_6D_6): δ (ppm) 25.7, 31.6, 32.3, 32.8, 68.4, 97.1, 165.1.

IR (cm^{-1}): 3648 (m), 3254 (s), 3112 (m), 1557 (m), 1516 (s), 1499 (s), 1433 (s), 1405 (s), 1359 (m), 1308 (m), 1281 (m), 1251 (s), 1217 (s), 1206 (s), 1127 (m), 1105 (m), 1036 (s), 1012 (m), 991 (s), 992 (m), 889 (m), 799 (s), 779 (s), 725 (m), 668 (m).

Synthesis of $[\{Sr_2(OMes)_2(\mu\text{-}OMes)_2(\eta^2\text{-}en)_3(\eta^1\text{-}en)(H_2O)\}_2(\mu\text{-}en)]\cdot 3en$ (5). Compound **5** was prepared in a manner identical with that of **3**. A total of 0.18 g (2 mmol) of strontium metal was stirred in 10 mL of ethylenediamine for 2 h. A total of 0.41 g (3 mmol) of HOMes was dissolved in 40 mL of THF and 0.02 mL (1 mmol) of water (stock solution of ethylenediamine with a known concentration), and the resulting solution was transferred to the reaction flask. The workup proceeded as mentioned for **3**. Several attempts to convert OH_2 to OH^- by refluxing the solution for several hours in a high-boiling solvent did not afford the intended hydroxide. Colorless crystals of **5** suitable for X-ray crystallography were obtained within 1 week at −20 °C. Yield: 0.66 g, 0.30 mmol, 80.7% based on HOMes. Mp: 93−95 °C.

^{1}H NMR (C_6D_6): δ (ppm) 6.90 (s, 16 H, *m*-H), 2.35 (s, 48 H, *p*-Me), 2.30 (s, 24 H, *o*-Me), 2.09 (s, 48 H, en), 0.59 (s, br, 32 H).

^{13}C NMR (C_6D_6): δ (ppm) 18.75, 21.20, 44.65, 123.22, 124.59, 129.78, 160.19.

IR (cm^{-1}): 3335 (sharp, w), 3270 (sharp, w), 2912 (s), 1599 (w), 1583 (w), 1458 (s), 1376 (m), 1301 (m), 1252 (m), 1155 (w), 1003 (w), 976 (w), 927 (w), 851 (w), 791 (w), 748 (w), 721 (w).

Synthesis of $Mg(PMDTA)(OMes)_2$ (6). Compound **6** was prepared as described for **1** using route b: 0.68 g (5 mmol) of HOMes, 40 mL of hexane, −78 °C, 3.33 mL of a 1 M $({}^{n/sec}Bu)_2Mg$ solution, and 10 mL of THF. The solution was stirred for 3 h at low temperature, followed by the addition of 0.03 g (1.67 mmol) of water and 2 mL (10 mmol) of PMDTA, affording a clear, yellow solution. Colorless crystals suitable for X-ray crystallographic studies were obtained at −20 °C within 1 week. Yield: 0.98 g, 2.05 mmol, 82.3% based on HOMes. Mp: >375 °C.

^{1}H NMR (C_6D_6): δ (ppm) 6.68 (4 H, *m*-H), 2.51 (m, 4 H, CH_2), 2.39 (m, 4 H, CH_2), 2.20 (s, 3 H, PMDTA), 2.14 (s, 6 H, *p*-Me), 2.13 (s, 12 H, PMDTA), 1.99 (s, 12 H, *o*-Me).

^{13}C NMR (C_6D_6): δ (ppm) 21.00, 41.95, 46.10, 48.21, 56.03, 56.94, 124.42.

IR (cm^{-1}): 2923 (s), 2854 (s), 2718 (w), 2360 (w), 1607 (w), 1466 (s), 1376 (m), 1348 (w), 1330 (m), 1278 (m), 1174 (w), 1152 (w), 1103 (w), 1058 (w), 1036 (w), 1013 (w), 974 (w), 956 (w), 934 (w), 910 (w), 856 (w), 828 (w), 813 (w), 796 (w), 779 (w), 749 (w), 722 (w).

X-ray Crystallographic Studies. X-ray-quality crystals for all compounds were grown as described in the Experimental Section. Crystal mounting and data collection procedures have been described previously.[16] Monochromated Mo Kα radiation (λ = 0.710 73 Å) was employed in all cases. All non-hydrogen atoms, with the exception of some disordered or restrained positions, were refined anisotropically. Disorder was handled by including split positions for the affected groups and refinement of the respective occupancies. Further details about the refinements and how disorder was handled are outlined in the Supporting Information. Because of unresolvable disorder in compounds **2** and **3**, THF or ethylenediamine was removed from the refinement using the function squeeze in the program package *PLATON*.[17] Hydroxide hydrogen positions in **1**, **2**, **4**, and **5** were located in difference maps and included in the refinement using restraints. Hydrogen positions were refined with O−H distances of 0.773 Å for compound **1**, 0.665 Å for compound **2**, 0.670 and 0.702 Å for compound **4**, and between 0.756 and 0.815 Å for compound **5**. O−H hydrogen atoms for **3** were placed in calculated positions. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. 608630−608635 (compounds **1**−**6**). Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. [fax (+44) 1223-336-033; e-mail deposit@ccdc.cam.ac.uk].

Powder X-ray Diffraction Study. Powder X-ray diffraction data were collected on a Bruker AXS D8 Advance automated diffractometer equipped with a Goebel mirror and capillary stage using Cu Kα radiation. The crystalline powder was carefully packed in the glass capillary in the drybox and then placed in the goniometer head. The step size was 0.02° in 2θ from 2° to 60°.

Results and Discussion

Synthetic Aspects. Compound **1** was obtained in high yield and purity using two different synthetic routes. Both the treatment of magnesium aryloxide with freshly prepared magnesium hydroxide and the treatment of alkylmagnesium with alcohol to obtain the aryloxide followed by the addition of water afforded identical reaction products. The first route (eqs 1a−c) involves the preparation of the two reagents (eqs 1a and 1b); if combined, they afford the final product **1** (eq 1c).

$$3({}^{n/sec}\mathrm{Bu})_2\mathrm{Mg} + 6\mathrm{HOMes} \xrightarrow[-78\ ^\circ\mathrm{C}]{\mathrm{THF}} 3\mathrm{Mg(OMes)}_2 + 6\mathrm{BuH} \tag{1a}$$

$$({}^{n/sec}\mathrm{Bu})_2\mathrm{Mg} + 2\mathrm{H_2O} \xrightarrow[-78\ ^\circ\mathrm{C}]{\mathrm{THF}} \mathrm{Mg(OH)}_2 + 2\mathrm{BuH} \tag{1b}$$

$$3\mathrm{Mg(OMes)}_2 + \mathrm{Mg(OH)}_2 \rightarrow [\mathrm{Mg_2(OMes)_3(OH)(THF)_2}]_2 \tag{1c}$$

The alternative synthetic route is a straightforward, one-pot procedure, affording compound **1** in good yield and purity, despite the “less controlled” reaction conditions. A total of 4 equiv of dialkylmagnesium and 6 equiv of alcohol are combined and stirred for 2 h, followed by the addition of water (eq 2). The extension of the alkane elimination route toward the heavier alkaline earth metals is difficult. While dibenzyl reagents are available for calcium, strontium, and barium,[18] their multistep synthesis, high reactivity, and low solubility in all solvents but THF, paired with the strict requirement to work at low temperature, make them less attractive starting materials. Therefore, direct metalation was chosen to prepare the heavier metal congeners. Early direct metalation attempts using alkaline earth metal shavings in THF did not proceed well. The reactions were sluggish, with only low yields and typically impure reaction products. In contrast, metal activation in either anhydrous ammonia or ethylenediamine afforded the products in good yield and purity. To this effect, the metals were dissolved in the respective solvent and stirred before being treated with an alcohol/water mixture [compounds **3** (eq 4) and **5** (eq 6)], or the aryloxide/pyrazolate was allowed to form before water was added [compounds **2** (eq 3), **4** (eq 5), and **6** (eq 6)]. We speculate that the first step in the formation of the hydroxides involves the coordination of water that is subsequently deprotonated to form $\mathrm{OH^-}$. Curiously, in the aqua complex **5**, water is not deprotonated and remains a Lewis donor even under forcing conditions. The absence of the thermodynamically favored water deprotonation cannot be rationalized by acidity or steric arguments, but rather, water is held in a hydrogen-bonding embrace by the solvent of crystallization, ethylenediamine, providing the rationale for the inertness of the water protons.

$$4({}^{n/sec}\mathrm{Bu})_2\mathrm{Mg} + 6\mathrm{HOMes} \xrightarrow[\mathrm{Hex/THF}\ (-78\ ^\circ\mathrm{C})]{\mathrm{H_2O}} [\mathrm{Mg_2(OMes)_3(OH)(THF)_2}]_2 + 8\mathrm{BuH} \tag{2}$$

$$4\mathrm{Ca} + 6\mathrm{HOMes} \xrightarrow[\mathrm{THF}]{2\mathrm{H_2O}} [\mathrm{Ca_2(OMes)_3(OH)(THF)_3}]_2 + 4\mathrm{H_2} \tag{3}$$

$$4\mathrm{Ca} + 6\mathrm{HOMes} \xrightarrow[\mathrm{en\ (reflux)}]{2\mathrm{H_2O}} [\mathrm{Ca_2(OMes)_3(OH)(en)_2}]_2 + 4\mathrm{H_2} \tag{4}$$

$$2\mathrm{Ca} + 4\mathrm{H}{}^t\mathrm{Bu_2Pz} \xrightarrow[\mathrm{NH_3/THF}]{\mathrm{H_2O}} [\mathrm{Ca_2}({}^t\mathrm{Bu_2Pz})_3\mathrm{(OH)(THF)}]_2 + 4\mathrm{H_2} \tag{5}$$

$$4\mathrm{Sr} + 8\mathrm{HOMes} \xrightarrow[\mathrm{en\ (reflux)}]{2\mathrm{H_2O}} [\mathrm{Sr_2(OMes)_4(en)_4(H_2O)}]_2(\mu\text{-en}) + 4\mathrm{H_2} \tag{6}$$

Compounds **1**−**4** rely on the use of a moderately sterically demanding ligand, as represented by the aryloxide −OMes or the pyrazolate $-{}^t\mathrm{Bu_2Pz}$ in conjunction with the effective Lewis donors THF and ethylenediamine. The reproducible complex stoichiometry and geometry, independent of 2:1, 3:1, or 4:1 ligand/water ratios, indicate this formulation to be especially robust, suggesting that compounds of this type might be considered intermediates in the sol−gel process. It is worth noting that species **1** was also obtained upon treatment of the dimeric heteroleptic $[\mathrm{BuMg(NHMes^*)}]_2$

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(16) Englich, U.; Ruhlandt-Senge, K. *Chem.*—*Eur. J.* **2000**, *6*, 4063−4070 and references cited therein.

(17) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7−13.

(18) (a) Fiel, F.; Harder, S. *Organometallics* **2000**, *19*, 5010−5015. (b) Harder, S.; Fiel, F.; Weeber, A. *Organometallics* **2001**, *20*, 1044−1046. (c) Fiel, F.; Harder, S. *Organometallics* **2001**, *20*, 4616−4622. (d) Weeber, A.; Harder, S.; Britzinger, H. *Organometallics* **2000**, *19*, 1325−1332.

Table 1. Crystallographic Data for Compounds **1**−**6**

	1	**2**	**3**	**4**	**5**	**6**
formula	$C_{78}H_{116}Mg_4O_{14}$	$C_{78}H_{116}Ca_4O_{14}$	$C_{76}H_{116}Ca_4N_8O_8$	$C_{74}H_{132}Ca_4N_{12}O_4$	$C_{95}H_{184}N_{23}O_{10}Sr_4$	$C_{27}H_{45}MgN_3O_2$
fw	1374.95	1438.03	1430.09	1414.24	2159.13	467.97
a (Å)	24.5045(6)	13.1767(15)	12.3900(9)	13.816(2)	25.559(6)	12.7034(6)
b (Å)	13.9953(4)	14.5719(17)	13.8979(10)	14.250(2)	19.512(5)	13.6576(7)
c (Å)	24.3557(6)	14.7956(17)	14.9393(11)	25.075(4)	24.723(6)	15.6115(8)
α (deg)		60.771(2)	116.3660(10)	76.093(3)		
β (deg)	109.8670(10)	80.596(2)	91.2332(2)	75.236(3)	111.880(5)°	96.199(1)
γ (deg)		81.263(2)	110.3100(10)	64.205(3)		
V (Å^3)	7855.6(4)	2437.3(5)	2113.8(3)	4250.4(11)	11441(5)	2692.7(2)
Z	4	1	1	2	4	4
space group	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2(1)/c$	$P2(1)/c$
d_{calc} (g/cm^3)	1.163	0.980	1.123	1.105	1.253	1.154
linear abs coeff (mm^{-1})	0.106	0.270	0.309	0.304	1.915	0.093
T (K)	88	96	91	94	93	95
2θ range, deg	3.40−50.00	3.22−50.00	3.12−50.00	3.32−50.00	3.56−50.00	3.98−56.58
no. of indep reflns	6919	8591	7437	14969	17385	6683
no. of param	454	437	433	891	1222	316
R1, wR2 (all data)	0.1000, 0.2113	0.0967, 0.1942	0.0825, 0.1736	0.1512, 0.2043	0.0864, 0.1164	0.0512, 0.1107
R1, wR2 ($>2\sigma$)	0.0663, 0.1882	0.0667, 0.1790	0.0599, 0.1635	0.0748, 0.1683	0.0478, 0.1113	0.0414, 0.1047

(Mes* = 2,4,6-$^tBu_3C_6H_2$) with a HOMes/water mixture,[19] indicating the strong propensity for the formation of the $[M_4(ligand)_6(OH)_2]$ formulation. Furthermore, alkaline earth metal pyrrolates were also observed to display an analogous tetranuclear stoichiometry and geometry.[19] Compounds **2** and **3** were initially obtained by inadvertent introduction of water. Despite the trace amounts of water present, the $[M_4(ligand)_6(OH)_2]$ complex stoichiometry was observed, but only in low yields. Subsequently, both compounds were prepared rationally using the correct reagent ratio to give the target compounds in good yields.

In an effort to study the donor influence on the formation of the $[M_4(ligand)_6(OH)_2]$ complex, a selection of donors, including THF, DME, TMEDA, and PMDTA, were introduced. Interestingly, the addition of TMEDA to the reaction mixture of magnesium aryloxide and water in THF did not result in donor exchange, but rather **1** was isolated in all instances. Only the tridentate donor PMDTA coordinated to the metal, affording the five-coordinated aryloxide monomer **6**. The aryloxide **6** does not hydrolyze, independent of the amount of water present or the reaction conditions applied. Clearly then, the combination of the tridentate donor and bulky alcohol provides sufficient kinetic metal stabilization to effectively prevent the thermodynamically preferred hydrolysis. Similar results are obtained if the ligand size increases, but sterically less demanding donors or those with lower denticity are utilized. Examples include the sterically demanding alcohols HO−BHT (BHT = 2,6-di-*tert*-butyl-4-methylphenyl), HO-2,6-$^iPr_2C_6H_3$, and HO-2-$^iPrC_6H_4$.[20] In all cases, the monomeric aryloxides of the type $Mg(donor)_n(OR)_2$ (R = 2,6-$^iPr_2C_6H_3$, donor = THF, $n = 3$;[13] R = BHT, donor = THF, $n = 2$;[20] R = 2-$^iPrC_6H_4$, donor = DME, $n = 1$)[20] or dimeric complexes $[Mg(THF)_2(O\text{-}2\text{-}^iPrC_6H_4)_2]_2$ were inert toward hydrolysis.[20]

Compound **2** was obtained by combining ammonia-activated calcium metal with alcohol. The mixture was stirred to allow for the formation of aryloxide, followed by the addition of water. In an effort to analyze the potential of ethylenediamine as a metal-activating solvent and circumvent work with the condensed gas NH_3, calcium metal was stirred for 2 h in ethylenediamine, followed by the simultaneous introduction of water and alcohol to afford compound **3** in good yield and purity, indicating yet again the propensity for the formation of $[M_4(ligand)_6(OH)_2]$. Clearly demonstrating its potential as a metal activator and thus allowing work at ambient temperature, ethylenediamine might not be ideal for all applications because of the formation of a strong M−N bond. In contrast, ammonia coordination appears to be more labile, and NH_3 can often be removed by brief evacuation and application of heat and/or vacuum or reflux in a high-boiling solvent such as toluene. The facile coordination of ethylenediamine to the calcium center also demonstrates the effect of steric crowding at the nitrogen atom with regard to base strength: the methyl-substituted analogue TMEDA does not coordinate.

Structural Aspects. Crystallographic information and data collection parameters for compounds **1**−**6** are summarized in Table 1. A compilation of selected geometrical parameters for all compounds is provided in Table 2, while Figures 1−6 illustrate the structural principles observed in compounds **1** and **3**−**5**. An illustration of compound **2** can be found in the Table of Contents Synopsis. The hydrogen atoms on the hydroxides and water in compounds **1**, **2**, and **4**−**6** were located in the difference maps and included in the refinement. Restraints were used to refine the O−H distances. The presence of hydroxide in compounds **1**−**4** and water in compound **5** was further confirmed by a strong, broad band around ~3250 cm^{-1} in the IR spectra.

Compounds **1**−**3** all contain tetranuclear arrangements with two hydroxides in apical positions and six aryloxides, some of which are in terminal, and therefore bridging, positions. Upon first inspection, compounds **1**−**3** look rather similar, but different point group symmetries (**1**, C_2; **2** and **3**, i) result in two distinct structure types, with the metals in different positions. Figure 1 illustrates the differences between the two arrangements. In **1**, two fused three-rung ladders with one bridging hydroxide in the center are held in a butterfly arrangement by the second bridging hydroxide,

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[19] Vargas, W.; Fry, N.; Ruhlandt-Senge, K., in preparation.
[20] Teng, W.; Ruhlandt-Senge, K., unpublished results.

Table 2. Selected Bond Distances (Å) for Compounds **1**−**6**

compound	M−ligand (Å)	M−OH/H_2O (Å)	M−donor (Å)
1	1.908(3),[a,c] 1.999(3)−2.020(2)[a,d]	1.944(2), 2.089(2), 2.202(1)[b]	2.096(2)−2.111(2)[h]
2	2.167(2),[a,c] 2.300(2)−2.351(2)[a,d]	2.322(3), 2.331(2), 2.349(3)[b]	2.386(2)−2.461(2)[h]
3	2.226(2),[a,c] 2.316(2)−2.338(2)[a,d]	2.334(2)[b]	2.525(3)−2.650(3)[i]
4	2.278(4)−2.372(4)[k,c] 2.413(4)−2.457(4)[k,d] 2.407(4)−3.151(4)[k,e] 2.416(4)−2.475(4)[k,f] 2.528(4)−2.627(4)[k,g]	2.276(4), 2.289(4), 2.308(4)[b]	2.389(4), 2.416(3)[h]
5	2.409(3)−2.447(3),[a,c] 2.483(3)−2.546(3)[a,d]	2.532(4), 2.570(4)[j]	2.771(4)−2.833(4)[i]
6	1.880(9), 1.939(9)[a,c]	NA	2.223(1)−2.385(1)[i]

[a] OMes. [b] OH. [c] Terminal. [d] Bridging. [e] η^1:η^2 bridging. [f] η^2:η^2 bridging. [g] η^2:η^4 bridging. [h] O(THF). [i] N(PMDTA, en). [j] H_2O. [k] *t*Bu_2pz.

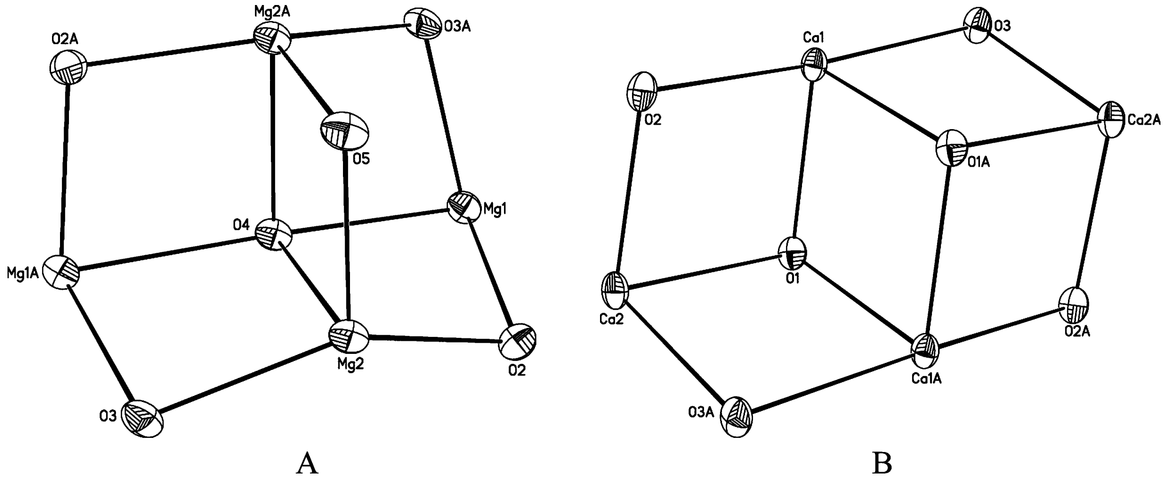

Figure 1. Graphical representation of the core of compounds **1** and **2**. Ellipsoids show 30% occupancy.

with an approximate 90° angle between the two ladder planes. Accordingly, one hydroxide bridges all four metal centers, while the second one only connects to two. In compounds **2** and **3**, the metals are located in diagonal positions on opposite faces of a cuboidal arrangement, resulting in a staircase-like arrangement. In here, each hydroxide bridges three metal centers.

The donor coordination in the target compounds depends on the metal radius and the type of donor, with one THF coordinating to each of the metal centers in **1**, while the larger calcium center in **2** accommodates two THF groups in one and one THF in the second position. The small chelating ethylenediamine in **3** coordinates in a bidentate fashion to each of the two independent metal centers.

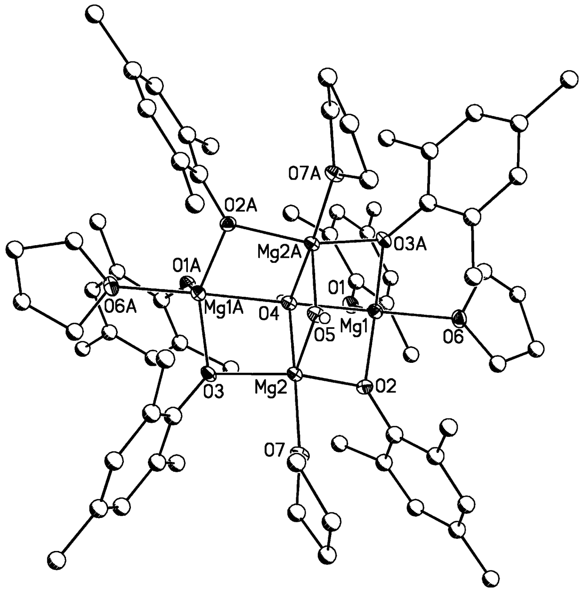

Figure 2. Graphical representation of compound **1**. Ellipsoids show 30% occupancy. The solvent of crystallization and hydrogen atoms, except those on hydroxide, have been omitted for clarity.

1, illustrated in Figure 2, has two independent metal centers, both displaying a distorted trigonal-bipyramidal geometry. Mg1 is bound to one terminal and two bridging aryloxides, in addition to one hydroxide and a THF donor. Mg2 is coordinated by two bridging aryloxides, two hydroxides, and one THF. The three aryloxides bound to Mg1 are oriented in the equatorial plane with MesO−Mg1−OMes angles ranging from 116.55(11) to 121.71(10)°, while the THF donor and the hydroxide ligand occupy the axial positions [O(THF)−Mg1−OH 173.22(12)°]. Mg1−OMes distances are shorter involving the terminal [1.908(3) Å] rather than the bridging aryloxides [2.015(2) and 2.020(2) Å]. The M−OH bonds [2.202(1) Å] are slightly longer than the Mg1−O(THF) distances [2.111(2) Å], reflecting the bridging nature of the former. Mg2 geometry is comprised of two bridging aryloxides and one hydroxide in the equatorial plane; a second bridging hydroxide and THF are located in the axial positions. The presence of differently sized ligands in the equatorial plane results in a significant deviation from ideal geometry, with angles ranging from 141.86(11)° between the two sterically demanding aryloxides down to 105.18(8)° involving the hydroxide moiety. The

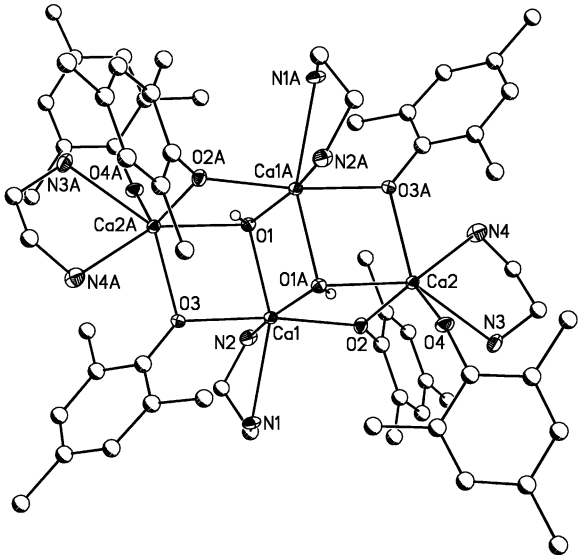

Figure 3. Graphical representation of compound **3**. Ellipsoids show 30% occupancy. The solvent of crystallization, toluene, and hydrogen atoms, except those on the hydroxide functions, have been removed for clarity.

O(THF)−Mg2−OH trans angle is 174.33(10)°. With the bridging Mg2−OMes distances very similar to those on Mg1 [1.999(2) and 2.018(2) Å], a significant difference in the Mg−OH distance is observed, with 1.944(2) Å for the hydroxide in the equatorial position and 2.089(2) Å for that in the axial position. Remarkably, both are significantly shorter than the Mg1−OH distance [2.202(1) Å], a fact explained by the less crowded environment at Mg2.

The role of steric crowding at the metal is also expressed in the calcium complex **2**, where two THF donors coordinate to the sterically less crowded metal center (Ca1), resulting in a distorted octahedral geometry. The coordination of only one THF to Ca2 retains the distorted trigonal-bipyramidal geometry as observed in **1**.

2, shown in the Table of Contents Synopsis, and **3**, exhibited in Figure 3, display very similar structural features, also represented in Figure 1B. In compound **2**, the equatorial plane at Ca2 consists of three aryloxides: two bridging [2.310(2) and 2.300(2) Å] and one terminal [2.167(2) Å)], with angles ranging from 108.67(9)° to 125.53(10)°. The trans angle [O(THF)−Ca2−OH] is observed at 167.96(9)°. The bond lengths at the octahedral Ca1 center reflect the increased coordination number with Ca1−OMes distances of 2.305(2) and 2.351(2) Å. Ca−OH distances are quite similar in length, with Ca1−OH 2.321(3) and 2.348(3) Å. As expected, the M−donor bonds are longer [Ca1−O(THF) 2.443(3) and 2.461(2) Å]. The significant deviation from octahedral geometry at Ca1 is expressed by equatorial angles ranging from 74.78(10)° to 118.33(9)° and a trans angle of 171.02(9)°.

In compound **3**, one ethylenediamine donor is coordinated to each calcium center, affording distorted octahedral geometry for both. Analogous to **1** and **2**, one metal center (Ca2) is coordinated by three aryloxide ligands (two bridging and one terminal), one hydroxide, and one ethylenediamine, binding in a bidentate mode. Of those, the three aryloxides as well as one of the ethylenediamine nitrogens occupy the equatorial plane, while the second ethylenediamine nitrogen and the hydroxide moiety occupy the axial positions. Again, distortion from ideal geometry is evident, with equatorial angles ranging from 77.80(9)° to 113.42(9)°. The trans angle of 146.77(9)° further indicates a significant degree of distortion. Distorted octahedral geometry is also observed for Ca1, involving the coordination of two bridging aryloxides [trans angle 173.07(8)°] and two hydroxides, as well as the bidentate ethylenediamine in the equatorial plane with angles between 69.19(9)° and 119.69(9)°. Not surprisingly, the narrower angles involve the ethylenediamine donors. Ca1−OMes and Ca1−OH distances are very similar to those of **2** with 2.329(2), 2.338(2), and 2.334(2) Å. The two Ca1−N distances are observed at 2.525(3) and 2.638(3) Å. In analogy with **1**, the terminal Ca2−OMes distances [2.226(2) Å] are slightly shorter than the bridging ones [2.316(2) and 2.346(2) Å]. Again, the Ca2−OH distance is elongated [2.410(2) Å] because of steric crowding. The Ca2−N distances are 2.629(3) and 2.650(3) Å.

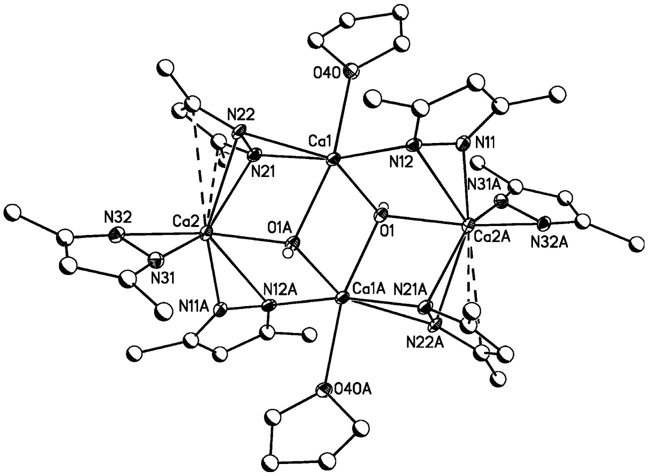

Figure 4. Graphical representation of compound **4**. Only one of the two independent molecules in the asymmetric unit is shown. Ellipsoids show 30% occupancy. Methyl groups on ^{t}Bu in the ligand and hydrogen atoms, except those on hydroxide, have been removed for clarity.

The overall tetranuclear geometry $[M_4(ligand)_6(OH)_2]$ (M = Ca, Sr) observed in **2** and **3** also appears in the calcium pyrazolate complex **4**, further indicating the favorable formulation of this type of compound. Furthermore, hydroxide may be replaced by the isolobal fluoride to provide yet again similar tetranuclear stoichiometry and geometry, as seen in $Ca_4(Me_2Pz)_6F_2(DME)_4$.[21]

Compound **4** (Figure 4) displays two independent molecules in the asymmetric unit, of which only one is shown. In analogy to **2** and **3**, there is a center of symmetry in the core of the aggregate with two symmetry-independent metal centers. Therefore, the two hydroxides each bridge three metal centers with Ca−O1 2.276(4)−2.342(4) Å. Two calcium centers are bridged by a pyrazolate in a μ-η^1:η^2 fashion for Ca1A and Ca2 [Ca−N 2.407(4)−3.151(4) Å] and a μ-η^2:η^4 mode for Ca2 and Ca1 [Ca−N 2.416(4)−2.627(4) Å]. If bonding is considered through the N−N centroids, the formally six-coordinate Ca1 shows a distorted

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[21] Hitzbleck, J. Ph.D. Thesis, Syracuse University, Syracuse, NY, 2004.

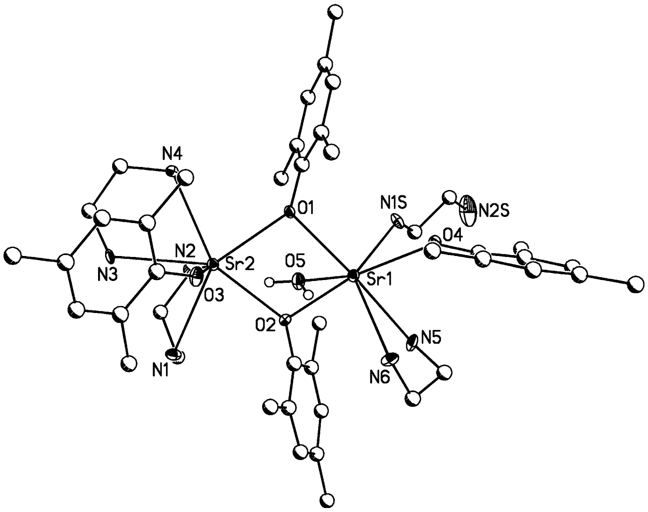

Figure 5. Graphical representation of compound **5**. Ellipsoids show 30% occupancy. Hydrogen atoms, except those on water, have been removed for clarity.

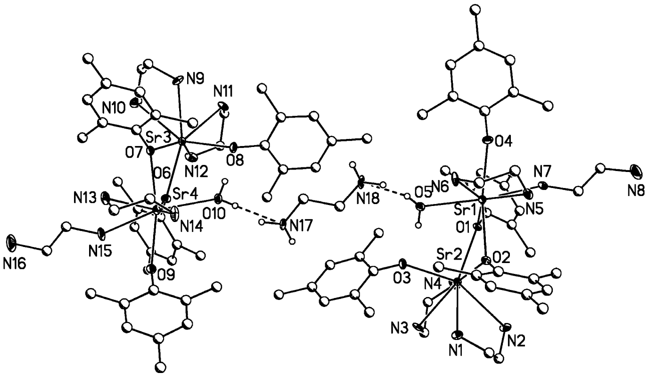

Figure 6. Graphical representation of **5** showing the hydrogen-bonded connection of two strontium dimers by ethylenediamine. Hydrogen atoms, except those on water and ethylenediamine, have been removed for clarity.

trigonal-bipyramidal coordination environment with the hydroxide O1 and the η^1- and η^2-bridging pyrazolate occupying the equatorial positions and the symmetry-generated O1A and the THF donor in the axial positions [trans angle 164.87(12)°]. Ca2, on the other hand, is nine-coordinate with two η^2-bonded pyrazolates, one in a terminal position [Ca−N 2.279(4) and 2.364(4) Å] and one bridging to Ca1A, and the hydroxide in the basal plane of a distorted pyramidal coordination environment; the side-on coordination of the tilted ligand occupies the apical position. The Ca−N bond lengths of the terminal η^2-pyrazolate are significantly shorter [0.043(8)−0.872(8) Å] than those of the bridging ligands. The π-bonded pyrazolate shows close Ca−C contacts [3.065(5)−3.440(4) Å] within the sum of the van der Waals radii, although Ca(2)−C(24) 3.440(4) Å is close to the upper limit and should only be considered as a weak interaction, an interpretation also confirmed by the wide Pz(cen)−NN(cen)−Ca angle (116.2°), reducing the capacity for π bonding.

5, illustrated in Figures 5 and 6, displays two independent molecules in the asymmetric unit. Figure 5 illustrates the overall geometry of the dimeric molecule, where two seven-coordinate, but inequivalent, metal centers are observed. Each metal center is bound to one terminal [2.409(3)−2.447(3) Å] and two bridging OMes ligands [2.483(3)−2.546(3) Å]. The environment at Sr2 is completed by two bidentate ethylenediamine donors: Sr1 binds η^2 to one ethylenediamine and η^1 to the other, with the seventh position filled by water [Sr−OH_2 2.532(4) and 2.570(4) Å]. Sr−N distances for the η^2-bound ethylenediamines range from 2.743(4) to 2.817(4) Å, with longer distances [2.822(4) and 2.853(4) Å] for the η^1-bound ethylenediamines. Two such dimers are associated via hydrogen bonding involving the water on Sr and a solvent of crystallization, ethylenediamine (Figure 6). The hydrogen-bonded embrace of water provides a rationale for the inertness of water toward the thermodynamically preferred deprotonation.

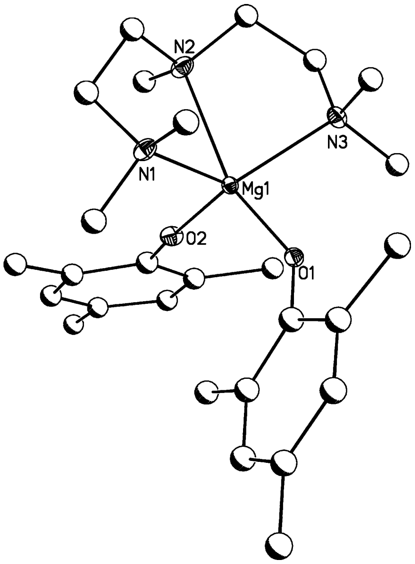

Figure 7. Graphical representation of compound **6**. Ellipsoids show 30% occupancy. Hydrogen atoms have been removed for clarity.

The five-coordinated aryloxide **6** (Figure 7) consists of a significantly distorted trigonal bipyramid with two nitrogen atoms (N1 and N3) from the tridentate PMDTA donor and one aryloxide (MesO2) in the equatorial plane, while the second aryloxide (MesO1) and the third PMDTA nitrogen atom (N2) are located in the axial positions. The distortion from ideal geometry is significant because of the narrow bite angle from the multidentate PMDTA with N−M−N angles at 75.93(4)° and 77.33(4)°. A further expression of the deviation from ideal geometry is the trans angle of 157.01(4)° and the equatorial angles ranging from 106.52(5) to 125.15(4)°. Mg−O distances are quite different, with 1.888(9) and 1.939(9) Å, expressing the steric crowding at the metal center. Nevertheless, these values are in good agreement with a series of five-coordinated magnesium aryloxides with Mg−O distances of 1.887(1) Å for $Mg(py)_3(O\text{-}2,6\text{-}Me_2C_6H_3)_2$ (py = pyridine), 1.897(2) Å for $Mg(THF)_3(O\text{-}2,6\text{-}(CHMe_2)_2C_6H_3)_2$, and 1.914(2) Å for $Mg(THF)_3(O\text{-}1,3,5\text{-}Cl_3C_6H_2)_2$.[22]

Compounds **1**−**4** are not the first alkaline earth metal compounds displaying a $[M_4(ligand)_6(anion)_2]$ tetranuclear core,[23−31] but they represent a small but growing number of

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(22) Albaric, L.; Hovnanian, N.; Julbe, A.; Guizard, C.; Alvarez-Larena, A.; Piniella, J. F. *Polyhedron* **1997**, *16*, 587−592.

such complexes bearing hydroxide. The only prior discrete, well-characterized hydroxides include $[\{OC_6H_2{}^tBu_2CHN(CH_2)_2NH_2\}Sr(\mu_3\text{-salean}{}^tBuH_2)Sr(\mu_3{-}OH)]_2$,[8] where a multidentate ligand effectively prevents further association. The related heterobimetallic $[MZr(OH)(O^iPr)_5(^iPrOH)_3]_2$ (M = Sr, Ba) also display a tetranuclear arrangement.[11] With only moderately sized monodentate ligands effectively stabilizing the metal centers, the unique nature of compounds **1−4** becomes evident. Apparently, the tetranuclear arrangement provides sufficient kinetic stabilization to prevent further hydrolysis even if excess of water is present. The unique nature of **1−4** as discrete, soluble complex species comprised of monodentate ligands and hydroxide is underscored if considering the typical occurrence of hydroxides as highly aggregated, inhomogeneous, insoluble residues. A sole example of a dimeric hydroxide, $[(Tp^{Ar,Me})Mg(\mu\text{-}OH)]_2$, is stabilized by the large tridentate tris(pyrazolyl)hydroborato ligand, preventing it from further aggregation.[7]

Conclusion

We here present four unique alkaline earth metal tetranuclear species of stoichiometry $[M_4(\text{ligand})_6(OH)_2(\text{donor})_n]$ (M = Mg, Ca). These compounds represent the first examples of well-defined homometallic alkaline earth metal molecular hydroxides bearing monodentate ligands. The formation of the $[M_4(\text{ligand})_6(OH)_2]$ tetranuclear geometry by ligands as diverse as aryloxide, pyrazolate, or pyrrolate, along with the introduction of significant stoichiometric variations (water/ligand), indicates a strong prevalence for the formation of this particular tetranuclear system, suggesting that the $[M_4(\text{ligand})_6(OH)_2(\text{donor})_n]$ arrangement might represent important intermediates in the hydrolysis of molecular species in sol−gel applications. This hypothesis will need to be verified by further studies involving a larger selection of ligands in combination with the heavier alkaline earth metals.

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Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths, bond angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for compounds **1−6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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