Alkaline-Earth-Metal Oxides

DOI: 10.1002/anie.200904054

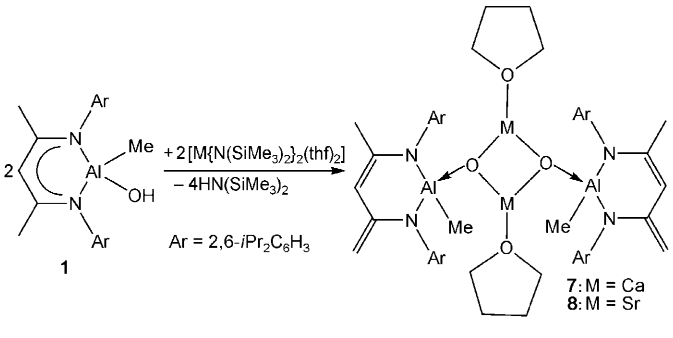
Soluble Molecular Dimers of CaO and SrO Stabilized by a Lewis Acid**

Sankaranarayana Pillai Sarish, Sharanappa Nembenna, Herbert W. Roesky,* Holger Ott, Aritra Pal, Dietmar Stalke, Sudipta Dutta, and Swapan K. Pati

Dedicated to Professor Alan H. Cowley on the occasion of his 75th birthday

Oxides of alkaline earth metals, especially calcium oxide, have been known since ancient times. The heavier alkaline-earth-metal oxides, such as calcium oxide (commonly known as quick lime) and strontium oxide, are prepared by heating the corresponding carbonates. Calcination of $CaCO_3$ appears to have been carried out in the Stone Age to judge by the remains of kilns that have been found. The Romans achieved a high degree of expertise in its use as a building material. Strontium oxide is mainly important as a source of other strontium salts. These oxides have a broad range of application in material science and technology. For instance, SrO finds application in cathode ray tubes, as it can absorb dangerous UV light. Strontium oxide aluminate doped with suitable metals can act as a photoluminescent phosphor. CaO and SrO are also catalysts for the Tishchenko reaction.[1] However, these inorganic compounds are insoluble in organic solvents, and making them available to organometallic chemistry is a synthetic challenge owing to their high lattice energy (CaO 816 $kcal\,mol^{-1}$, SrO 769 $kcal\,mol^{-1}$). For this reason, and also because of their high melting points (CaO 2707 °C, SrO 2430 °C),[2] they are not useful as precursors for organometallic compounds. A well-defined synthetic strategy is needed to obtain these types of complexes. Organometallic oxides can act as catalysts and can serve as model compounds for the fixation of catalytically active species on oxide surfaces and can thus help to clarify structure–activity relationships.[3] Such knowledge would help with the design of good heterogeneous catalysts, which are always preferred by industry. Thus, we became interested in trapping or incorporating molecular inorganic oxides into an organometallic or organic matrix. These lipophilic complexes can be studied using characterization techniques available for organometallic complexes. A suitable synthesis of these complexes starts with their hydroxide complexes as precursors. The unique property of β-diketiminate ligands (herein, L = $CH(CMe\text{-}2,6\text{-}i\mathrm{Pr}_2C_6H_3N)_2$) to stabilize unusual coordination sites has been successfully applied in the syntheses of various well-defined hydroxide complexes of main-group metals such as aluminum,[4] gallium,[5] and germanium.[6] Soluble heavy alkaline-earth-metal hydroxide complexes of calcium ($[\{LCa(\mu\text{-}OH)(thf)\}_2]$[7] and strontium $[LSr(thf)(\mu\text{-}OH)_2Sr(thf)_2L]$[8]) have been reported. Using the strontium hydroxide $[LSr(thf)(\mu\text{-}OH)_2Sr(thf)_2L]$ as a precursor, we were able to assemble the heterobimetallic oxide $[\{LSr(\mu\text{-}O)Zr(NMe_2)_3\}_2]$ containing strontium and zirconium.[8] The previously prepared calcium and strontium hydroxides, however, turned out to be useless precursors for the preparation of soluble CaO and SrO compounds. Therefore, we decided to use [LAlMe(OH)] (**1**)[4b] as a source for oxygen, because we observed that [LAlMe(Cl)] (**2**) in the presence of the Lewis base $[LSrN(SiMe_3)_2(thf)]$ (**3**) is converted to $[L^1Al(Me)(thf)]$ (**4**) (L^1 = $CH\{C(CH_2)\}(CMe)(2,6\text{-}i\mathrm{Pr}_2C_6H_3N)_2$) upon deprotonation of a methyl group of L.[9] Subsequently, we treated **1** with $[Ca\{N(SiMe_3)_2\}_2(thf)_2]$ (**5**) and $[Sr\{N(SiMe_3)_2\}_2(thf)_2]$ (**6**) to yield $[\{L^1Al(Me)(\mu\text{-}O)Ca(thf)\}_2]$ (**7**) and $[\{L^1Al(Me)(\mu\text{-}O)Sr(thf)\}_2]$ (**8**).

Herein, we report the synthesis, characterization and theoretical investigation of the first soluble molecular CaO and SrO complexes (**7** and **8**, respectively). Compound **7** was obtained by the reaction of **1** with **5** in a molar ratio of 2:2 in THF/*n*-hexane (1:1) at 0 °C, and **8** was prepared by reaction of **1** and **6** in the same ratio in THF at room temperature (Scheme 1). $[L^1Al(Me)]$ is formed by deprotonation of **1** with **5** or **6** with concomitant formation of $HN(SiMe_3)_2$. Simultaneously, the oxygen atom of **1** is transferred to the alkaline



Scheme 1. Preparation of calcium and strontium oxide complexes.

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[*] Dipl.-Chem. S. P. Sarish, Dr. S. Nembenna, Prof. Dr. H. W. Roesky, Dr. H. Ott, Dr. A. Pal, Prof. Dr. D. Stalke
Institut für Anorganische Chemie, Universität Göttingen
Tammannstrasse 4, 37077 Göttingen (Germany)
Fax: (+49) 551-39-3373
E-mail: hroesky@gwdg.de
S. Dutta, Prof. Dr. S. K. Pati
Theoretical Sciences Unit and New Chemistry Unit, JNCASR
Bangalore, 560064 (India)

[**] Support of the Deutsche Forschungsgemeinschaft is highly acknowledged. S.D. acknowledges the CSIR for a research fellowship and S.K.P. acknowledges the CSIR and DST, Govt. of India for a research grant.

Supporting information for this article, including synthetic details, physical data, and theoretical calculations, is available on the WWW under http://dx.doi.org/10.1002/anie.200904054.

earth metal to form CaO and SrO cores. [L^{1}Al(Me)] acts as a Lewis acid and coordinates to the oxygen atoms in **7** and **8**. This type of deprotonation is the key step for generating **7** and **8**.

Compound **7** is a colorless solid and **8** is a pale greenish-yellow solid. Both are soluble in benzene, toluene, and THF. Both **7** and **8** were characterized by NMR spectroscopy, EI mass spectrometry, elemental analysis, and X-ray structural analysis. The ^{1}H NMR spectrum of **8** showed broad signals at room temperature. Therefore, the ^{1}H NMR spectroscopy experiment was conducted at low temperature to give a better resolution of the resonances. The Al–Me protons of **7** and **8** resonate at $\delta = -1.05$ and -1.06 ppm, respectively. The signals at $\delta = 1.58$ (**7**) and 1.73 ppm (**8**) and at $\delta = 3.98$, 3.45 (**7**) and 3.36, 2.79 ppm (**8**) can be attributed to the CH_3 and CH_2 groups on the L^1 backbone. The IR spectra of **7** and **8** show bands at 1619 and 1624 cm^{-1}, which can be assigned to the C=C bond. No molecular ion peaks were observed in the mass spectra for compounds **7** and **8**, but fragment ions were detected.

Compounds **7** and **8** crystallize in the triclinic space group $P\bar{1}$ and the monoclinic space group Cc, respectively, both with two molecules in the asymmetric unit (Figure 1 and Figure 2).[10] The structures reveal the dimeric nature of both compounds resulting in the formation of almost planar four-membered Ca_2O_2 and Sr_2O_2 rings, which are connected to two terminal L^{1}AlMe units. The calcium and strontium atoms are tetracoordinate (coordinated by one oxygen atom of thf, one interaction to the ligand backbone, and two oxygen atoms of the Al–O group), and both adopt a distorted square-planar geometry. The aluminum atoms are also tetracoordinate (coordinated by two nitrogen atoms of L^1, the methyl carbon atom, and an oxygen atom) and generate two six-membered C_3N_2Al rings owing to the bidentate nature of L^1. The coordination polyhedra of the aluminum atoms can best be described as highly distorted tetrahedra. The terminal C–C bond lengths in the ligand backbone (C1–C4 1.510(5), C3–C5 1.369(5) (**7**) and C1–C4 1.516(7), C3–C5 1.348(7) Å (**8**)) are indicative of a single and a double bond, respectively. The bond lengths within L^1 are in the range of those known in the literature, except for the two N–C bonds (N1–C1 1.355(4), N2–C3 1.395(4) (**7**) and N1–C1 1.354(6), N2–C3 1.410(6) Å (**8**)), which differ slightly from each other.[11] The two Ca–O and Sr–O bond lengths in the M_2O_2 core are different (on average 2.175, 2.259 (**7**) and 2.323, 2.394 Å (**8**)). The longer bonds are similar to those found in [{LCa(μ-OH)(thf)}$_2$] (2.225(6)$_{av}$ Å)[7] and [LSr(thf)(μ-OH)$_2$Sr(thf)$_2$L] (2.402(2)$_{av}$ Å).[8]

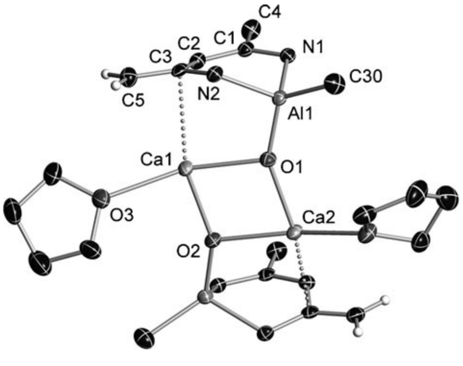

Figure 1. Core structure of [{L^{1}Al(Me)(μ-O)Ca(thf)}$_2$] (**7**); anisotropic displacement parameters are shown at the 50% probability level. Selected bond lengths [Å] and angles [°] of one half of a formula unit in the asymmetric unit: Al1–O1 1.740(2), Al1–N1 1.898(3), Al1–N2 1.900(3), Al1–C30 1.959(4), Ca1–O1 2.255(2), Ca1–O2 2.179(2), Ca1–O3 2.415(3), Ca1–C3 2.680(3), C3–C5 1.369(5); O1-Ca1-O2 82.47(9), O1-Al1-N2 104.24(12), N1-Al1-N2 98.14(13), Ca1-O1-Ca2 97.69(9), Ca1-O2-Ca2 97.26(9). Noncoordinating *n*-hexane molecules, substituents on the nitrogen atoms, and all hydrogen atoms (except those at C5 and C35) are omitted for clarity

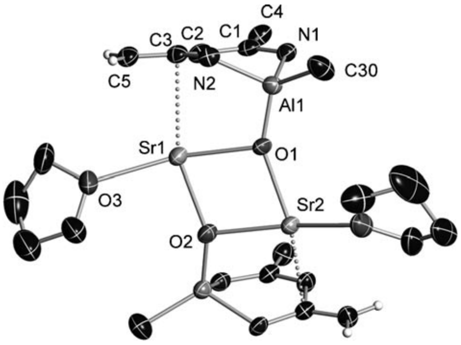

Figure 2. Crystal structure of [{L^{1}Al(Me)(μ-O)Sr(thf)}$_2$] (**8**); anisotropic displacement parameters are shown at a 50% probability level. Selected bond lengths [Å] and angles [°] of one half of a formula unit in the asymmetric unit: Al1–O1 1.729(3), Al1–N1 1.895(4), Al1–N2 1.906(4), Sr1–O1 2.391(3), Sr1–O2 2.324(3), Sr1–O3 2.567(3), Sr1–C3 2.787(4), C3–C5 1.348(7); O1-Sr1-O2 81.15(11), O1-Al1-N2 105.91(17), N1-Al1-N2 96.96(17), Sr1-O1-Sr2 98.89(12), Sr1-O2-Sr3 98.66(12). Noncoordinating THF molecules, substituents on the nitrogen atoms, and all hydrogen atoms (except those at C5 and C35) are omitted for clarity.

For a detailed understanding of the electronic structure and bonding properties of **7** and **8**, we performed ab initio density functional theory calculations as implemented in the Gaussian 03 package.[12] We have adopted a hybrid B3LYP[13] exchange and a correlation functional with the LANL2DZ[14] basis set. The molecular structures from the X-ray diffraction experiments served as the starting point for the calculations. Since the hydrogen atom positions from the X-ray structural determination are not comparable to the gas phase, we relaxed all the hydrogen atoms. The calculations for natural atomic orbitals (NAO) and natural bond order (NBO) were performed to investigate the charge localization, bonding, and hybridization characteristics of the structures under consideration.

We find that although the aluminum atoms of individual rings in both **7** and **8** are surrounded by two nitrogen atoms of the bidentate ligand L^1, one methyl carbon atom, and one oxygen atom in a slightly distorted tetrahedral fashion, the bonding characteristics of Al show a mixture of covalent and ionic characters with more contribution from the ionic part. This situation is evident from the localization of charges on the individual atoms (see the Supporting Information). The Wiberg bond order analysis also shows a diminished covalency of the bonds (Supporting Information). This ionic character can further be argued from the molecular orbital wave functions in Figure 3, which show the absence of delocalization over these bonds. However, the Ca_2O_2 or Sr_2O_2 rings in between two L^{1}Al moieties show complete ionic character with approximately +1.9 e charge on each of the

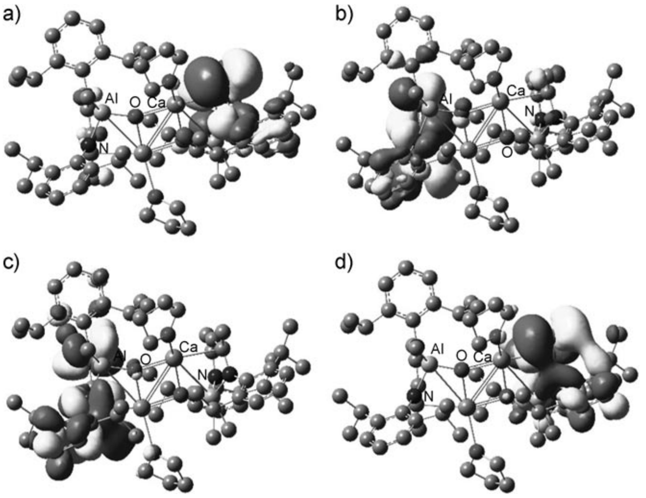

Figure 3. a) HOMO−1, b) HOMO, c) LUMO, and d) LUMO+1 of **7** with energies −4.49, −4.48, −0.14, and −0.11 eV, respectively. All hydrogen atoms are omitted for clarity. The corresponding MOs of **8** are given in the Supporting Information.

cations (Supporting Information). Interestingly, the reduction of the charge on the oxygen atoms (−1.6 instead of −2.0) indicates a charge transfer towards the Al atoms arising from their Lewis acidic character.[15] The oxygen atoms of the thf ligands reside within the coordination sphere of Ca^{2+}/Sr^{2+} cations solely owing to Coulombic attraction. For the same reason, the π-electron cloud of the methylene groups from the ligand backbones also come within bonding distance of the cations. These arguments are consistent with the NBO analysis as well (Supporting Information). A preference to delocalize electrons over the ligand backbones is observed (Figure 3). In fact, the experimental observations of single- and double-bond character in the terminal C−C bonds in the ligand backbones are consistent with the Wiberg bond order analysis (Supporting Information). Owing to the presence of the symmetric ligands on either side, the highest occupied molecular orbital (HOMO) becomes almost degenerate with the HOMO−1, as does the lowest unoccupied molecular orbital (LUMO) with the LUMO+1, as can be seen in Figure 3.

In summary, the reaction of aluminum methyl hydroxide **1** with $[M\{N(SiMe_3)_2\}_2(thf)_2]$ (M = Ca, Sr) gave the unprecedented heterobimetallic oxides **7** and **8** and reveals alkaline-earth-metal oxide in an organometallic matrix. Formation of these two complexes is accompanied by the deprotonation of one methyl group in the ligand backbone. The stability and good solubility of **7** and **8** are requirements for the application of these compounds in catalytic reactions, motivated by the recent finding of calcium compounds in hydroamination reactions.[16] Furthermore, detailed theoretical calculations suggest that the oxygen atoms of the thf ligands and the π-electron cloud of the methylene groups of the ligand backbone come within the coordination sphere of Ca^{2+}/Sr^{2+} cations to stabilize the Ca_2O_2/Sr_2O_2 clusters in the organic matrix through Coulombic attraction.

Received: July 22, 2009

Keywords: alkaline earth metals · calcium · hydroxides · oxides · strontium

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[10] a) Crystal data for **7**·0.85*n*-hexane: $C_{73}H_{114}Al_2Ca_2N_4O_4$, $M_r = 1246.90$, $0.10 \times 0.08 \times 0.06$ mm, triclinic, space group $P\bar{1}$, $a = 17.771(1)$, $b = 17.815(1)$, $c = 25.285(2)$ Å, $\alpha = 103.393(2)$, $\beta = 106.785(2)$, $\gamma = 90.117(2)^\circ$, $V = 7435.3(10)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.114$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 0.224$ mm^{-1}, $T = 100(2)$ K, $2\theta_{max} = 50^\circ$, 94970 reflections measured, 26248 independent ($R_{int} = 0.0593$), $R1 = 0.067$ ($I > 2\sigma(I)$), $wR2 = 0.184$ (all data), max. res. density peaks: 1.11 to −0.58 e Å^{-3}. b) Crystal data for **8**·1.7 THF: $C_{75}H_{116}Al_2N_4O_6Sr_2$, $M_r = 1391.31$, $0.2 \times 0.1 \times 0.1$ mm, monoclinic, space group *Cc*, $a = 25.915(1)$, $b = 25.999(1)$, $c = 23.384(1)$ Å, $\beta = 94.443(1)^\circ$, $V = 15708.5(7)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.177$ Mg m^{-3}, $\mu(Cu_{K\alpha}) = 2.377$ mm^{-1}, $T = 100(2)$ K, $2\theta_{max} = 120^\circ$, 81493 reflections measured, 21355 independent ($R_{int} = 0.0909$), $R1 = 0.041$ ($I > 2\sigma(I)$), $wR2 = 0.112$ (all data), max. res. density peaks: 1.20 to −0.55 e Å^{-3}. CCDC 739370 (**7**), 739371 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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