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Hexa-coordinated Strontium Silylamide Complex Stabilized by Tetradentate Alkoxy Ligand

Sheby Mary George,[†] Eun Ae Jung,[†] Hyo-Suk Kim,[†] Myoung Soo Lah,[‡] Bo Keun Park,[†]
Chang Gyoun Kim,[†,*] and Taek-Mo Chung[†,*]

[†]*Thin Film Materials Research Center, Korea Research Institute of Chemical Technology, Daejeon 34114,*
*Republic of Korea. *E-mail: cgkim@krict.re.kr; tmchung@krict.re.kr*
[‡]*Interdisciplinary School of Green Energy, Ulsan National University of Science and Technology,*
Ulsan 44919, Republic of Korea
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The heavier group 2 metal bis(trimethylsilyl)amides [M(btsa)$_2$; M = Mg, Ca, Sr, and Ba] are efficient catalysts for hydroamination reactions, but their extreme sensitivity to air and moisture makes them experimentally inconvenient. Therefore, the substitution of one btsa ligand of M(btsa)$_2$ for a sterically bulky amidinate or a β-diketiminate ligand was accepted as a worthy strategy for increasing the stability of the complex while retaining its reactivity.[1–6] The bulky amidinate and diketiminate ligands that are used to substitute one btsa group of M(btsa)$_2$ effectively stabilize smaller metal cations (Mg and Ca), whereas the bigger metal centers (Sr and Ba) have a propensity to assume a six-coordinated (rather than a three- or four-coordinated) state. This makes partially substituted heavier alkaline-earth metal amides far from stable for easy use, which reiterates the necessity of having a reasonably stable, partially substituted strontium bis(trimethylsilyl)amide for smooth handling while retaining its reactivity. Here we describe the synthesis of a dimeric strontium complex with six-coordinated metal centers, which contains two bis(trimethylsilyl)amides groups and two tetradentate alkoxide ligands.

The synthesis of the complex [Sr(mmmdo)(btsa)]$_2$ (**1**) consists of the careful substitution of one btsa ligand of [Sr(btsa)$_2$ · 2DME] (DME = dimethoxyethane) for 2-(methoxymethyl)-2-methyl-4,7-dioxa-1-octanolate (mmmdo) (Scheme 1). The product was obtained in a yield of 92%, and crystals suitable for X-ray diffraction were grown from a toluene solution at −30 °C. All previously reported partially substituted strontium bis(trimethylsilyl)amides display four- and five-coordinated metal centers due to the steric bulk of the ligands used to stabilize those complexes. In complex **1**, the tetradentate alkoxy ligand mmmdo proves to be highly coordinating, as it uses all four donor atoms. It is also compact enough to fit in the sterically demanding ligand environment that surrounds the metal center. The octahedral coordination of the metal centers shows that **1** is in the most stable form among these types of complexes, and the complete removal of DME indicates that the metal center is saturated.

Complex **1**

Scheme 1. Synthesis of complex **1**.

Single-crystal X-ray analysis shows that complex **1** crystallizes in the monoclinic space group *P*21/*n* and that it exists in the dimeric form (Figure 1). The two btsa groups occupy opposite ends of the molecule to minimize steric interactions, whereas the two mmmdo ligands cover the metal centers like umbrellas from the other sides, thus forming a stable structure. The complete utilization of all four donor atoms of the mmmdo ligands ensures that the metal centers are well protected. The alkoxy oxygens of the two mmmdo ligands bridge two strontium atoms to form the dimer. The strontium atoms in **1** are in a distorted octahedral environment, as the bond angles around Sr display large deviations from ideal octahedral geometry; this is primarily due to the bulky btsa groups. The distance between strontium and the btsa nitrogen atom (Sr1–N1) is 2.554(4) Å (Table 1), which is slightly longer than that found for similar complexes containing one btsa group ([{(^{i}Pr)$_2$ATI}Sr{N(SiMe$_3$)$_2$}(THF)$_2$)],[5] ((^{i}Pr)$_2$ATI = *N*-isopropyl-2-(isopropylamino)troponiminate) 2.482(3) Å; LSrN(SiMe$_3$)$_2$(THF) (L = CH(CMe-2,6-^{i}Pr$_2$C$_6$H$_3$N)$_2$),[7] 2.446(2) Å; and [Sr(demamp)(btsa)]$_2$,[8] 2.5012(15) Å). The metal–metal distance observed in **1** (3.7995(11) Å) is shorter than those in previously reported oxygen-bridged dinuclear strontium complexes [Sr$_2$(tmhd)$_4$(HOCH$_2$CH$_2$OMe)$_2$][9] (4.039(2) Å) and [Sr$_2$(tmhd)$_4$(dmaeH)$_2$(μ$_2$-dmaeH)$_2$] (dmae = *N*,*N*-dimethylaminoethanol)[10] (4.435(2) Å), whereas it is longer than the Sr···Sr distance of 3.7119(6) Å in [Sr(demamp)(tmhd)]$_2$.[8] A similarly substituted dimeric complex of strontium ([Sr(demamp)(btsa)]$_2$)[8] with five-coordinated metal centers shows a Sr···Sr distance of 3.8193(3) Å, which is similar to that found for **1**. The fact that the Sr—N bond length in **1** is comparable to those in similar complexes that are used as catalysts in hydroamination chemistry, as well as the rare six-coordination of the metal center, makes **1** an interesting compound in this field of chemistry.

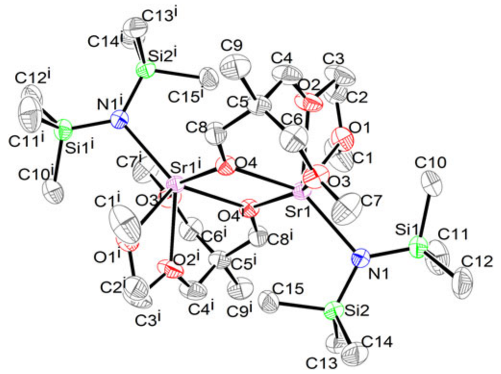

Figure 1. ORTEP diagram of complex **1**.

The ^1H NMR spectra of complex **1** show singlet peak for the two btsa groups at 0.44 ppm, which is a significant downfield shift from that of $Sr(btsa)_2.2DME$ where the btsa groups show peak at 0.32 ppm. The mmmdo $-CCH_3$ protons in **1** appear at 0.32 ppm, which displays large upfield shift from the free ligand where these protons resonate at 0.93 ppm. The methoxy protons of the mmmdo ligand in **1** resonate at 3.27 and 3.59 ppm, which are downfield shifts comparing to the free mmmdoH. The $-CCH_2O$ protons next to the assymetric center in mmmdo ligand in **1** display doublets of doublets for each of its protons similarly to those in mmmdoH but with large downfield shifts at 3.95 and 4.30 ppm, whereas the remaining $-CH_2-$ protons from the mmmdo in **1** appear as multiplets in the spectra and display an upfield shift compared to the free mmmdoH. The notable absence of $-OH$ peak in the spectra of **1**, which appears as triplet in free mmmdoH at 2.74 ppm, and considerable peak shifts in mmmdo ligand protons in **1** with respect to mmmdoH confirm that the reaction is complete and formation of **1** is successful. The absence of O–H peaks in the FT-IR spectra of **1** and presence of strong C–H peaks further supported the successful formation of complex **1**, whereas the microanalysis conducted on crude samples confirm the purity of **1**.

In conclusion, we have discovered a structurally interesting strontium complex, which has been obtained by the partial substitution of one of the amide groups of strontium bis(trimethylsilyl)amide for tetradentate alcohol (mmmdoH). The six-coordinated metal centers in **1** are expected to be more stable than the strained four- and five-coordinated metal centers in known partially substituted strontium bis(trimethylsilyl) amide complexes.

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Supporting Information. The structure file has been added to the Cambridge Structural Database as a CIF file under number CCDC 996428. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Selected bond lengths and Bond angles for **1**.

Bond lengths (Å)	
Sr(1)–O(4)	2.411(3)
Sr(1)–O(4)i	2.429(3)
Sr(1)–N(1)	2.554(4)
Sr(1)–O(2)	2.570(3)
Sr(1)–O(3)	2.603(3)
Sr(1)–O(1)	2.656(3)
Sr(1)···Sr(1)i	3.800(1)
Bond angles (°)	
O(4)–Sr(1)–O(4)i	76.6(1)
O(4)–Sr(1)–N(1)	140.7(1)
O(4)i–Sr(1)–N(1)	108.5(1)
O(4)–Sr(1)–O(2)	72.8(1)
O(4)i–Sr(1)–O(2)	114.2(1)
N(1)–Sr(1)–O(2)	131.7(1)
O(4)–Sr(1)–O(3)	74.2(1)
O(4)i–Sr(1)–O(3)	147.9(1)
N(1)–Sr(1)–O(3)	86.5(1)
O(2)–Sr(1)–O(3)	69.2(1)
O(4)–Sr(1)–O(1)	118.6(1)
O(4)i–Sr(1)–O(1)	85.6(1)
N(1)–Sr(1)–O(1)	100.6(1)
O(2)–Sr(1)–O(1)	62.4(1)
O(3)–Sr(1)–O(1)	120.3(1)

Electronic Supporting Information (ESI) for this paper includes detailed experimental, spectral, and structural details.

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