Unusual Reactivity of Silicon Grease Towards Metal Alkoxides: Serendipity for Structural Chemistry

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Dedicated to Professor Christoph Janiak on the Occasion of his 60th Birthday

Controlled synthesis of moisture sensitive metal alkoxides demands the use of silicon grease for the inert synthetic manipulation of starting materials using glass apparatus to avoid adventitious hydrolysis. Spontaneous reaction of the siloxane units (OSi(Me)2) with the synthesized alkoxides often leads to molecular metal alkoxides based siloxane frameworks. These spontaneous incorporation of siloxane units into homo- and heterometallic alkoxide building blocks lead to the formation of new multinuclear homo- and heterometallic alkoxide-siloxide compounds

\[ \text{[Ce}_2(\text{OiBu})_2(\text{Me}_2\text{Si}(\text{OiBu})\text{O})_2(\text{NO}_3)_2] \text{ (1),} \]
\[ \text{[Zr}((\text{OiPr})_2(\text{Me}_2\text{Si}O)_2\text{Sr}(\text{Zr}((\text{OiPr})_2)_2) \text{ (2) and} \]
\[ \text{[Sn}(_3\text{Ir}_2\text{O}_3)(\text{Me}_2\text{Si}((\text{OiPr})_2) \text{O})((\text{OiPr})_2)_2] \text{ (3). Multifunctional coordination properties of these siloxane units enable the molecular approach to synthetically demanding polymetallic complexes for potential MO}_2\text{SiO}\text{ nanocomposites fabrication.} \]

Introduction

The fundamental interest in nanostructured materials with well-defined size, morphology and composition is a persisting driving force for the developments in chemical processing of new materials, which demands new precursors with multielemental compositions for specific material preparation. In recent years, enormous efforts have been made in the construction of heterometal alkoxides, which display the target material composition already at the molecular level.[1–20] These molecular control of synthesized complexes offer the possibility of single-source precursor fabrication for target ternary and quaternary phase preparation.[1–20] Metal alkoxides are versatile precursors for oxide-ceramics largely due to their unique structural diversity, intrinsic propensity towards hydrolysis, presence of preformed strong M–O bonds and defined decomposition mechanism.[2,11,12] The preparation of mixed-metallic complexes with pre-defined metal ratio appropriate for the desired materials synthesis (e.g., [MgAl2(OR)3] for MgAl2O4, R=Bu, iPr)[20] is often not a straightforward preparative task, and strongly influenced by different parameters like chosen ligands, reaction temperatures, solvents and combined metal.[2,11,12] In particular, the synthesis of heterotrimetallic alkoxides with structurally characterized compounds limited to [{Cd(OiPr)3}M2(M2(OR)3)3, M=Sn, Pb; M=Ti, Zr, Hf][21–26] [{M(OR)3}2(HOiPr)Ba [{M(OR)3}(M=Al, Ga; M=Hf; M=Zr)][25] and [{EuK3TiO4(OiBu)2}(OMe/OH)(HOiBu)][26] is nearly an unexplored field.

The ability of dimethylsiloxo groups (Me2SiOR) to act as chelating as well as bridging ligands makes them attractive reagents for connecting several metal centers. Furthermore, these bridging ligands offer a reliable connection between different sort of metal centers, forming multinuclear species. The formation of isolated structure motives is initialize by the chemical activation of the Si–O bond as well as the chemical nature and the steric profile of the R group of the corresponding dialkylalkoxo groups, that influence the polarity and reactivity of the Si–O bond.[27–38] Hetero- and monometallic siloxanes, containing the anionic ligands \([R_3\text{SiO}]^-, [R_2\text{SiO}]^2-, [R_3\text{SiO}O]_3^-, [R_3\text{SiO}]^-, \text{ etc., constitute an important class of compounds due to their potential applications in catalysis and material science.}\)[39–42] In addition, the ability of stabilizing reduced early transition metal centers is known for silica crown ether compounds.[43]

The incorporation of siloxane ligands with their ability to bridge different metal centers facilitate the formation of multinuclear metal alkoxide-siloxide complexes as observed in accidently synthesized siloxide compounds based on an incorporated monomeric or oligomeric dimethylsiloxane unit \(\text{[Me}_2\text{SiO}]_n\).[38,44] The partial solubility of silicone grease in organic solvents is a well-known evil in laboratory routine that in some cases can act as a source of structural bananza by forming heteroleptic compounds with alkoxo- and siloxo-units.[38–40,46–48] The possible in-situ activation of silicon grease enables the formation of polymeric dimethylsiloxane or cyclic siloxanes that can react with homoleptic metal alkoxides. Several cases of participation of silicone grease in a number of...
reactions have been reported so far,\textsuperscript{38,45} however only few reports for the incorporation of grease fragments in the molecular structure of metal alkoxides have been published before.\textsuperscript{47–49} The already structurally characterized examples include the monometallic polymer $[\text{Ti}_2\{\text{Me}_2\text{SiO}\}_2\text{O}]_{10}^{19}$ which contains a dinuclear, dianionic $[(\text{R})\text{SiO}_2\text{O}]^{2-}$ unit, and the heterobimetallic complex $[\text{V}\text{Li}_2\text{O}_6\text{ONep}_2\text{SiMe}_2\text{ONep}]_2$ (Nep = Neopentyl).\textsuperscript{50} In the latter case, the formation of the siloxide complex was described to occur via nucleophilic addition of the lithium alcoholate at the siloxane accompanied by the generation of a $(\text{Me}_2\text{SiONep})\text{O}^{-}$ unit followed by segregation of the distinctive metallic species.

In this work, synthesis and structural characterization of three new mono (Ce)- and heterobimetallic (Zr–Sr, In–Sn) metal alkoxides, stabilized by adventitious incorporation of dimethylsiloxane units, is described. The unintended integration of the chelating groups $(\text{Me}_2\text{Si}(\text{R})\text{O})^{-}$ $(\text{R}=\text{OtBu}, \text{OiPr})$ and $(\text{Me}_2\text{SiO})^{2-}$ in the organometallic framework resulted in the isolation of new structural motifs, which provides impetus for the design of new heterometallic compounds.

Results and Discussion

The dimeric complex $[\text{Ce}_2\text{OtBu}_2\{\text{Me}_2\text{Si(OtBu)}\}_2\{\text{NO}_3\}_2]$ (1) was obtained either by the reaction of cerium(IV) ammonium nitrate (CAN) with 6 equiv of KOTBu or by the attempted synthesis of the bimetallic alkoxide $[\text{SnCe(OtBu)}_2]_2$\textsuperscript{50} starting from CAN, 2 equiv of $[\text{Na}_2\text{Sn(OtBu)}_2]$ and NaOTBu. Both syntheses were performed in THF, which is known to dissolve low-oligomeric fragments of silicon grease such as the cyclic compounds octamethylcyclotetrasiloxane $(\text{Me}_8\text{SiO}_4)$ and hexamethyldicyclosiloxane $(\text{Me}_6\text{SiO})_2$\textsuperscript{41}. The formation of the $(\text{Me}_2\text{Si}-(\text{OtBu})\text{O})^{-}$ anion, observed in the molecular structure 1, could be described as an insertion of the dimethylsiloxane unit $(\text{Me}_2\text{SiO})$ in an $M$–OtBu-bond. A possible mechanistic pathway would include the nucleophilic attack of alkali-metal tert-butoxide on the silicon centers followed by an incorporation of the silanolate group in the rare earth metal complex via a salt elimination reaction (Figure 1).

The centrosymmetric, heteroleptic cerium(IV) siloxide crystallized in the monoclinic space group $C 2/c$ (No. 15, Table 1) with four molecules in the unit cell. Both lanthanide centers exhibit pentagonal bipyramidal coordination geometry and were linked via one common edge with inversion center lying in the middle of the central Ce-O$_2$ ring (Figure 2). The metal atoms are bridged by the o xo-functions of the silico ligands with an intermetallic distance of 3.864(9) Å, comparable with the cerium-cerium distance in the dimeric alkoxides.

![Figure 1](image1.png)

**Figure 1.** Postulated mechanism of the formation of $[\text{M}(\text{Me}_2\text{Si(OtBu)}\text{O})]$ unit $(\text{M}=\text{Na}, \text{K})$ by the reaction of $[\text{M(OtBu)}]$ $(\text{M}=\text{Na}, \text{K})$ with dissolved low-oligomeric fragments of silicon grease in THF and the synthesis of $[\text{Ce}_2\text{OtBu}_2\{\text{Me}_2\text{Si(OtBu)}\}_2\{\text{NO}_3\}_2]$ (1).

![Figure 2](image2.png)

**Figure 2.** Molecular structure of 1 (hydrogen atoms are omitted for clarity). Selected lengths (Å) and angles (deg): Ce–O1 2.037(4), Ce–O2 2.039(4), Ce–O3 2.280(4), Ce–O4 2.569(4), Ce–O5 2.516(5), Ce–O6 2.543(4), Ce–Ce 3.864(9), O1–Ce–O2 157.4(2), O3–Ce–O4 59.2(1), O3–Ce–O3’ 69.5(2), O5–Ce–O6 50.1(2), O4–Ce–O6 105.5(2).
[Ce(ORBu)$_3$][51] and [Ce(OCMe$_2$)$_3$Pr)$_2$][52]. In order to prevent unfavorable inter-ligand repulsions of the sterically crowded tert-butoxide groups on both sides of the bridge an asymmetric bridging motive with one short (2.280(4) Å) and one elongated Ce–O bond (2.421(4) Å) is formed which is further manifested in the small Ce–O–C and O–Ce–O angles of the trans standing alkoxo ligands. Together with the bridging oxygen atoms, the tert-butylin function of one siloxy group and one nitrato ligand constitute the nearly planar pentagonal base of the coordination polyhedron. The interplanar bond angles showed significant deviation from the ideal value caused by restrictions, that are induced by the bite angle of the bidentate ligands and the compulsion of the edge sharing structural motive. The Ce–O bond lengths of the alkoxo and nitrato ligands are in good agreement with the distances observed for other cerium nitrato alkoxo complexes.

The reaction of [(F$_2$C)$_2$Cd(Zr$_2$(OPr)$_9$))][54] with [Sr(OPr)$_3$][56] resulted in the isolation of the bimetallic alkoxide [Zr$_2$(OPr)$_9$][Me$_2$SiO$_2$]Sr(Zr$_2$(OPr)$_9$)][56] (2). The preferred incorporation of the strontium atom into the [Zr$_2$(OPr)$_9$] subunit was also observed in this structural motive. The insertion of [Me$_2$SiO$_2$]$^2$ units[44] into the metal alkoxide framework resulted in the formation of an inorganic SiSrO$_2$-ring, whereas the bidentate siloxo ligands bridged the different metal centers via the electron rich oxo-functions. The formed [Sr(Me$_2$SiO$_2$)] units seem to promote the nucleophilic attack of alkali earth metal iso-propoxide onto the silicon centers resulting in molecular structure 2 (Figure 3).

The NMR spectroscopic analysis of multinuclear alkoxides with more sterically demanding alkoxide functions like isopropano is always challenging because of the strong overlapping of the terminal and bridging methine and methyl protons and carbons, making NMR analysis not the preferred analysis method. Single crystals of compound 2 suitable for X-ray diffraction analysis were obtained from a solution of toluene kept at −18 °C. 2 crystallized in the triclinic space group P T (No. 2, Table 1) with two molecules per unit cell. This heptanuclear compound consisted of two [Sr(Zr$_2$(OPr)$_9$)]$^2$ units, which were bridged by one [Zr(OPr)$_8$][Me$_2$SiO$_2$]$^3$ fragment (Figure 4). All zirconium atoms were distorted octahedrally coordinated, whereas the coordination sphere of the strontium atoms represented a capped octahedron. The octahedron of the central zirconium atom of the [Zr(OPr)$_8$][Me$_2$SiO$_2$]$^3$ unit shows a slightly distortion of cis angles about 83.1(2)–98.1(2)° and trans angles of 177.5–177.9(2)°. The Zr–O bond lengths in the [Sr(Zr$_2$(OPr)$_9$)]$^2$-subunit showed the expected order Zr–O$_{terminal}$ < Zr–O$_{cis}$ < Zr–O$_{trans}$ O < Zr–μ$_2$O < Zr–μ$_3$O. The Sr–O distance of the bridging iso-propoxo ligands was significantly shorter than the Sr–O bond length of the dimethylsiloxo group, which can be attributed to the poor donor properties of the siloxane oxygen atoms.[57,58]

A ligand-exchange reaction based on concomitant alcoholysis of individual metal silylamides was examined as a potential synthetic route to heterometallic alkoxides.[11,12,16,18,19,59-64] The heterometallic compound [Sn$_4$In$_4$O$_2$][Me$_2$Si(O)OPrO]OPr$_3$$_2$ (3)
obtained by the alcoholysis of \([\text{In}\{\text{N(SiMe}_3)_2\}_3]\) and \([\text{Sn}\{\text{N-(SiMe}_3)_2\}_2\}_2]\) produced the oxo-alkoxide \([\text{O(iPr)}_2\text{In}\{\text{Me}_2\text{Si(O(iPr)}_2\}O}\]) that is probably formed by the insertion of \text{Me}_2\text{SiO} into the \(\text{O(iPr)}\)\text{In(O(iPr)}_2\) bond (Figure 5). In contrast to 1 and 2, the \{\text{Me}_2\text{Si(O(iPr))O}\}^{-} anion is present in a terminal position.

The metal oxo-alkoxide \([\text{Sn}_2\text{In}_2\text{O}_2\{\text{Me}_2\text{Si(O(iPr))O}\}{\text{O(iPr)}_2}\}_{2}\) crystallized in a monoclinic crystal system (space group \(P2_1/c\), Table 1) with two molecules per cell unit (Figure 6). The formation of an oxo species could be explained by ether elimination, which was observed for other metal alkoxides such as \([\text{In}_2\{\mu_2\text{-O}\}\{\mu_2\text{-O(iPr)}_2\}_2\{\mu_2\text{-O(iPr)}_2\}O\text{O(iPr)}_2\}_{2}\)\(^{6,5,6}\).

The \text{In}2 metal center with one coordinated \{\text{O(iPr)}_2\text{In}\{\text{Me}_2\text{Si(O(iPr)}_2\}O}\}^{-} unit is connected with two other indium and tin atoms through two oxygen atoms (\(\mu_2\text{-O}\) and \(\mu_4\text{-O}\)) and three \(\mu\text{-O(iPr)}\) ligands in a distorted octahedral coordination. Whereas the indium atoms are six-fold coordinated building face-sharing octahedral coordination sphere, the bivalent pseudo tetragonal tin centers are coordinated by three oxygen atoms, one \(\mu_3\text{-O}\) atom and two \(\mu_4\text{-O(iPr)}\) ligands, which is typically observed for bivalent group 4 cations. Indium oxygen bond lengths for \{\text{OSiMe}_2\text{O}\text{iPr)}_2\}_{2}\) octahedron showed following order: \text{In}2\text{-O terminal < In2\text{-O}_{\text{metallic}} < In2\text{-O}_{\text{metallic}} < In2\text{-O}_{\text{metallic}}\}_{2}\) with \text{In}2\text{-O bond length of (OSiMe}_2\text{O(iPr)}_2\}_{2}\) group being the shortest (2.032(9) Å), whereas the longest bond distance was observed for \text{In}2\text{-O}_{\text{metallic}}\text{-O (for }\mu_3\text{ 2.112(6) Å and }\mu_4\text{ 2.280(9) Å).}
To illuminate the coordination of \( \text{Me}_2\text{SiO} \) units, provided by grease in synthesis reaction with metal alkoxides, systematic activation of dimethylsiloxane and silicon grease with different reaction conditions have been performed. The hydrolysis of dimethylsiloxane was tried to initialize by the addition of alcohol in acidic as well as alkaline conditions in CAN solutions. In addition, the reaction time (60 h) and temperature (reflux) were increased to enhance the implementation of the siloxane unit. All reaction products were analyzed by \( ^{29}\text{Si} \) NMR spectroscopy (Supporting Information, Figure S1), showing no shifting and therefore no incorporation of the dimethylsiloxane group in the metal complexes, respectively. That indicates that the formation of the mentioned compounds 1–3 was only observed in the solid structure to verify the stability of the compounds by the coordination of the \( \text{Me}_2\text{SiO} \). Therefore, the chemical activation and implementation of dimethylsiloxane in metal alkoxides seems to be initialized by metal rearrangement of heterometallic compounds and long-time crystallization processes. The unexpected formation of alkoxide-siloxide offers the accessibility to unique molecular structure motives, however,
the direct synthesis route is quite challenging although it was reported before.\[38\]

## Materials and Methods

All reactions were performed under nitrogen atmosphere using a modified Stock vacuum line taking utmost precautions to prevent adventitious hydrolysis. All glass equipment were stored in a drying oven at 140 °C before use and were heated in vacuum additionally to remove finally all impurities of adherent moisture. Solvents were purified by reported methods.\[39\] Poly(dimethylsiloxane) was used without further purification (i.e. DESil, Aldrich); Cerium(IV) ammonium nitrate (CAN, (NH\(_4\))\(_2\).Ce(NO\(_3\))\(_6\), Aldrich, 98.5%) was dried in dynamic vacuum for 7 hours; KOtBu and [Sr(OiPr\(_2\))\(_4\)] were synthesized by dissolving the metal in a mixture of toluene and the corresponding alcohol (tert-buty alcohol or iso-propyl alcohol); KOtBu was purified by vacuum sublimation. The amides [In(N(SiMe\(_3\))\(_2\))\(_2\)] and [Sn(N(SiMe\(_3\))\(_2\))\(_2\)] were synthesized following published procedures.\[58,60\]

\(^1\)H (300.1 MHz) and \(^{29}\)Si (59.6 MHz) chemical shifts are reported in parts per million (ppm) relative to external tetramethylsilane references. Microanalysis for C, H, N and S were carried out using a Hekatek CHNS EuroEA 3000 Analyzer with Helium as carrier gas. Data collection for X-ray crystal structure determination were performed on a STOE IPDS II diffractometer using graphite-monochromated Mo-K\(_\alpha\) radiation (\(\lambda = 0.71073\) Å). The data were corrected for Lorentz and polarization effects. A numerical absorption correction based on crystal-shape optimization was applied for all data.\[39\] The programs used in this work are Stoe’s X-AREA,\[52\] including X-RED and X-Shape for data reduction and absorption correction\[53\] and the WinGX suite of programs\[54\] including SIR-92\[55\] and SHELXL-97\[56\] for structure solution and refinement. The hydrogen atoms were placed in idealized positions and constrained to ride on their parent atom. The last cycles of refinement included atomic positions for all atoms, anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms. Graphics for publication were prepared using DIAMOND.\[50\]

### Reaction of KOTBu, (NH\(_4\))\(_2\).Ce(NO\(_3\))\(_6\), and (Me\(_2\)SiO\(_3\)) in acidioc solution

To a solution of 0.64 g (1.2 mmol) Cerium ammonium nitrate [(NH\(_4\))\(_2\).Ce(NO\(_3\))\(_6\)] in 15 mL THF a solution of 0.75 g (6.72 mmol) KOTBu in THF was added and the resulting yellow solution was separated from the white precipitate by decantation. An excess of (Me\(_2\)SiO\(_3\)) (0.32 g), 5 mL ethanol and 5 mL hydrochloric acid were added. After stirring overnight, the solution was evaporated to dryness under reduced pressure (10\(^{-3}\) mbar) to obtain a dark yellow solid. \(^{29}\)Si–NMR (benzene-d\(_6\), 298 K, 59.6 MHz) \(\delta/\text{ppm}:-21.8\).

### Reaction of KOTBu, (NH\(_4\))\(_2\).Ce(NO\(_3\))\(_6\), and (Me\(_2\)SiO\(_3\)) for 60 h at room temperature

To a solution of 0.48 g (0.8 mmol) Cerium ammonium nitrate [(NH\(_4\))\(_2\).Ce(NO\(_3\))\(_6\)] in 15 mL THF a solution of 0.59 g (5.2 mmol) KOTBu was added and the resulting yellow solution was separated from the white precipitate by decantation. An excess of (Me\(_2\)SiO\(_3\)) (0.27 g) was added as well as and after stirring for 60 h the solution was evaporated to dryness under reduced pressure (10\(^{-3}\) mbar) to obtain a dark yellow solid. \(^{29}\)Si–NMR (benzene-d\(_6\), 298 K, 59.6 MHz) \(\delta/\text{ppm}:-21.8\).

### Reaction of KOTBu, (NH\(_4\))\(_2\).Ce(NO\(_3\))\(_6\), and (Me\(_2\)SiO\(_3\)) under reflux. To a solution of 0.41 g (0.7 mmol) Cerium ammonium nitrate [(NH\(_4\))\(_2\).Ce(NO\(_3\))\(_6\)] in 15 mL THF a solution of 0.50 g (4.4 mmol) KOTBu was added and the resulting yellow solution was separated from the white precipitate by decantation. An excess of (Me\(_2\)SiO\(_3\)) (0.23 g) was added as well as and after stirring at 60 °C overnight, the solution was evaporated to dryness under reduced pressure (10\(^{-3}\) mbar) to obtain a dark yellow solid. \(^{29}\)Si–NMR (benzene-d\(_6\), 298 K, 59.6 MHz) \(\delta/\text{ppm}:-21.8\).

### Reaction of [F\(_2\)C\(_6\)].Cd(Zr\(_{2}\)(OiPr\(_2\)))\(_2\) and [Sr(OiPr\(_2\))\(_4\)]

0.50 g (0.53 mmol) [F\(_2\)C\(_6\)].Cd(Zr\(_{2}\)(OiPr\(_2\)))\(_2\) were dissolved in 10 mL toluene and 0.16 g (0.78 mmol) [Sr(OiPr\(_2\))\(_4\)] in toluene (4 mL) were added. After stirring over night at room temperature all volatiles were removed under reduced pressure (10\(^{-3}\) mbar) and the product (2) was obtained as a light yellow solid.

### Reaction of [In(N(SiMe\(_3\))\(_2\))\(_2\)] and [Sn(N(SiMe\(_3\))\(_2\))\(_2\)]

0.13 g (0.23 mmol) [In(N(SiMe\(_3\))\(_2\))\(_2\)] and [Sn(N(SiMe\(_3\))\(_2\))\(_2\)] in 10 mL toluene was added to a solution of 0.10 g (0.23 mmol) [In(N(SiMe\(_3\))\(_2\))\(_2\)] in 10 mL toluene. After the addition of 5 mL of dry iso-propyl alcohol the colorless solution was stirred overnight at 70 °C. All volatiles were removed under reduced pressure (10\(^{-3}\) mbar) and the product (3) was obtained as colorless crystals from a solution in toluene.

## Conclusions

This paper reports the structural investigations of alkoxide-siloxide complexes of tetravalent cerium, zirconium and trivalent indium serendipitously formed in the adventitious reaction of the starting materials with silicon grease used for lubricating the glass joints. The unexpected incorporation of the dimethylsiloxane units (Me\(_2\)Si(OR))\(_2\) (R=Pr, tBu) and (Me\(_2\)SiO\(_3\)) in the molecular structures of mono- and heterobimetallic alkoxides opened up new insights in the broad spectrum of possible heteroleptic polymeric coordination compounds that can act as model intermediates in co-hydrosythesis of metal alkoxides and siloxides involved in the sol-gel processing of MO<sub>x</sub>-SiO<sub>y</sub> nanocomposites. The targeted synthesis of such complexes out of defined molecular educts
such as cyclic siloxanes (Me$_2$SiO)$_n$ and (Me$_2$SiO)$_4$ can lead to new synthetic rationale for mixed-metal alkoxide siloxides. In contrast, the target implementation of (Me$_2$SiO) units into metal alkoxide complexes is a challenging process, which seems to be influenced by equilibrium processes whereby slow reaction and long-term crystallization processes resulting in unique alkoxide-siloxide complexes. However, these findings also point at the necessity of precautions that must be taken, when using silicon grease during the synthesis of metal organic compounds containing polar metal-ligand bond.

Supplementary Materials

These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC 994695, 994696 and 2047810) via www.ccdc.cam.ac.uk/data_request/cif.

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