

Si–O–based inorganic ring systems containing f-elements: structural characterization of novel siloxanediolates of the lanthanides and actinides†

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Depending on the reaction conditions and the ionic radius of the lanthanide ion, tetraphenyldisiloxanediol, $(\text{Ph}_2\text{SiOH})_2\text{O}$, reacts with $[\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}_3\{\text{LiCl}(\text{thf})_3\}_3]$ ($\text{Ln} = \text{Eu}, \text{Gd}, \text{Sm}$) to afford novel heterobimetallic rare earth disiloxanediolates, some of which can be regarded as 'inorganic lanthanide metallocenes'; a ring expanded uranium(vi) derivative, $[\text{U}\{\text{Ph}_2\text{Si}(\text{OSiPh}_2\text{O})_2\}_2\{(\text{Ph}_2\text{SiO})_2\text{O}\}]$ **4**, is formed upon treatment of uranocene, $[\text{U}(\eta^8\text{-C}_8\text{H}_8)_2]$, with $(\text{Ph}_2\text{SiOH})_2\text{O}$.

The chemistry of metallasiloxanes derived from silanediols, disiloxanediols and related Si–OH species is an area of active research¹ because such compounds are valuable precursors for metal oxides and silicates^{2,3} as well as models for silica-supported heterogeneous catalysts.^{1,4,5} A particularly useful ligand is the tetraphenyldisiloxanediolate dianion, $[(\text{Ph}_2\text{SiO})_2\text{O}]^{2-}$, which gives rise to a variety of unusual and unexpected structures especially when combined with alkali metals⁶ and early transition metals.^{2b,6,7} Apparently this ligand has not yet been employed in f-element chemistry, with $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{thf})(\mu\text{-OSiMe}_2\text{OSiMe}_2\text{O})\text{Sm}(\text{C}_5\text{Me}_5)_2(\text{thf})]^{18}$ being the only closely related rare earth siloxane derivative. We report here the synthesis of novel lanthanide and uranium complexes derived from $[(\text{Ph}_2\text{SiO})_2\text{O}]^{2-}$.

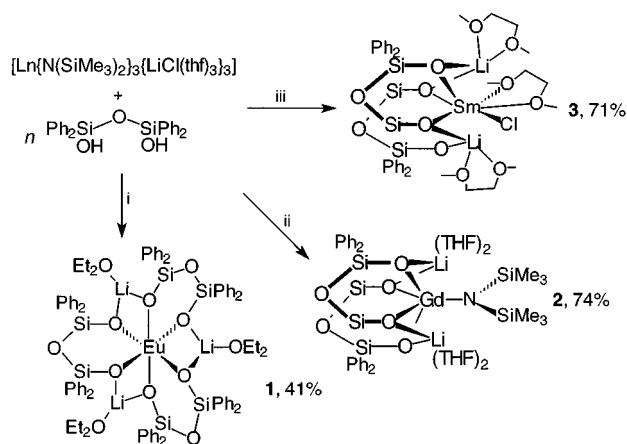
Treatment of $[\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}_3\{\text{LiCl}(\text{thf})_3\}_3]$ ($\text{Ln} = \text{Eu}, \text{Gd}, \text{Sm}$) (prepared from LnCl_3 and 3 equiv. of $\text{LiN}(\text{SiMe}_3)_2$ in thf solution⁹) with $(\text{Ph}_2\text{SiOH})_2\text{O}$ ¹⁰ in different stoichiometries afforded the new lanthanide disiloxanediolates **1–3** (Scheme 1). The use of *in situ* prepared lanthanide silylamide reagents in order to maintain the necessary high Li ion concentration is

essential for the success of the preparations. The colorless crystalline solids have been fully characterized by elemental analyses, spectroscopic data and X-ray crystallography.[§]

The X-ray structure of **1** (Fig. 1) shows a heterobimetallic metallasiloxane, in which the central Eu ion is octahedrally surrounded by three mono-anionic chelating $(\text{Et}_2\text{O})\text{Li}\{(\text{Ph}_2\text{SiO})_2\text{O}\}^-$ units.

The molecular structures of **2** and **3** (Figs. 2 and 3) are especially remarkable. Both complexes are disubstituted lanthanide metallasiloxanes comprising two lithium disiloxanediolate ligands while retaining one functional ligand [Cl or $\text{N}(\text{SiMe}_3)_2$, respectively]. The latter should make these compounds susceptible for further reactions. It is noteworthy that the outcome of these preparations depends not only on the stoichiometry but also on the size of the Ln^{3+} ion (Gd vs. Sm). In each case the coordination sphere of lithium is completed by addition of solvent molecules. The most striking feature of the gadolinium and samarium complexes, however, is their similarity with certain lanthanide metallocenes such as $(\text{C}_5\text{Me}_5)_2\text{LnN}(\text{SiMe}_3)_2$ ¹¹ (*cf.* **2**) or $(\text{C}_5\text{Me}_5)_2\text{LnCl}(\text{thf})$ ¹² (*cf.* **3**). There is only one other report on Li-containing anionic ligands formally replacing the cyclopentadienyls in lanthanide metallocenes, *i.e.* the $[(\text{dad})\text{Li}]^-$ units ($\text{dad} = 1,4\text{-diazadiene dianion}$).¹³ It can be anticipated that the lithium disiloxanediolate units in the 'inorganic lanthanide metallocenes' **1–3** are quite robust spectator ligands owing to the presence of only Ln–O bonds.

For the synthesis of a related uranium cyclometallasiloxane the long-known sandwich complex uranocene, $[\text{U}(\eta^8\text{-C}_8\text{H}_8)_2]$,¹⁴ was chosen as soluble starting material. Replacement of both cyclooctatetraenyl ligands upon treatment with an excess of $[(\text{Ph}_2\text{SiOH})_2\text{O}]$ (an unprecedented reaction pathway



Scheme 1 Synthesis of complexes **1–3**. Reagents and conditions: i, $\text{Ln} = \text{Eu}$, $n = 3$, toluene– Et_2O ; ii, $\text{Ln} = \text{Gd}$, $n = 2$, thf; iii, $\text{Ln} = \text{Sm}$, $n = 2$, DME (four phenyl groups in **2** and **3** have been omitted for clarity).

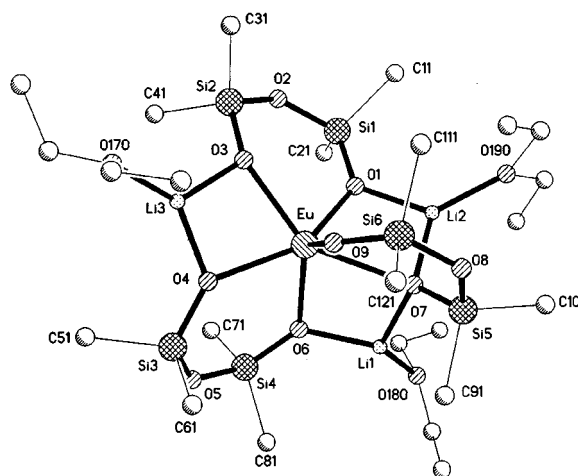


Fig. 1 Molecular structure of complex **1**

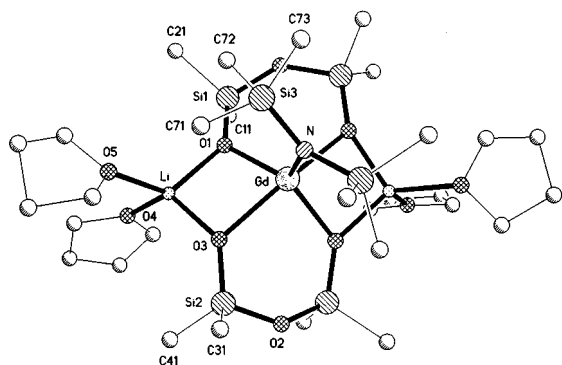


Fig. 2 Molecular structure of complex 2

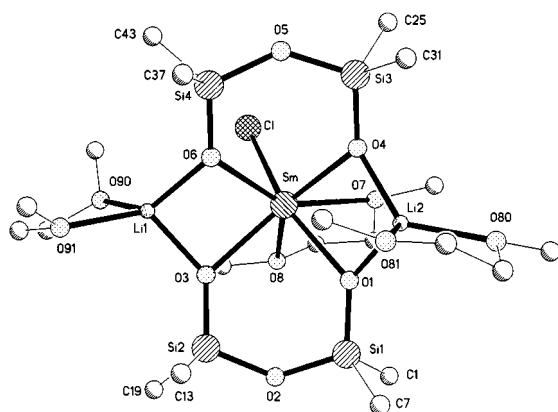


Fig. 3 Molecular structure of complex 3

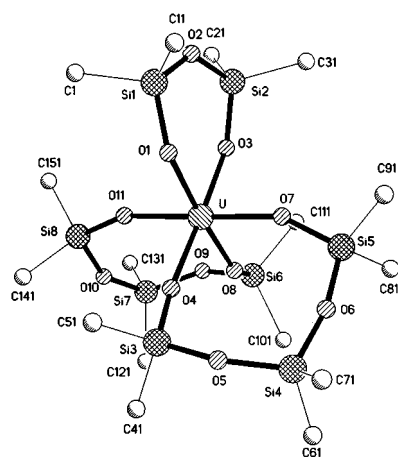


Fig. 4 Molecular structure of complex 4

for uranocene) resulted in the formation of colorless $[U\{Ph_2Si(OSiPh_2O)_2\}_2\{(Ph_2SiO)_2O\}]$ **4** in 80% yield.

An X-ray structure analysis (Fig. 4) revealed the presence of a hexacoordinated uranium(VI) cyclometallosiloxane containing expanded trisiloxanediolate chelating ligands. This type of ring expansion has been reported earlier and studied in detail by Sullivan and coworkers.^{7c} However, compound **4** represents the first example of a mixed-ligand complex containing both the ring expanded ligand and the original tetraphenyldisiloxanediolate dianion.

We conclude that siloxanediolate ligands derived from $(Ph_2SiOH)_2O$ are interesting new spectator ligands for f-elements which in the case of the lanthanides make inorganic analogues of synthetically useful lanthanide metallocenes available.

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Notes and References

† Dedicated to Professor Michael F. Lappert, as a mark of friendship and respect, on the occasion of his 70th birthday.

§ Crystal data: The measurements on **1**, **3** and **4** were performed at -100°C using a Siemens SMART CCD diffractometer with Mo-K α X-radiation ($\lambda = 0.71073\text{ \AA}$). The data on **2** were collected on a Siemens P4 diffractometer at -100°C .

1: $C_{84}H_{90}EuLi_3O_{12}Si_6$, $M = 1632.88$, triclinic, space group $P\bar{1}$, $a = 13.6639(2)$, $b = 14.5015(2)$, $c = 24.234(2)\text{ \AA}$, $\alpha = 83.541(2)$, $\beta = 86.713(2)$, $\gamma = 61.980(2)^\circ$, $U = 4222.28(7)\text{ \AA}^3$, $Z = 2$, $D_c = 1.284\text{ Mg m}^{-3}$, $F(000) = 1692$, $\mu(\text{Mo-K}\alpha) = 0.885\text{ mm}^{-1}$. 51 321 reflections, of which 20 536 were independent ($R_{\text{int}} = 0.039$). $R1 = 0.0394$ (conventional) and $wR2 = 0.0939$ (all data), with goodness of fit = 1.065 (SHELXTL software).¹⁵

2: $C_{70}H_{90}GdLi_2NO_{10}Si_6$, $M = 1445.10$, monoclinic, space group $C2/c$, $a = 22.2584(12)$, $b = 14.4469(8)$, $c = 23.486(2)\text{ \AA}$, $\beta = 106.427(6)^\circ$, $U = 7244.0(7)\text{ \AA}^3$, $Z = 4$, $D_c = 1.325\text{ Mg m}^{-3}$, $F(000) = 3004$, $\mu(\text{Mo-K}\alpha) = 1.070\text{ mm}^{-1}$. 13 420 reflections, of which 6377 were independent ($R_{\text{int}} = 0.035$). $R1 = 0.0295$ (conventional) and $wR2 = 0.0726$ (all data), with goodness of fit = 0.980 (SHELXTL software).¹⁵

3: $C_{60}H_{70}ClLi_2O_{12}Si_4Sm$, $M = 1295.20$, monoclinic, space group $P2_1/c$, $a = 17.34960(10)$, $b = 17.3002(2)$, $c = 21.2440(3)\text{ \AA}$, $\beta = 98.133(1)^\circ$, $U = 6312.29(12)\text{ \AA}^3$, $Z = 4$, $D_c = 1.363\text{ Mg m}^{-3}$, $F(000) = 2668$, $\mu(\text{Mo-K}\alpha) = 1.106\text{ mm}^{-1}$. 36 094 reflections, of which 12 814 were independent ($R_{\text{int}} = 0.040$). $R1 = 0.0564$ (conventional) and $wR2 = 0.1450$ (all data), with goodness of fit = 1.118 (SHELXTL software).¹⁵

4: $C_{106}H_{106}N_2O_{12}Si_8U$, $M = 2062.68$, monoclinic, space group Cc , $a = 25.0349(5)$, $b = 14.6569(2)$, $c = 29.4351(5)\text{ \AA}$, $\beta = 109.869(1)^\circ$, $U = 10157.8(3)\text{ \AA}^3$, $Z = 4$, $D_c = 1.349\text{ Mg m}^{-3}$, $F(000) = 4224$, $\mu(\text{Mo-K}\alpha) = 1.752\text{ mm}^{-1}$. 34 298 reflections, of which 16 973 were independent ($R_{\text{int}} = 0.023$). $R1 = 0.0258$ (conventional) and $wR2 = 0.0597$ (all data), with goodness of fit = 1.07 (SHELXTL software).¹⁵ CCDC 182/998.

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