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Heterobimetallic uranyl(VI) alkoxides of lanthanoids: formation through simple ligand exchange†

Dennis Grödler,[a] Martin L. Weidemann,[b] Andreas Lichtenberg,[a] Tobias Greven,[a] Robin Nickstadt,[a] Malek Haydo,[a] Mathias Wickleder,[a] Axel Klein,[a] Dirk Johrendt,[b] Sanjay Mathur,[a] Markus Zegke*[a] and Aida Raauf*[a]

Lanthanoid and actinoid silylamides are versatile starting materials. Herein we show how a simple ligand exchange with *tert*-butanol leads to the formation of the first trimeric heterobimetallic uranyl(VI)–lanthanoid(III) alkoxide complexes. The μ^3 coordination of the endogenous uranyl oxo atom results in a significant elongation of the bond length and a significant deviation from the linear uranyl arrangement.

Although the chemistry of high-valent uranyl ($\mathrm{O{=}U{=}O^{2+}}$) accounts for 55% of all U structures reported in the CSD, not much attention has been paid to its alkoxide chemistry over the last 30 years. Only a few uranyl alkoxide compounds were structurally characterised in the 1950s by Bradley *et al.* and in the 1980s by Sattelberger *et al.*[1,2] In contrast, far more alkoxide structures of the lower-valent uranium (U(IV)–U(V))[3–6] species have been reported, because the preparation of uranyl alkoxides is accompanied by synthetic difficulties, *e.g.* solvolytic disproportionations, in which the cleavage of an oxo-unit takes place, while a second oxo-component is cleaved thermally to result in the formation of $[\mathrm{U(OR)_6}]$ and $[\mathrm{U_2O_5(OR)_2(HOR)_2}]$.[1] During the 1980s, coordinatively unsaturated alkoxides were reported to undergo ligand redistribution, resulting in oxo-alkoxide clusters.[2] Mononuclear uranyl alkoxides could only be stabilised by coordinating sterically demanding ligands like $\mathrm{Ph_3PO}$ by Burns *et al.* in 1992 and aryloxides by Barnhardt *et al.* in 1995.[7,8] Even though uranyl-lanthanoid assemblies have been investigated in different systems,[9–12] the heterobimetallic alkoxides have been rarely investigated, and, to the best of our knowledge, only few complexes such as $[\mathrm{Li(THF)_2U(O}^t\mathrm{Bu)_6}]$, $[\mathrm{Li(Et_2O)U(O}^t\mathrm{Bu)_6}]$ and $[\mathrm{KU_2(O}^t\mathrm{Bu)_9}]$ have been reported, where alkali metals are bridged *via* $\mathrm{O}^t\mathrm{Bu}$ ligands to U(IV) or U(V) centres and none of them contain uranyl ($\mathrm{O{=}U{=}O^{2+}}$) units.[13,14] The compound $[\mathrm{Zr_2(O}^i\mathrm{Pr)_9U(C_8H_8)}]$ prepared from $[\mathrm{Zr_2(O}^i\mathrm{Pr)_9}]\mathrm{UI_2(THF)}$ by Evans in 2001 is the only known heterobimetallic alkoxide that contains U(III) and a transition metal.[15] A CSD search on uranium bridged to lanthanoids *via* oxygen revealed only 19 examples, but none of these structures can be classified as an alkoxide. Most of them are reduced uranyl oxo-bridged complexes. In 2011 Arnold *et al.* first reported the reduction of a uranyl(VI) polypyrrolic Schiff-base macrocyclic complex $[\mathrm{UO_2(THF)(H_2L)}]$ by Sm(II) silylamide $[\mathrm{SmN''_2(THF)_2}]$ ($\mathrm{N''} = \mathrm{N\{Si(CH_3)_3\}_2}$) or by sterically induced reduction with $\mathrm{YN''_3}$ resulting in $[\{\mathrm{UO_2M(py)_2(L)}\}_2]$ (M = Y, Sm) (L = "*Pacman*" type calix pyrrole macrocycle). The series was later extended to M = Sc, Ce, Sm, Eu, Gd, Dy, Er, Yb and Lu in 2013.[16,17] Additionally, they were also able to isolate a small series of linear, oxo-bridged trinuclear compounds *e.g.* $[\{\mathrm{UO_2(py)_5}\}_2(\mathrm{LnI_4})]\mathrm{I}$ (Ln = Sm, Dy) containing a uranyl(V) by reduction of $[\mathrm{UO_2Cl_2(THF)_2}]$ with Ln(II) (Ln = Sm, Dy) halides in 2017.[18] The only other known compounds are phosphate- or mellitate-bridged clusters.[19,20]

Particularly important in this context is also the activation of the uranyl(VI) dication, which, due it its $\mathrm{O{=}U{=}O}$ bond strength with a notional bond order of three and a mean U–O bond dissociation enthalpy of 604 kJ $\mathrm{mol^{-1}}$ is one of the most stable oxo-cations.[21,22] Over the last 15 years the reduction chemistry of uranyl(VI) has seen a renaissance, and particularly the coordination of hetero metal atoms to the uranyl oxo atoms has resulted in a variety of reduced uranium complexes that show catalytic activity,[23] cation-cation interactions (CCIs),[24] thermally, photochemically or chemically reduced uranyl(V) centres and significantly elongated U–O bonds and paramagnetism attributable to the $5f^1$ state.[25–28] Many of these complexes have been stabilised with auxiliary ligands, such as macrocycles, bipyridine/phenantroline-type[29] or dipyrrin-type[30] ligands but also with just coordinating solvent molecules.[31]

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[a] *Department of Chemistry, Institute for Inorganic Chemistry, University of Cologne, Greinstr. 6, 50939 Cologne, Germany. E-mail: m.zegke@uni-koeln.de, ajamil@uni-koeln.de*

[b] *Department of Chemistry, Ludwig-Maximilians-University of Munich, Butenandtstraße 5-13 (D), 81377 Munich, Germany*

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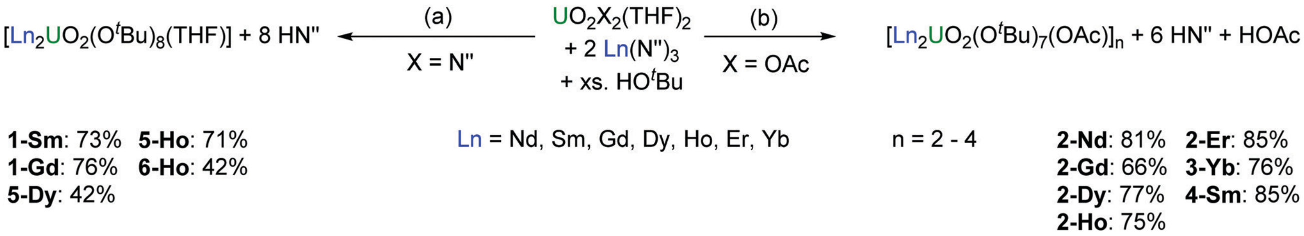


Scheme 1 Synthesis of mixed uranyl-lanthanoid alkoxides by reaction of either $[UO_2N''_2(THF)_2]$ or $[UO_2(OAc)_2(THF)_2]$ with the respective $[LnN''_3]$ (Ln = Nd, Sm, Gd, Dy, Ho, Er, Yb) to afford the monomeric cluster $[Ln_2UO_2(O^tBu)_8(THF)]$ (a) or the acetate-bridged $[Ln_2UO_2(O^tBu)_7(OAc)]_n$ (b).

We have revisited this chemistry herein, and present the first heterobimetallic uranyl-lanthanoid alkoxides with the general formula $[Ln_2UO_2(O^tBu)_n(L)]$ (L = OAc, $n = 7$; L = THF, $n = 8$), obtained by the reaction of $[UO_2(L)_2(THF)_2]$ (L = OAc, N″) with the corresponding metal silylamides $Ln(N'')_3$ (Ln = Nd, Sm, Gd, Dy, Ho, Er, Yb) in THF followed by adding an excess of *tert*-butanol (Scheme 1). The products resulting from the reaction of $[UO_2(OAc)_2(THF)_2]$ with LnN''_3 are oligomers by acetate-bridging of the trinuclear-monomeric unit $[Ln_2UO_2(O^tBu)_7(OAc)]_x$ (x = 2–4) whereas the reaction of $[UO_2N''_2(THF)_2]$ with LnN''_3 resulted in a merely trinuclear-monomeric complex.

The compounds were analysed structurally by scXRD and were investigated by Physical Properties Measurement System (PPMS). We have been able to isolate a variety of clear red-orange single crystals by careful crystallisation from saturated benzene or toluene solutions at 4 °C.

All $[Ln_2UO_2(O^tBu)_n(L)]$ (Ln = Nd, Gd, Dy, Ho; L = OAc, $n = 7$; L = THF, $n = 8$) complexes show similar bonding motifs (Fig. 1). The molecular structure consists of two lanthanoid centres and one uranyl subunit linked through three μ^2-O^tBu groups to form a triangle which is capped by one μ^3-O^tBu on the one side and by one uranyl oxygen (μ^3-$O_{endo}{=}U{=}O_{exo}$) on the other side. Moreover, the uranyl centre possesses one terminal O^tBu group to complete a distorted octahedral configuration and each Ln centre possesses one terminal O^tBu-group. To saturate the coordination sphere of the Ln centre, the acetate group is bridged to the next $[Ln_2UO_2(O^tBu)_7(OAc)]$ unit, resulting in the formation of an oligomeric structure $[Ln_2UO_2(O^tBu)_7(OAc)]_n$ (Scheme 1(b)). In contrast, starting from $[UO_2N''_2(THF)_2]$ results, due to the absence of the acetate group, in a Ln atom possessing an additional terminal O^tBu group. The coordination sphere of the second Ln centre is completed by a THF molecule resulting in the trinuclear complex $[Ln_2UO_2(O^tBu)_8(THF)]$ (Scheme 1(a)) displaying a distorted octahedral geometry around each Ln. In addition, the endogenous uranyl $O_{\mu^3}{=}U{=}O$ bond lengths are elongated to 1.866–1.902 Å, respectively, when compared to non-oxo-coordinated uranyl compounds (O=U=O 1.78 Å) (see Fig. S29, ESI†). This is in

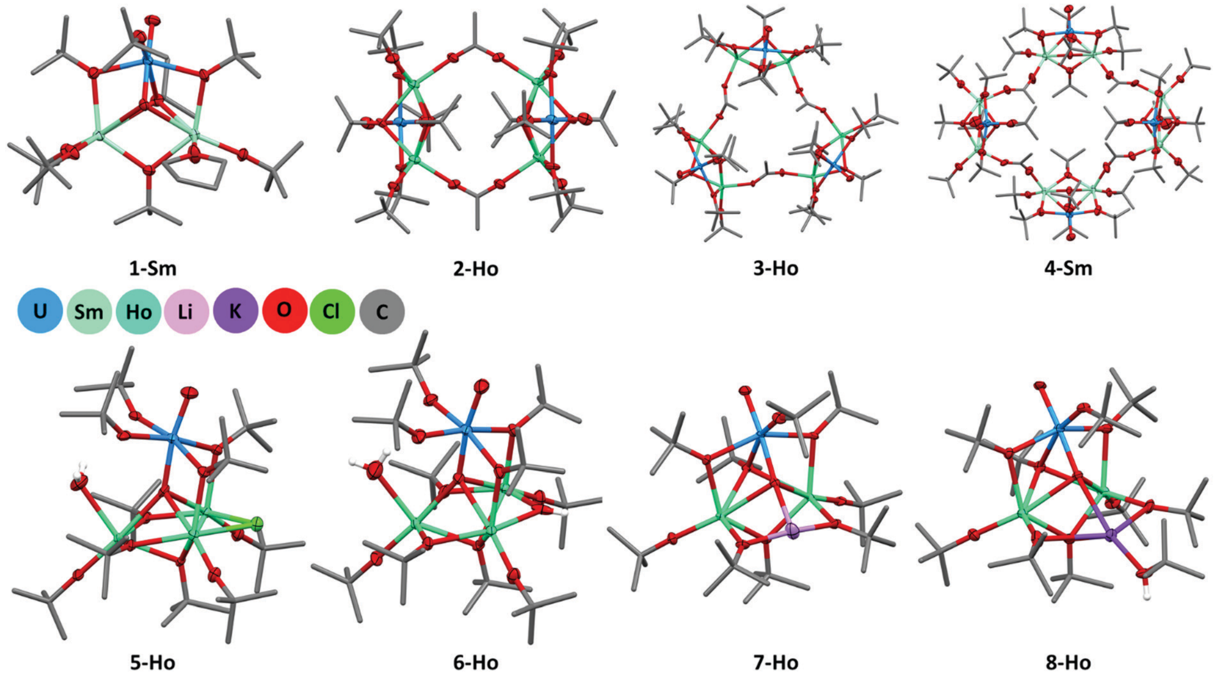


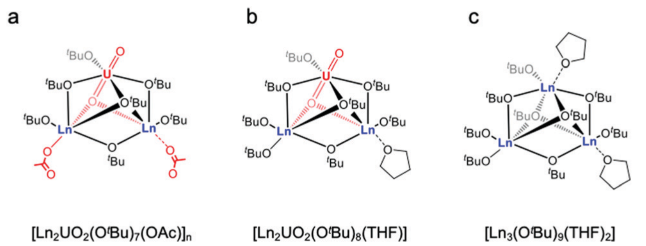
Fig. 1 Selected molecular structure of the monomeric **1-Sm**, dimeric **2-Ho**, trimeric **3-Ho**, tetrameric **4-Sm**, chloride and hydroxide inclusion **5-Ho** and **6-Ho** and alkali metal inclusion **7-Ho** and **8-Ho** alkoxides. Thermal ellipsoids are shown at 50% probability level and hydrogen atoms have been omitted for clarity.

the range of various uranyl(V) complexes,[32] even though C. J. Burns *et al.* have shown that significant uranyl lengthening and bending can occur in uranyl(VI) oxometallate clusters.[33] We can only hypothesise at this stage that this is due to the smaller radii of later lanthanoid ions, which are harder Lewis acids and therefore a better acceptor for the also hard uranyl oxygen. The O=U=O bond angle is also bent to below 170°. Previous studies have shown that the O=U=O unit can deviate significantly from a linear arrangement given the right ligand environment. For further details see the overview by Hayton and the references therein.[34] The latter study also shows that this influences the colour of the compound. As deviations from the linear arrangement are rare it is quite remarkable that our samples consistently show O=U=O bond angles below 170° (see Fig. S30, ESI†).

The trinuclear "Ln_2U" unit resembles the molecular structure of previously reported trimeric Ln *tert*-butoxides $[Ln_3(O^tBu)_9(THF)_2]$[35] with one Ln component being replaced by the uranyl unit in our compounds, and consequently a tridentate O^tBu group and a coordinating THF molecule are replaced by the uranyl oxygen units (Scheme 2).

Comparing the Ln series we observed that with increasing atomic number the Ln–O_{μ^3} coordination shortens from 2.626 Å (**2-Nd**) to 2.447 Å (**3-Yb**) as a consequence of the decreasing ionic radius. This results in an elongation of O_{μ^3}=U to about 1.88 Å in **3-Yb** (see Table S1, ESI†). In addition, we found different crystals of the material leading to an expanded connectivity between the acetate-bridges, depending on how long the complexes were crystallised for. When the compound was crystallised in a period of 1–2 days only crystals of monomeric constitution were isolated, but after two weeks clusters with up to four $[Ln_2UO_2(O^tBu)_7(OAc)]$ units were found for Ln = Sm and three $[Ln_2UO_2(O^tBu)_7(OAc)]$ units for Ln = Ho and Yb, the latter crystallising in the cubic space group *Pa*$\bar{3}$ (see SI for details).

In addition, the reaction between $[UO_2N''_2(THF)_2]$ and LnN''_3 is also prone to side reactions if unsublimed starting materials are used, as observed by the isolation of complexes with chloride or alkali metal inclusions (Fig. 1). Because these complexes contain unique connectivity of the metal centres, these were then made on purpose. To provide 1 equiv. of chloride 1/3 equiv. of the respective $LnCl_3{\cdot}6H_2O$ salt was added to a reaction mixture with sublimed LnN''_3. Utilising the hydrated $LnCl_3$ salt proved to be a useful method to keep the content of water as low as possible but at the same time providing a coordinating water molecule which is a necessary feature of $[Dy_3UO_2(O^tBu)_{10}Cl(H_2O)]$ **5-Dy** and $[Ho_3UO_2(O^tBu)_{10}Cl(H_2O)]$ **5-Ho**. Both **5-Dy** and **5-Ho** could not be isolated when water was completely excluded even though THF is present in the reaction mixture that could saturate the coordination sphere of the Ln centre. By looking at the space filling of the *tert*-butanol ligands it becomes evident that a THF molecule does not have enough space in this gap. **5-Dy** and **5-Ho** both crystallise in the orthorhombic space group *Pnma*. Their structures can be described as an $[UO_2(O^tBu)_2]$ moiety binding to a $[Ln_3(O^tBu)_8Cl]$ trimer *via* coordination of the uranyl oxygen to three lanthanoid centres and two bridging μ^2-O^tBu to two of the three Ln atoms. The third Ln atom shows a coordinating water molecule to saturate the coordination sphere. The bond distances of 2.481(4) Å for both **5-Dy** and **5-Ho** fit well with other Ln water bonds found in the literature and are in accordance with the oxidation state of the metal centres.[36,37] Alkali metal inclusions were reproduced by adding one additional equiv. of MN'' (M = Li, K) to a reaction mixture of $[UO_2N''_2(THF)_2]$ and LnN''_3. Because of the small ionic radius of Li, it fits into the small gap of the former endogenous *tert*-butoxides, whereas K possesses a protonated *tert*-butanol ligand to saturate the coordination sphere. In general, we found that complexes containing later Ln decompose rather quickly, sometimes before crystallisation can set in, identified by a colour change from orange to red, or undergo side reactions more readily than those with early Ln. The UV-vis absorption spectra (see Fig. S26, ESI†) for $[Gd_2UO_2(O^tBu)_7(OAc)]_2$ (**2-Gd**) and $[Ho_2UO_2(O^tBu)_7(OAc)]_2$ (**2-Ho**) showed an absorption at 270 nm for (**2-Gd**) and 275 nm for **2-Ho**, respectively. Additional bands were observed at 362 nm and 450 nm. The pattern of the UV-vis absorption spectra is in accordance with the spectra of uranyl formohydroxamate reported by Albrecht-Schmitt *et al.* but show a hypsochromic shift to 450 nm corresponding to a low intensity charge transfer band compared to typical uranyl compounds.[21,38] The hydrolysis curve for **2-Ho** was determined by the decreasing absorption of the complex after exposure to atmospheric moisture (see Fig. S27 and S28, ESI†).



Scheme 2 Illustrations of the molecular structure of (a) trinuclear monomeric unit $[Ln_2UO_2(O^tBu)_7(OAc)]_n$, (b) trinuclear compound $[Ln_2UO_2(O^tBu)_7(THF)]$ and (c) comparison with the homometallic lanthanoid *tert*-butoxide $[Ln_3(O^tBu)_9(THF)_2]$.

PPMS studies of the susceptibility and magnetisation between 2.1 and 300 K confirmed that $[Gd_2UO_2(O^tBu)_7(OAc)]_2$ (**2-Gd**), $[Dy_2UO_2(O^tBu)_7(OAc)]_2$ (**2-Dy**) and $[Ho_2UO_2(O^tBu)_7(OAc)]_2$ (**2-Ho**) are paramagnetic according to the Curie–Weiss rule[39] with effective magnetic moments of 7.92(1), 10.36(1) and 10.32(1) μ_B, respectively. These values agree with the expected moments for Gd^{3+}, Dy^{3+} and Ho^{3+} (Table 1), which suggests, considering charge neutrality with uranium being U(VI), that the rare-earth ions are the only active magnetic species in these compounds.

Negative values of the Weiss constant θ (Fig. S24, ESI†) and a slight flattening of χ_{mol} below 4 K indicate antiferromagnetic ordering of the Dy and Ho compounds.[41] In case of the Gd containing complex a negative θ value suggests antiferromagnetic ordering as well, though the transition temperature is apparently below the lower measurement limit.

Table 1 Comparison of the measured effective magnetic moments $\mu_{\mathrm{eff}}^{\mathrm{exp}}$ (μ_{B}) with typical magneton values from the literature $n_{\mathrm{eff}}^{\mathrm{exp}}$,[40] and calculated values

Magnetic centres	$\mu_{\mathrm{eff}}^{\mathrm{exp}}$ (μ_{B})	$n_{\mathrm{eff}}^{\mathrm{exp}}$	$g_J[J(J+1)]^{1/2}$
Gd^{3+}	7.92(1)	7.8–7.9	7.94
Dy^{3+}	10.36(1)	10.2–10.6	10.65
Ho^{3+}	10.32(1)	10.3–10.5	10.61

Isothermal magnetisation plots (Fig. S25, ESI†) are linear with the field at 300 K. In case of $[Gd_2UO_2(O^tBu)_7(OAc)]_2$ the curve saturates at a value near $g_JJ = 7$ for Gd^{3+}. The magnetisation of the Dy and Ho samples saturate against 5 μ_B, which is only half of the expected value $g_JJ = 10$ for Dy^{3+} and Ho^{3+}, possibly due to the antiferromagnetic order.

In conclusion, we have isolated the first trimeric heterobimetallic uranyl(VI)–lanthanoid(III) alkoxide complexes *via* a simple and straightforward ligand exchange. The μ^3 coordination of the endogenous uranyl oxo atom results in a significant elongation of the bond length and a significant deviation from the linear uranyl arrangement. This indicates that a coordination of lanthanoid atoms to the uranyl oxo-atoms may facilitate the reduction chemistry towards lower oxidation states of uranium, resulting in trimetallic systems with 5f–4f electron correlations. The magnetic susceptibilities obey the Curie–Weiss rule with effective magnetic moments compatible to Gd^{3+}, Dy^{3+} and Ho^{3+}, respectively, and indicate antiferromagnetic ordering below 4 K for the Dy^{3+} and Ho^{3+} compounds.

D. G.: Original draft, data curation, formal analysis, investigation, visualisation; M. W., A. L., T. G., R. N., M. H.: Data curation, formal analysis, investigation; S. M., M. W., A. K., D. J.: Funding acquisition, supervision, validation, resources, review & editing; M. Z., A. R.: conceptualisation, methodology, project administration, review & editing, supervision.

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Conflicts of interest

There are no conflicts of interest to declare.

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