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Berger, Erik; Westin, Gunnar

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Structure of a hepta-nuclear termetallic oxo-alkoxide: $\text{Eu}_3\text{K}_3\text{TiO}_2(\text{OBu}^t)_{11}(\text{OMe}/\text{OH})(\text{HOBu}^t)$

Erik Berger and Gunnar Westin

Department of Materials Chemistry, Ångström laboratory, Uppsala University, SE 75121 Uppsala, Sweden

+46 - 18 - 471 3740

+46 - 18 - 51 35 48

Gunnar.Westin@mkem.uu.se

Abstract

The novel termetallic oxo-methoxo-*tert*-butoxide $\text{Eu}_3\text{K}_3\text{TiO}_2(\text{OBu}^t)_{11}(\text{OMe}/\text{OH})(\text{HOBu}^t)$ (**1**) has been synthesised and structurally and spectroscopically characterised. Its unusual structure features an $\text{Eu}_3\text{K}_3\text{O}$ *fac*-octahedron, capped by a distorted K_3TiO tetrahedron on the K_3 face. The compound, crystallising in space group $P2_1/n$ with cell parameters $a=14.44\text{\AA}$, $b=23.58\text{\AA}$, $c=21.27\text{\AA}$ and $\beta=96.18^\circ$, is the result of incomplete metathesis between EuCl_3 and potassium and titanium *tert*-butoxides in combination with deliberate hydrolysis and decomposition. It provides one of few examples of termetallic lanthanide alkoxides, as well as of an alkoxide *tert*-butyl group decomposing into a methyl group.

Precursor chemistry, Oxo-alkoxide, Crystal structure, Alkoxide, Sol-gel precursor, Europium, Termetallic alkoxide, Structure

1. Introduction

Metal alkoxides have attracted much interest of materials scientists owing to their versatility as precursors to advanced multi-component ceramic materials prepared via sol-gel processing or chemical vapour deposition [1-6]. In sol-gel processing, use of alkoxides often allows for facile complete hydrolysis of the alkoxo ligands to yield inorganic gels or nano-particles that can be converted to oxide thin films and nano-particles at low temperatures in a controlled manner. In addition, their structures and properties can be changed by variation of the alkoxo groups and introduction of oxo atoms. Also, their ability to form heteronuclear molecules provides atomic scale mixing of the metal components of the target ceramic, and at the same time allows for controlled concerted precipitation of the oxide

components, thereby providing control over the materials' morphology. If carefully controlled, the high degree of homogeneity can be used to obtain metastable glassy or crystalline phases.

An area that has received considerable interest recently is the synthesis of lanthanide doped glasses and ceramics targeted for applications in e.g. signal enhancement and frequency up-conversion in fibers and integrated optic communication devices, lasers and fluorescent light emitters [7-11], nano-particular optic and magnetic bio-markers [12-13] and heterogeneous catalysts [14]. Lanthanide ions are also important components of electroceramics as silent spacer atoms in e.g. Dy-substituted PZT [15, 16], or as optically and magnetically active ions in e.g. colossal magneto resistant LCMO and LSCO films [17-22]. Several lanthanide alkoxides have been reported as active to highly active non-toxic catalysts or catalyst precursors in organic synthesis steps such as ring-opening polymerisation and olefin polymerisation [23-27].

Yet, although great advances have been made in alkoxide chemistry during recent years they still make up a class of compounds where much remains to explore to develop a level of understanding where molecular structures can be predicted [2-6]. Exploration of the various structures encountered among homo- and heterometallic alkoxides and oxo-alkoxides can provide information about the structure-directing factors, and thus aid in the optimising of heterometallic ceramic precursors and selective catalysts.

As part of our continuing study on lanthanide-containing heterometallic alkoxides, we recently focused on Eu alkoxides and have determined and analysed the structure of a novel heptanuclear termetallic oxo-*tert*-butoxide, displaying interesting features. The unusual structure is built around a central *fac*-Eu₃K₃O octahedron, with the potassium face shared by a tetrahedron, incorporating titanium into the structure. The compound is one of very few structurally determined termetallic lanthanide alkoxides (to our knowledge, only (Tb,Er)₄TiO(OPrⁱ)₁₄ [28] has been published¹). Also, the Eu alkoxides in general constitute a small group, starting with the report by Brown et al. [29] of formation of an Eu-isopropoxide assumed to have the formula Eu(OPrⁱ)₂ upon dissolution of europium metal. Pires de Matos et al. [30] and Evans et al. [31, 32] reported the

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¹ Results from Cambridge Structural Database v.5.30, November 2008 update (Cambridge Crystallographic Data Centre)

divalent Eu alkoxides with: methoxide, ethoxide, *iso*-propoxide and methoxy-ethoxide ligands; all formulated as $\text{Eu}(\text{OR})_2(\text{solvent})_x$ (solvent=THF [31], toluene [32] or none [30]). The structurally determined purely oxo-/hydroxo alkoxides of Eu are: $\text{Eu}^{\text{III}}_2\text{Eu}^{\text{III}}_2(\text{OPr}^i)_{10}(\text{HOPr}^i)_3 \cdot 2\text{HOPr}^i$ [33], $\text{Eu}^{\text{III}}\text{Eu}^{\text{III}}_4\text{O}(\text{OPr}^i)_{12}(\text{HOPr}^i) \cdot \text{HOPr}^i$ [34], $\text{Eu}_5\text{O}(\text{OPr}^i)_{13}$ [33], $\text{Eu}_4(\text{OCH}_2\text{CMe}_3)_{12}$ [35], $\text{EuAl}_3(\text{OPr}^i)_{12}$ [33] and $\text{Eu}^{\text{III}}\text{Ge}_2(\text{OBu}^t)_6$ [36], and $\text{Eu}_2\text{Ba}_6\text{O}_2(\text{OPr}^i)_{14}(\text{HOPr}^i)_2(\text{THF})_4$ [37], when including easily removed neutral ligands such as THF.

Here we describe the synthesis of $\text{K}_3\text{Eu}_3\text{TiO}_2(\text{OR})_{12}(\text{HOR})$ (**1**) and its characterisation by IR spectroscopy. The structure determined by single crystal X-ray techniques will be discussed and compared with other known structures.

2 Experimental

2.1. Equipment and chemicals

The syntheses and re-crystallisations, the sample preparations for spectroscopic studies and the mounting of crystals for single-crystal X-ray data collection were performed in a glove-box containing dry, oxygen-free argon (Braun MB200). All glassware were dried at 150°C for at least one hour before being taken into the glove-box. The toluene (Scharlau, $\leq 0.03\%$ H_2O) and *tert*-butanol (Scharlau, $\leq 0.1\%$ H_2O) were dried by distillation over CaH_2 . The anhydrous EuCl_3 (99.9%-Eu O, STREM chemicals) and $\text{Ti}(\text{OBu}^t)_4$ (99.95%-Ti) were used as purchased. The potassium was cleaned from its surface crust before use.

The metal and chlorine elemental contents (Eu, K, Cl, Ti) were obtained from air-hydrolysed samples taken out of the glove-box, by use of a scanning electron microscope (SEM, Zeiss LEO 440) with an energy-dispersive X-ray spectrum analyser (EDS, EDAX). The IR spectra were obtained in the range $4000\text{--}370\text{ cm}^{-1}$, with a Fourier transform infrared (FT-IR) spectrometer (Perkin-Elmer Spectrum One) as paraffin mulls between KBr discs. Single-crystal data collection was performed on a single-crystal diffractometer with CCD-detector (Bruker AXS D8).

2.2. Synthesis of (1)

0.258 g (6.60 mmol) K was dissolved in 20 mL of 1:1 (vol:vol) *tert*-butanol:toluene followed by addition of 0.384 g (1.13 mmol) titanium *tert*-butoxide, and subsequent drop-wise addition of 2.5 ml 0.44 M H₂O in 1:1 (vol:vol) *tert*-butanol:toluene (1.1 mmol) under vigorous stirring. After addition of 0.568g (2.20 mmol) EuCl₃, the mixture was stirred for more than two days. EDS analysis of the solution part showed virtually no europium, whereas the sediments consisted mainly of Eu and Cl. After heating at 60°C for three days, the solution part contained Eu, K and Ti in ratios of about 2:4:1. The mixture was then centrifuged to sediment the solid part (EDS: Cl>K>Eu) and the solution part transferred to another flask. Successive replacement of the solvent by *tert*-butanol, by means of repeated evaporations in vacuo and addition of *tert*-butanol, resulted in the formation of a white precipitate. The solution part was removed, and the white precipitate redissolved in ca. 6 mL 1:10 (vol:vol) *tert*-butanol:toluene. Within two weeks, crystals of **1** had formed from this solution. EDS analysis of these crystals gave a composition of ca. 3:3:1 (Eu:K:Ti). No Cl or other elements were detected.

FT-IR data for identification (nujol, cm⁻¹): 3670, 3370(broad), 2809(weak), 1361, 1351, 1228sh, 1214sh, 1204, 1195sh, 1183sh, 1050, 1035, 1022sh, 1002sh, 989, 964, 937, 891, 855, 792, 779, 766, 759, 583, 534sh, 521, 499sh, 489, 478, 460.

2.3. Structure determination of (1)

Colourless crystals with dimensions up to 0.5x0.5x0.5 mm were glued with a small amount of paraffin in glass-capillaries, which were subsequently melt-sealed and transferred to the single-crystal diffractometer. Intensity data (ω -2 θ scans) were collected with the Bruker AXS SMART APEX software at 170 K using Mo-*K*_α radiation. Data reduction and Lorentz and polarisation corrections were performed by the Bruker AXS SAINT software.

Systematic absences in the collected diffraction data were consistent with the centro-symmetric monoclinic space group *P*2₁/*c* (No. 14). The non-conventional *P*2₁/*n* setting was chosen as the more convenient setting.

A portion of the reflections (<2% of all data, <0.2% of unique reflections) were rejected on the basis of drastically reduced intensities caused by unfortunate crystal support, beam stopper and detector geometry. The high redundancy of the data was then used to correct the data for apparent errors such as absorption (crystal, crystal support), variation in the irradiated crystal volume, incident beam inhomogeneity and crystal decay and reject obvious outliers, using the SADABS program [38].

Selected crystallographic and experimental data together with the refinement details are given in **Table 1**. Cell parameters are given for the crystal used for final structure refinement, but with standard errors reflecting the spread between different crystals.

The structure was solved using direct methods and refined against F^2 using the computer programs SHELXS and SHELXL versions 2008/04 and 2008/01, respectively [38]. Residual electron density maps were double-checked with the DUPALS package [39].

All non-hydrogen atoms were refined anisotropically. After location of most hydrogen atoms at nearly ideal positions in the residual electron density maps, all hydrogen atoms except two were refined at ideal positions using riding models (instruction AFIX 34 for *tert*-butyl groups, AFIX 137 for the methyl group on O3) with thermal displacement parameters 1.2 times the U_{eq} of their respective pivot atom. One hydrogen atom needed for charge balance could not be located unambiguously, and one hydrogen atom partially occupying the site of the methyl group on O3 was not included in the model either.

Table 1 Crystallographic data and structure refinement parameters for $\text{Eu}_3\text{K}_3\text{TiO}_2(\text{OR})_{12}(\text{OR}')\text{H}$

Empirical formula	$\text{C}_{49} \text{H}_{112} \text{Eu}_3 \text{K}_3 \text{O}_{15} \text{Ti}$
Formula weight (g/mol)	1562.5
Crystal system, space group	Monoclinic, $P2_1/n$
Unit cell dimensions ($\text{\AA}$, deg)	$a=14.439(31)^a$ $\alpha=90$
	$b=23.577(30)^a$ $\beta=96.176(24)^a$
	$c=21.268(32)^a$ $\gamma=90$
Unit cell volume ($\text{\AA}^3$)	7197.9(3)
Z	4
Calculated density (g/cm^3)	1.442
Absorption coefficient (mm^{-1})	2.91 for MoK_α

Diffractometer	Bruker AXS D8
Radiation wavelength (Å)	0.71073 (MoK _α)
Data collection temperature (K)	170
Crystal colour	Colourless to pale
Crystal habit	Roughly equant
Crystal size (mm ³)	0.35 × 0.35 × 0.21
Theta range for data collection (deg)	1.63 - 28.37
Limiting indices	-19 ≤ h ≤ 19, -31 ≤ k ≤ 31, -28 ≤ l ≤ 28
Total reflections measured	181023
Absorption correction	Empirical (SADABS 2008)
Apparent max./min. transmission	0.75/0.57 = 1.3
λ/2 correction factor	0.0015
Reflections with I-⟨I⟩ _{eq} /σ>4.0	15
Reflections h0l with odd h+l	2287 highest I/I _{max} =0.3% (0 0 -25)
Reflections 0k0 with odd k	102 highest I/I _{max} =0.5% (0 -21 0)
Used reflections / unique / R _{int}	178619 / 17066 / 0.0535
Data / restraints / parameters	17066 / 0 / 678
R indices (all) ^b	R ₁ =0.0445 wR ₂ =0.0781
R indices (F _O ² >2σ) ^b	R ₁ =0.0361 wR ₂ =0.0752
Largest diff. peak and hole (eÅ ⁻³)	1.218 / -0.522

^a non-biased standard deviations of 6 data collections (5 crystals)

^b $R_1 = \Sigma||F_O| - |F_C|| / \Sigma|F_O|$; $wR_2 = \{ \Sigma[w(F_O^2 - F_C^2)] / \Sigma[w(F_O^2)^2] \}^{1/2}$;

$w = 1/[\sigma^2(F_O^2) + (aP)^2 + bP]$, where $P = (F_O^2 + 2F_C^2)/3$, $a=0.0344$, $b=7.0790$

3. Results and Discussions

3.1. Synthesis

The original synthesis was targeted at europium titanium oxo *tert*-butoxides with overall Eu:Ti:oxo composition 2:1:1. However, the intended metathesis reaction between potassium and titanium alkoxides and europium chloride with precipitation of potassium chloride did not proceed to completion even after extended heating at 60°C. Instead, an Eu-K-Ti-oxo-alkoxide (**1**) was found with an Eu:K:Ti:oxo ratio of 3:3:1:2 and with one *tert*-butyl group replaced by a methyl group. Reaction 1 summarizes the overall reaction forming **1**, after dissolution of potassium in toluene-*tert*-BuOH, including non-reacting species and ignoring the nature of the decomposition reaction from OBU^t to OMe:

Thus, apart from KCl, by-products should include unreacted EuCl_3 and $\text{Ti(OBu}^t)_4$, possibly involving heterometallic Eu-Ti-K chloro-alkoxides. The elemental analysis results for the sediments after centrifugation were consistent with a mixture of mainly KCl and some EuCl_3 . After solvent replacement and removal of the alcohol phase from **1**, the IR spectra for this alcohol phase (dried samples in nujol) showed a superposition of peaks from $\text{Ti(OBu}^t)_4$ and **1** along with a few unidentified peaks.

3.2 Spectroscopy

IR spectroscopy has proven very useful for identifying structurally similar ethoxide and *iso*-propoxides [33, 34, 40-45]. The IR spectrum of **1** (Figure 1) shows peaks typical of *tert*-butoxo and methoxo groups assigned as: CH_3 umbrella modes ($\sim 1350 \text{ cm}^{-1}$) and C-C and C-O stretching and bending ($1210\text{-}800 \text{ cm}^{-1}$); as well as of Ti- and Eu-containing alkoxides, assigned as: Ti-O stretching ($\sim 580 \text{ cm}^{-1}$) and Eu-O stretching ($550\text{-}360 \text{ cm}^{-1}$) overlapped with various OH and alkoxo group modes. In the C-O + C-C region ($1210\text{-}1000 \text{ cm}^{-1}$), a distinction can be seen between the tertiary alkoxide peaks with a maximum at 1204 cm^{-1} and the methoxide peak at 1050 cm^{-1} . At higher wavenumbers, a composite peak with a maximum at $\sim 3370 \text{ cm}^{-1}$, attributed to O-H stretching, is observed, as well as a very sharp peak at 3670 cm^{-1} , interpreted as the -OH stretch mode of -OH groups, not participating in hydrogen bonding. In addition, various peaks are seen typical of CH_3 modes and C-C modes.

Fig. 1 IR spectrum of (1) as paraffin-mull

3.3. Structure

The molecular structure in ORTEP representation is shown in **Figure 2** and the atomic coordinates and bond valence sums [46,47] in **Table 2**. The $\text{Eu}_3\text{K}_3\text{TiO}_{15}$

metal-oxygen framework of the molecule consists of three six-coordinated europium atoms, three five- or six-coordinated potassium atoms and one four-coordinated titanium atom, held together by: one μ_6 -, one μ_4 -, seven μ_3 -, two μ_2 -bridging and four terminal oxygen atoms, all but the first two being part of alkoxo ligands. The structure can thus be written: $\text{Eu}_3\text{K}_3\text{Ti}(\mu_6\text{-O})(\mu_4\text{-O})(\mu_3\text{-OR})_7(\mu\text{-OR})_2(\text{t-OR})_4$, but for charge balance one of the OR groups should be protonated, which is supported by the presence of an O-H stretch band at 3370 cm^{-1} in the IR spectrum.

It can be seen that the thermal motion increases from the bary-centre to the periphery of the molecule, indicating that the inter-molecular bonds are weak and fairly non-directional allowing the molecules to vibrate freely as stiff rotors in their lattice positions. The OR groups attached to the Ti atom also seem to vibrate more than those on the $\text{Eu}_3\text{K}_3\text{O}$ octahedron.

The crystal packing of the molecules is shown in **Figure 3**. With 14 neighbours and intermolecular carbon-carbon distances of around $4\text{ \AA}$, the molecules are essentially close-packed, but it is possible to find voids in the structure with more than $3\text{ \AA}$ to the nearest hydrogen atoms.

Fig. 2 ORTEP representation of $\text{Eu}_3\text{K}_3\text{Ti}(\mu_6\text{-O})(\mu_4\text{-O})(\mu_3\text{-OMe/OH})(\mu_3\text{-OBu}^t)_6(\mu\text{-OBu}^t)_2(\text{t-OBu}^t)_4\text{H}$

Table 2 Atomic coordinates, displacement parameters ($\text{\AA}^2$), coordination numbers and bond valence sums (BVS, v.u.) for metal and oxygen atoms in **1**

Atom	x	y	z	U_{eq}	C.N.	BVS
Eu(1)	0.58318(1)	0.477821(6)	0.299425(7)	0.02007(4)	6	3.19
Eu(2)	0.77229(1)	0.378354(7)	0.327614(7)	0.02114(5)	6	3.20
Eu(3)	0.69542(1)	0.423881(7)	0.167912(7)	0.02241(5)	6	3.19
K(1)	0.44551(6)	0.38552(3)	0.18037(4)	0.0325(2)	6	0.84
K(2)	0.53043(6)	0.33659(3)	0.36506(4)	0.0311(2)	6	0.81
K(3)	0.67382(6)	0.27164(3)	0.20937(4)	0.0354(2)	5	0.81
Ti(1)	0.40956(4)	0.25147(3)	0.24581(3)	0.0278(1)	4	4.18
O(1)	0.6246(2)	0.3849(1)	0.2586(1)	0.0206(5)	6	1.39
O(2)	0.5088(2)	0.2904(1)	0.2470(1)	0.0322(6)	4	2.01
O(3)	0.7416(2)	0.4683(1)	0.2704(1)	0.0232(5)	3	2.20
O(4)	0.5645(2)	0.4807(1)	0.1871(1)	0.0264(5)	3	2.03
O(5)	0.6625(2)	0.4251(1)	0.3838(1)	0.0236(5)	3	2.05

O(6)	0.8016(2)	0.3593(1)	0.2215(1)	0.0267(5)	3	2.07
O(7)	0.6140(2)	0.3546(1)	0.1176(1)	0.0339(6)	3	1.96
O(8)	0.7173(2)	0.2928(1)	0.3443(1)	0.0309(6)	3	1.99
O(9)	0.4459(2)	0.4367(1)	0.3052(1)	0.0291(5)	3	1.97
O(10)	0.9042(2)	0.3900(1)	0.3801(1)	0.0312(6)	1	1.94
O(11)	0.7684(2)	0.4686(1)	0.1024(1)	0.0351(6)	1	1.94
O(12)	0.5844(2)	0.5625(1)	0.3327(1)	0.0325(6)	1	1.94
O(13)	0.3280(2)	0.2920(1)	0.1887(1)	0.0397(6)	2	2.06
O(14)	0.3826(2)	0.2562(1)	0.3297(1)	0.0460(7)	2	1.99
O(15)	0.4208(2)	0.1792(1)	0.2219(2)	0.0488(7)	1	2.09

Fig. 3 The crystal packing of the molecules, represented by their $\text{Eu}_3\text{K}_3\text{TiO}_2$ cores, in projection parallel to the c axis. The light and dark grey molecules form two layers positioned around $z=-0.25$ and $z=+0.25$ respectively

Selected bond lengths and angles are listed in **Table 3** and **Table 4**. The metal-oxygen bond lengths all obey the generally observed trend $\text{M-t-O} < \text{M-}\mu\text{-O} < \text{M-}\mu_3\text{-O} < \text{M-}\mu_4\text{-O} < \text{M-}\mu_6\text{-O}$ [5]. The bond valence sums (BVS, Table 2) [46] were 3.19 and 4.18 for the Eu and Ti atoms, respectively, which fits the expected 3 and 4 valences well. These valences are also corroborated by the absence of a strong yellow to red colour or dark blue colour in the crystals and solutions expected for the lower valence ions, Eu^{2+} and Ti^{3+} , respectively.

Table 3 Selected bond lengths in **1**

Atoms	Distance (Å)	Bond valence		Atoms	Distance (Å)	Bond valence
Eu(1)-O(1)	2.454	0.36		K(1)-O(1)	2.921	0.12
Eu(2)-O(1)	2.460	0.35	$\mu_6\text{-O}$	K(2)-O(1)	2.989	0.10
Eu(3)-O(1)	2.456	0.36		K(3)-O(1)	2.982	0.10
			$\mu_4\text{-O}$	K(1)-O(2)	2.756	0.18
Eu(1)-O(3)	2.443	0.37		K(2)-O(2)	2.725	0.20
Eu(2)-O(3)	2.461	0.35	$\mu_3\text{-OMe}$	K(3)-O(2)	2.631	0.26
Eu(3)-O(3)	2.445	0.37		Ti(1)-O(2)	1.699	1.37
Eu(1)-O(4)	2.376	0.44		K(1)-O(4)	2.821	0.15

Eu(1)-O(5)	2.374	0.45	μ_3 -OBu ^t	K(2)-O(5)	2.826	0.15
Eu(2)-O(5)	2.359	0.47		K(3)-O(6)	2.765	0.18
Eu(2)-O(6)	2.383	0.44				
Eu(3)-O(6)	2.364	0.46		K(1)-O(7)	2.988	0.10
Eu(3)-O(4)	2.388	0.43		K(1)-O(9)	2.916	0.12
				K(2)-O(9)	2.889	0.13
Eu(1)-O(9)	2.222	0.67		K(2)-O(8)	2.966	0.10
Eu(2)-O(8)	2.210	0.70	μ_3 -OBu ^t	K(3)-O(8)	2.914	0.12
Eu(3)-O(7)	2.219	0.68		K(3)-O(7)	2.831	0.15
Eu(1)-O(12)	2.118	0.89		K(1)-O(13)	2.800	0.16
Eu(2)-O(10)	2.119	0.89	μ -OBu ^t	K(2)-O(14)	2.893	0.13
Eu(3)-O(11)	2.116	0.90	t-OBu ^t	Ti(1)-O(13)	1.862	0.88
Ti(1)-O(15)	1.790	1.07		Ti(1)-O(14)	1.870	0.86

Table 4 Selected bond angles in **1**

Atoms	Angle	Atoms	Angle
Eu(1)-O(1)-Eu(2)	94.2°	K(1)-O(1)-K(2)	89.2°
Eu(1)-O(1)-Eu(3)	94.7°	K(1)-O(1)-K(3)	92.0°
Eu(2)-O(1)-Eu(3)	94.9°	K(2)-O(1)-K(3)	94.0°
Eu(1)-O(1)-K(3)	179.6°	K(1)-O(2)-K(2)	98.4°
Eu(2)-O(1)-K(1)	176.1°	K(1)-O(2)-K(3)	104.0°
Eu(3)-O(1)-K(2)	177.4°	K(2)-O(2)-K(3)	109.2°
Eu(1)-O(12)-C(12)	177.8°	K(1)-O(2)-Ti(1)	101.5°
Eu(2)-O(10)-C(10)	178.6°	K(2)-O(2)-Ti(1)	104.0°
Eu(3)-O(11)-C(11)	178.7°	K(3)-O(3)-Ti(1)	134.0°
Ti(1)-O(15)-C(15)	164.7°		
O(2)-Ti(1)-O(13)	101.9°	O(4)-K(1)-O(13)	173.5°
O(2)-Ti(1)-O(14)	102.5°		
O(2)-Ti(1)-O(15)	114.6°	O(5)-K(2)-O(14)	171.2°
O(13)-Ti(1)-O(14)	114.2°		
O(13)-Ti(1)-O(15)	111.9°	O(6)-K(3)-O(15)	159.9°
O(14)-Ti(1)-O(15)	111.2°	O(7)-K(3)-O(8)	125.3°

The titanium atom is tetrahedrally coordinated by four oxygen atoms, with O-Ti-O angles being close to tetrahedral, ranging from 102° to 115°. The TiO₄ tetrahedron shares two of its edges with potassium polyhedra.

All three europium atoms are octahedrally coordinated by oxygens to: one terminal alkoxo group, four μ_3 -bridging alkoxo groups and the central oxo-atom. Four out of eight faces of each EuO₆ octahedron are shared with neighbouring EuO₆ and KO_n octahedra.

Two potassium atoms are six-coordinated (K1 and 2), whereas one atom is five-coordinated (K3), with the latter more closely bonded to the tetrahedral oxygen atom. The BVS values are very similar for the three K atoms ranging 0.81-0.84, which are typical values for K⁺. The K- μ_6 -O bond lengths of 2.9-3.0 Å in **1**, are comparable to those in similar oxo-alkoxides such as K₄Zr₂O(OPrⁱ)₁₀ (2.8 Å) [48] and K₄Sb₂O(OBu^t)₈(THF)₄ (2.6-3.0 Å) [49]. The K- μ_4 -O bonds of **1** are somewhat shorter: 2.63 Å for the five coordinated K atom and 2.73 – 2.75 to the six-coordinated K atoms.

It is notable that the ligands of both the five and the six coordinated K-ions occupy less than a hemisphere. This is also found for several other large alkali-ions such as K, Rb and Cs in alkoxide chemistry, e.g., K₄Zr₂O(OPrⁱ)₁₀ [48], M₂Er₄O(OPrⁱ)₁₂ (M = K, Rb, Cs; unpublished results) and K₄Li₄(OBu^t)₈ [50]. This may seem unusual when comparing with ions having p-, d- and f-orbital influenced outer shells directing the ligands around the metal ion, or s-shell ions where the inter-ligand repulsions can easily be reduced by separating non inter-tied groups as far from each other as possible. Here the ligands are bridging several metal atoms, which restrict them to being close to either the Eu₃K₃ octahedron or the K₃Ti tetrahedron, resulting in the observed coordination.

It is also noted that the two kinds of oxo ion in **1** have very different BVS values: 2.0 for μ_4 -O, compared to 1.4 for μ_6 -O. The value of 2.0 corresponds to what is expected for oxo ions and suggests that the charge on the oxygen atom is about the same as on a μ_5 -O in e.g. Eu₄TiO(OPrⁱ)₁₄ (BVS 1.8; unpublished results), Eu₅O(OPrⁱ)₁₃ (BVS 2.0) [33] and Eu₅O(OPrⁱ)₁₂(HOPrⁱ) (BVS 2.0) [34] or on μ_6 -O in Ba₆Li₃O₂(OBu^t)₁₁(THF)₃*THF (BVS 1.8 and 2.1) [51], Na₂Gd₄O(OBu^t)₁₂ (BVS 1.8) [52] and Cs₂Er₄O(OPrⁱ)₁₂ (BVS 2.1). The value of 1.4, on the other hand, is unusually low and approaching the level of the

protonated μ_5 -O in $\text{YNa}_8\text{OH}(\text{OBu}^t)_{10}$ (BVS 0.8) [53]. It is however unlikely that the central six coordinated oxo-ion is protonated taking the even and crowded coordination geometry into consideration. Further, an even lower BVS is found on the central oxygen atom in $\text{H}_4\text{Ba}_6\text{O}(\text{OC}_2\text{H}_4\text{OMe})_{14}$ (BVS: 1.1) [54] which is even less likely to have a μ_6 -OH considering its even C_i symmetry of the molecule. The authors placed three protons as part of μ_3 -OH groups, while the fourth was not placed.

Of the 13 alkoxo-oxygen atoms, 12 are part of *tert*-butoxo ligands and one (O3) is part of a methoxo ligand. However, the structure determination shows less electron density than expected from a methyl group in the latter position and hence the position may be partially occupied by a hydroxo group. This is corroborated by the sharp IR peak at 3670 cm^{-1} . The electron density then suggests that almost half of the methyl groups are replaced by hydroxo groups.

All Eu-O-C angles for terminal alkoxo groups are roughly equal to 180° and the corresponding terminal Ti-O-C angle is also fairly close to 180° .

Large Ln-O-R angles are common for Ln-alkoxides and terminal M-O-C angles of 164 - 177° are found for $\text{Eu}_5\text{O}(\text{OPr}^i)_{13}$ [33]. With the sterically demanding *tert*-butoxides such as $\text{Dy}_3(\text{OBu}^t)_9(\text{HOBu}^t)_2$ [15] even the protonated ligands show angles of more than 170° , whereas Ti-O-C angles in titanium *tert*-butoxides can reach down to 150° even for ligands not participating in hydrogen bonding (e.g. $\text{Ti}_{18}\text{O}_{27}(\text{OH})(\text{OBu}^t)_{17}$ [55]).

There should be one protonated OR ligand in the molecule to obtain charge neutrality. As discussed above, bond valence sum calculations can sometimes be used for identification of protonated ligands through the lowering of the oxygen valency, as found in alkoxides like $\text{Eu}_2\text{Eu}_2(\text{OPr}^i)_{10}(\text{HOPr}^i)_3$ (BVS 1.1-1.3 for four $\text{H}_{0.75}\text{OPr}^i$) and $\text{Eu}_4\text{EuO}(\text{OPr}^i)_{12}(\text{HOPr}^i)$ (BVS 1.3-1.4 for HOPr^i). In the present case, however, it did not provide us with any strong clue for the position of the H atom in **1**, as all calculated alkoxo ligand oxygen valences are close to 2 (1.9-2.2). Furthermore, analysis of bond angles and structure did not help in making a good assumption on the position of the H atom either. It seems most likely that it is placed in the K_3 -Ti region of the molecule at a μ_2 or terminal OBu^t oxygen.

Molecular build-up. Figure 4 highlights the metal-oxygen part of the molecule consisting of two oxo-centred polyhedra: an Eu_3OK_3 octahedron and a K_3OTi tetrahedron, fused together via a triangular K_3 face. The octahedron is quite regular with Eu-O distances ranging 2.45-2.46 Å and K-O distances ranging 2.92-2.99 Å. In addition, opposite Eu-O-K angles are close to 180° and a high degree of three-fold symmetry is maintained throughout the $\text{Eu}_3\text{K}_3\text{O}$ atom-group, in spite of the lack of rotation symmetry around the titanium atom. Even the methyl groups in the OBu^t ligands conform well to the threefold symmetry law.

The tetrahedron is distorted from ideal symmetry with the apical titanium atom pointing in the direction of two of the potassium atoms, with which it shares one alkoxo bridge each. The central oxygen atom is instead drawn closer towards the third potassium atom.

Fig. 4 M_xO polyhedron view of **1**, carbon and hydrogen atoms omitted

3.4. Comparisons

The central part of **1** containing a single M_6O oxo-centred octahedron finds many examples in alkoxide chemistry such as: $\text{Na}_2\text{Gd}_4\text{O}(\text{OBu}^t)_{12}$ [52], $\text{K}_4\text{Zr}_2\text{O}(\text{OPr}^i)$ [48], and $\text{Cs}_2\text{Er}_4\text{O}(\text{OPr}^i)_{12}$ (unpublished results). This structural motif of six metal ions around a central O^{2-} ion is often found with large, electropositive ions rendering the metal ions very weakly electron withdrawing. Whereas for *Zr-iso-propoxides*, three- or four-coordinated oxo-O ions are normally found [2-4, 6], and for *Ln-iso-propoxides*, five-coordinated oxo-O ions are often found (e.g. $\mu_5\text{-O}$ in $\text{Eu}_5\text{O}(\text{OPr}^i)_{13}$), the same elements may form $\mu_6\text{O}$ -centered $\text{M}_{6-x}\text{A}_x\text{O}$ structures when combined with highly electropositive alkali atoms (e.g. $\text{K}_4\text{Zr}_2\text{O}(\text{OPr}^i)_{10}$ [48], $\text{M}_2\text{Ln}_4\text{O}(\text{OR})_{12}$ ($\text{M} = \text{K}, \text{Rb}, \text{Cs}$)). Thus, with three K^+ and three Eu^{3+} ions in **1**, the M_6O structure is not unexpected. Oxo-centred M_4O tetrahedra however, are normally found with rather highly charged metal ions such as Zr^{4+} - and Ti^{4+} [2-4, 6], and for these elements, the tetrahedra do not tend to share faces.

We have not found another example of the specific motif of **1** showing an oxo-centred M_6O octahedron and an M_4O tetrahedron sharing a common face in the literature among alkoxides and related complexes. However, there is a close resemblance to $\text{Ba}_6\text{Li}_3\text{O}_2(\text{OBu}^t)_{11}(\text{THF})_3 \cdot \text{THF}$ [51], in which an octahedron

(Ba₆O) and a cone-shaped prismoid with a central six coordinated oxo-O atom (Ba₃OLi₃) share a common triangular face, as shown in **Figure 5**.

Fig. 5 Structure of: (left) Eu₃K₃TiO₂(OBu^t)₁₁(OMe/OH)(HOBu^t) (**1**) and (right) Ba₆Li₃O₂(OBu^t)₁₁(THF)₃*THF [51]

4. Conclusions

A new hepta-nuclear termetallic oxo-oxo alkoxide, Eu₃K₃TiO₂(OBu^t)₁₁(OMe/OH)(HOBu^t) (**1**), has been synthesised through metathesis, hydrolysis and decomposition reactions all together. It is the first example of a termetallic lanthanide alkoxide reported as far as we can find and has an unusual structure containing two fused oxo-centered groups: *fac*-Eu₃K₃O and K₃TiO, respectively. The central part of the structure consisting an Eu₃K₃O unit, is expected for an oxo-alkoxide with such a high average electropositive character and there are examples in the literature of this kind of structures. However, the Ti tetrahedron attached to a K₃ face of the Eu₃K₃O octahedron is an unusual feature that might give insight on the construction of larger oxo-alkoxide units by joining stable molecular building blocks and the details of how charge density of oxo and alkoxo groups is distributed in oxo-alkoxides. The only closely related molecule found is Ba₆Li₃O₂(OBu^t)₁₁(THF)₃*THF, which has a Ba₃Li₃O trigonal prism fused to the Ba₆O octahedron. However, more examples are needed for a good understanding of the formation of oxo-alkoxide structures and compositions of this complexity.

CCDC file 749748 contains 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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Fig. 1 IR spectrum of (1) as paraffin-mull

Fig. 2 ORTEP representation of $\text{Eu}_3\text{K}_3\text{Ti}(\mu_6\text{-O})(\mu_4\text{-O})(\mu_3\text{-OMe/OH})(\mu_3\text{-OBu}^t)_6(\mu\text{-OBu}^t)_2(t\text{-OBu}^t)_4\text{H}$

Fig. 3 The crystal packing of the molecules, represented by their $\text{Eu}_3\text{K}_3\text{TiO}_2$ cores, in projection parallel to the c axis. The light and dark grey molecules form two layers positioned around $z=-0.25$ and $z=+0.25$ respectively

Fig. 4 M_xO polyhedron view of 1, carbon and hydrogen atoms omitted

Fig. 5 Structure of: (left) $\text{Eu}_3\text{K}_3\text{TiO}_2(\text{OBu}^t)_{11}(\text{OMe}/\text{OH})(\text{HOBu}^t)$ (1) and (right) $\text{Ba}_6\text{Li}_3\text{O}_2(\text{OBu}^t)_{11}(\text{THF})_3 \cdot \text{THF}$ [51]