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Potassium, Ytterbium(II), and Samarium(III) Alkoxide Complexes Containing the Tris((2-dimethylaminomethyl)phenyl)methoxide Ligand: Synthesis and Structures

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Abstract—The reaction of tris((2-dimethylaminomethyl)phenyl)methanol ((2-$Me_2NCH_2C_6H_4)_3COH$) with potassium hydride in THF at –35°C affords dimeric alkoxide {[(2-$Me_2NCH_2C_6H_4)_3CO$]K(THF)}$_2$ (**I**) in a yield of 90%. The reaction of compound **I** with $YbI_2(THF)_2$ (1 : 1, 25°C) gives the Yb(II) alkoxyiodide complex {[(2-$Me_2NCH_2C_6H_4)_3CO$]Yb(μ-I)$(THF)_2$}$_2$ (**II**) in a yield of 57%. Complex **II** in the crystalline state is dimeric due to two bridging iodide ligands. Unlike the Yb(II) compound, the exchange reaction of complex **I** with $SmI_2(THF)_2$ (1 : 1, 25°C) in THF followed by the addition of dimethoxyethane (DME) involves the oxidation of the metal to form the trivalent samarium complex [(2-$Me_2NCH_2C_6H_4)_3CO]_2SmI$ (**III**), which is isolated in a yield of 60%. The molecular structures of the complexes are determined by X-ray diffraction (XRD) (CIF files CCDC nos. 2259700 (**I**), 2259701 (**II**), and 2259702 (**III**)).

Keywords: ytterbium, samarium, potassium, alkoxide anion, tris((2-dimethylaminomethyl)phenyl)methoxide, synthesis

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INTRODUCTION

Continuous progress in studying a number of classes of highly reactive lanthanide compounds (alkyl, hydride, amide, etc.) designed for the use in homogeneous catalysis has been observed within the recent three decades [1–9]. Lanthanide complexes capable of forming stable derivatives in the oxidation state +2 (Sm, Eu, Yb) are of special interest due to their unique reactivity caused by two active centers: Ln–R bond (R = Alkyl, H, NR_2) and low-valent metal [6, 8–16]. At the same time, owing to a high electropositivity of lanthanides [17, 18] and predominantly ionic character of the metal–ligand interaction in their organic derivatives, the use of ligands forming stable organic anions is preferred to provide the stabilization of the coordination sphere of the metal. Just this explains the fact that to the recent time the cyclopentadienyl complexes have prevailed among the organic derivatives of lanthanides [18–22]. It is difficult to overestimate the role of the C_5Me_5 ligand in the lanthanide chemistry, and the use of this ligand gave a powerful impulse to the development of this field [22–24]. However, a number of drawbacks inherent in the cyclopentadienyl series derivatives and associated with the easy transfer of the η^5-bound Cp ligands between two metallocenters [25–27] and a tendency of mixed-ligand lanthanide complexes to the redistribution of ligands and formation of the homoligand derivatives [28, 29] put forward a task to design new types of the ligand environment capable of providing the kinetic stabilization of the metal complex. The tertiary alkoxide anion R_3CO^- has the electron-donating properties and can rigidly bind with the oxophilic metallocenter and, hence, can act as a convenient and easily modified alternative to the standard Cp platform. However, only several examples of mixed-ligand complexes containing alkoxide ligands are known to the present time [30–33], and their reactivity and catalytic activity remain unstudied. In 2022, the new tris(aryl)carbinolate ligand bearing additional donor NR_2 groups (R = Me, $(CH_2)_5$) has first been developed by our research group and was implemented in the Sc(III) chemistry [34].

In this work, we describe the study of the coordination of the tetrapodal ligand (2-$Me_2NCH_2C_6H_4)_3CO$ with Yb^{2+} and Sm^{2+} ions and the synthesis and structures of the potassium {[(2-$Me_2NCH_2C_6H_4)_3$-CO]K(THF)}$_2$ (**I**), ytterbium {[(2-$Me_2NCH_2C_6H_4)_3$-CO]Yb(μ-I)$(THF)_2$}$_2$ (**II**), and samarium [(2-$Me_2NCH_2C_6H_4)_3CO]_2SmI$ (**III**) alkoxide complexes.

EXPERIMENTAL

All compounds were synthesized and isolated in a vacuum apparatus using the standard Schlenk procedure. After drying over solid NaOH, THF and DME were purified from water and oxygen traces by distillation with sodium benzophenone ketyl. Hexane was distilled over the Na/K alloy. Deuterated benzene (C_6D_6) was dehydrated by metallic sodium, degassed, and condensed in vacuo. Tris((2-dimethylaminomethyl)phenyl)methanol was synthesized according to a published procedure [34]. The synthesis of $LnI_2(THF)_n$ (Ln = Yb, $n = 2$; Sm, $n = 3$) was carried out using a described procedure [35]. Commercially available KH (Aldrich) was used. IR spectra were recorded on a Bruker-Vertex 70 instrument. Samples of the compounds were prepared in a dry argon atmosphere (MBraun glove box) as suspensions in Nujol. ^{1}H, ^{13}C, and HSQC ^{1}H–^{13}C NMR spectra were recorded on Bruker Avance III and Bruker DPX-300 instruments (25°C, C_6D_6). Chemical shifts were presented in ppm relative to residual protons of the deuterated solvents. Elemental analysis was conducted on a Carlo Erba Model 1106 instrument. The contents of ytterbium and samarium were determined by complexonometric titration (Trilon B) using xylenol orange as the indicator [36].

Synthesis of potassium tris((2-dimethylaminomethyl)phenyl)methanolate tetrahydrofuranate (I). Potassium hydride KH (0.110 g, 2.78 mmol) was added with vigorous stirring to a solution of $(2\text{-}Me_2NCH_2C_6H_4)_3COH$ (1.000 g, 2.32 mmol) in THF (10 mL) cooled to –35°C. The reaction mixture was stirred at –35°C for 2 h with the periodical removal of the evolved hydrogen. Then the temperature of the mixture was brought to 25°C, and the mixture was left stirring for 24 h more. After which, the solution was filtered from a KH excess and concentrated to 5 mL. Colorless crystals of complex **I** were prepared by the slow diffusion of hexane (15 mL) to a solution of the complex in THF (5 mL). The mother liquor was decanted from the residue, and the crystals of the complex were dried at room temperature in vacuo for 2 h. The yield of complex **I** was 1.300 g (90%).

For $C_{32}H_{44}N_3O_2K$ (*FW* = 541.82)

Anal. calcd., %:	C, 70.94	H, 8.19	N, 7.76
Found, %	C, 70.70	H, 8.32	N, 7.70

^{1}H NMR (300 MHz; 25°C; C_6D_6; δ, ppm): 1.48–1.66 (m, 4H, β-CH_2, THF); 2.03 (s, 18 H, NMe$_2$); 3.26 (d, 3H, CH$_2$, $^2J_{H,H}$ = 13.9 Hz); 3.61 (t, 4 H, α-CH_2, THF); 3.96 (d, 3H, CH$_2$, $^2J_{H,H}$ = 14.8 Hz); 6.87 (br.s, 3H, CH-Ar); 7.02–7.10 (m, 3H, CH-Ar); 7.31–7.40 (m, 3H, CH-Ar); 7.89 (d, 3H, CH-Ar, $^3J_{H,H}$ = 7.0 Hz). ^{13}C NMR (75 MHz; 25°C; C_6D_6; δ, ppm): 25.57 (β-*C*H$_2$, THF); 45.44 (NMe$_2$); 62.91 (CH$_2$); 67.59 (α-*C*H$_2$, THF); 85.77 (*C*O); 126.02 (CH-Ar); 127.40 (CH-Ar); 128.78 (CH-Ar); 131.00 (CH-Ar); 139.70; 146.54. IR (ν, cm^{-1}): 1592 s, 1323 m, 1298 m, 1260 m, 1244 m, 1167 s, 1147 s, 1096 s, 1030 s, 986 m, 957 m, 911 s, 883 m, 850 s, 760 s, 642 s, 620 m, 519 m.

Synthesis of ytterbium bis(tris(2-dimethylaminomethyl)phenyl)methanolate ditetrahydrofuranate iodide (II). A solution of complex **I** (0.900 g, 1.75 mmol) in THF (10 mL) was added with vigorous stirring to a suspension of $YbI_2(THF)_2$ (1.000 g, 1.75 mmol) in THF (20 mL) at room temperature. The solution quickly turned orange, a precipitate of $YbI_2(THF)_2$ was dissolved, and a finely crystalline precipitate of KI was formed. The solution was stirred for 24 h, centrifuged, separated from the precipitate, and concentrated to 5 mL. Bright orange crystals of complex **II** were prepared by the slow diffusion of hexane (15 mL) to a THF solution (5 mL). The mother liquor was poured down, and the crystals of complex **II** were dried at room temperature in vacuo for 2 h. The yield was 0.828 g (57%).

For $C_{36}H_{52}N_3O_2IYb$ (*FW* = 874.79)

Anal. calcd., %	C, 49.43	H, 5.99	N, 4.80	Yb, 19.78
Found, %	C, 49.65	H, 6.07	N, 4.72	Yb, 19.56

^{1}H NMR (300 MHz; 25°C; C_6D_6; δ, ppm): 1.41 (br.s, 4H, β-CH_2, THF); 2.24 (s, 18 H, NMe$_2$); 2.98 (d, 3H, CH$_2$, $^2J_{H,H}$ = 12.9 Hz); 3.58 (br.s, 4H, α-CH_2, THF); 4.37 (d, 3H, CH$_2$, $^2J_{H,H}$ = 12.3 Hz); 6.67–6.95 (compl. m, 6H, CH-Ar); 7.08–7.11 (m, 3 H, CH-Ar); 7.44 (d, 3H, CH-Ar, $^3J_{H,H}$ = 6.9 Hz). ^{13}C NMR (75 MHz; 25°C, C_6D_6; δ, ppm): 25.36 (β-*CH*$_2$, THF); 45.99 (NMe$_2$); 64.39 (CH$_2$); 67.78 (α-*CH*$_2$, THF); 89.05 (*C*O); 125.65 (CH-Ar); 126.16 (CH-Ar); 128.53 (CH-Ar); 133.91 (CH-Ar); 137.10; 153.54. IR (ν, cm^{-1}): 1595 s, 1320 m, 1304 m, 1269 s, 1204 m, 1171 s, 1155 s, 1103 s, 1074 s, 1032 s, 988 m, 951 m, 911 s, 879 s, 839 m, 700 s, 642 s.

Synthesis of samarium(III) bis(tris(2-dimethylaminomethyl)phenyl)methanolate iodide (III). A solution of complex **I** (0.988 g, 1.82 mmol) in THF (10 mL) was poured with vigorous stirring to a suspension of $SmI_2(THF)_2$ (1.000 g, 1.82 mmol) in THF (10 mL) at room temperature. The solution color quickly changed from blue to dark brown, a precipitate of $SmI_2(THF)_2$ was dissolved, and a finely crystalline precipitate of KI was formed. The solution was stirred for 24 h more, centrifuged, separated from the precipitate, and concentrated to 3 mL. DME (1 mL) was added to the dark brown solution in THF, and the resulting mixture was left to stay at room temperature for 72 h. After 72 h, the solution became lighter, and a minor amount of yellow crystals of complex **III** pre-

Table 1. Main crystallographic data and refinement parameters for complexes **I–III**

Parameter	Value		
	I	**II**	**III**
Empirical formula	$C_{64}H_{88}N_6O_4K_2$	$C_{72}H_{104}N_6O_6I_2Yb_2$	$C_{56}H_{72}N_6O_2ISm$
FW	1083.60	1749.49	1138.44
T, K	120	120	100
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
Z	1	1	4
Z'	0.5	0.5	1
a, Å	11.118(5)	9.2277(11)	12.4521(4)
b, Å	12.402(6)	10.6156(13)	21.1603(7)
c, Å	12.661(6)	18.521(2)	22.7915(7)
α, deg	108.663(10)	90.729(3)	90
β, deg	106.243(10)	97.228(2)	103.150(2)
γ, deg	100.082(11)	90.671(3)	90
V, $Å^3$	1519.3(13)	1799.6(4)	5847.9(3)
ρ_{calc}, g cm^{-3}	1.184	1.614	1.293
μ, cm^{-1}	2.07	34.93	15.73
F(000)	584	872	2324
$2\theta_{max}$, deg	54	56	52
Number of measured reflections	16240	25784	59397
Number of independent reflections	6631	8664	11489
Number of reflections with $I > 3\sigma(I)$	2683	5746	9430
Number of refined parameters	360	407	619
R_1	0.0633	0.0428	0.0406
wR_2	0.1442	0.0869	0.1033
GOOF	0.892	0.963	1.041
Residual electron density (d_{max}/d_{min}), e $Å^{-3}$	0.300/–0.458	0.918/–0.789	2.015/–1.198

cipitated. The main amount of crystals of complex **III** was obtained by the slow diffusion of hexane (15 mL) to the mother liquor of the complex in a THF–DME (3 : 1, mL/mL) mixture. The mother liquor was poured down, and the crystals of the complex were dried at room temperature in vacuo for 2 h. The yield based on complex **I** involved in the reaction was 0.622 g (60%). Methyl vinyl ether $CH_3OCH=CH_2$ was found in the mother liquor by the GC/MS method.

For $C_{56}H_{72}N_6O_2ISm$ (*FW* = 1138.50)

Anal. calcd., %	C, 59.08	H, 6.37	N, 7.38	Sm, 13.21
Found, %	C, 59.30	H, 6.22	N, 7.46	Sm, 13.60

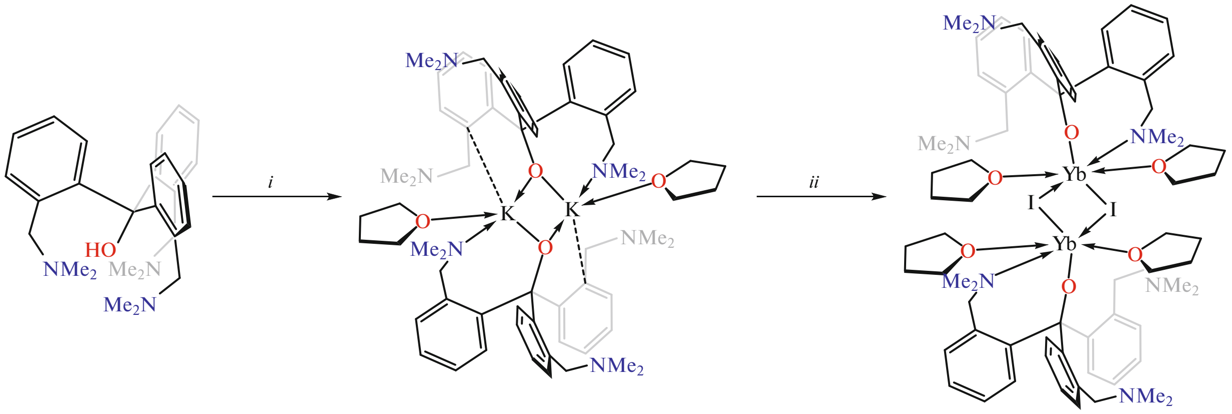
IR (ν, cm^{-1}): 1572 m, 1320 m, 1302 m, 1252 s, 1169 m, 1150 s, 1098 s, 1059 s, 1022 s, 984 s, 949 m, 918 s, 860 s, 818 m, 762 s, 698 m, 640 s, 615 m.

XRD of complexes **I** and **II** were carried out at 120 K on a Bruker APEX2 DUO CCD diffractometer, and that of complex **III** was conducted at 100 K on a Bruker D8 Quest CMOS diffractometer (MoK_α radiation, graphite monochromator, ω scan mode). The structures were solved using the ShelXT program [37] and refined by full-matrix least squares using the Olex2 program [38] in the anisotropic approximation for F^2_{hkl}. The positions of hydrogen atoms were calculated geometrically and refined in the isotropic approximation by the riding model [38]. The main crystallographic data and refinement parameters are given in Table 1.

The coordinates of atoms and full crystallographic parameters for compounds **I**, **II**, and **III** were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 2259700 (**I**), 2259701 (**II**), and 2259702 (**III**); http://www.ccdc.cam.ac.uk/).

RESULTS AND DISCUSSION

The reaction of $(2\text{-}Me_2NCH_2C_6H_4)_3COH$ [34] with KH in THF was conducted at –35°C for 2 h and then 24 h more at room temperature (Scheme 1). The reaction occurs with gaseous H_2 evolution and KH dissolution. Large colorless crystals of complex $\{[(2\text{-}Me_2NCH_2C_6H_4)_3CO]K(THF)\}_2$ (**I**) suitable for XRD were prepared in a yield of 90% by the slow diffusion of hexane to a solution of the complex in THF.



(**I**) 90% (**II**) 57%

Reagents: *i*. KH, THF, –35–25°C; *ii*. $YbI_2(THF)_2$, THF, 25°C

Scheme 1.

Complex **I** is insensitive to oxygen, but its hydrolysis occurs rapidly in a wet atmosphere to form the initial carbinol and potassium hydroxide. The complex is highly soluble in THF, restrictedly soluble in aromatic hydrocarbons (benzene, toluene), and insoluble in hexane. The molecular structure of complex **I** is shown in Fig. 1. Selected bond lengths and bond angles are listed in Table 2. According to the XRD data, complex **I** crystallizes in the triclinic space group (symmetry $P\bar{1}$). The molecule of compound **I** is a dimer in which the potassium ions are linked with each other by the bridging alkoxide anions (Fig. 1). Each potassium cation in complex **I** is coordinated by the alkoxide ligand via the μ^2-O, κ^1-N mode, whereas the remained NMe_2 groups are not coordinated to the metal. The central fragment K(μ^2-O)$_2$K is absolutely planar with the angles K(1)O(1)K(1) 95.55(7)° and O(1)K(1)O(1) 84.46(9)°. The K–O bond lengths (2.621(3) and 2.531(3) Å) are comparable with the values characteristic of the known potassium alkoxides (coordination number 4) [39]. Unlike the previously published potassium alkoxide complexes $[^t\text{BuOK}]_4$ [40], $[^t\text{AmylOK}]_4$ [41], $[\text{Ph}_2\text{CMeOK}]_4$ [39], and $[\text{Thienyl}_3\text{COK}]_4$ [42] with the tetrameric heterocubane structure, the dimeric structure of complex **I** is accomplished due to the polydentate nature and exclusive volume of the $(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_3\text{CO}^-$ anion. The coordination sphere of K^+ contains a THF molecule as well. Note the nonvalent interaction of the K^+ cation with one of three aromatic fragments of the tris(aryl)carbinolate ligand, which is expressed as a short contact of the potassium atom with the *ipso*-carbon atom (K–C_{ipso} 3.390(4) Å) (Fig. 1). This fact is somewhat unusual, since the donor amino group NMe_2 linked with the same aromatic fragment is not coordinated to the metal.

The proton NMR spectrum of complex **I** (C_6D_6, 25°C) contains the expected set of signals corresponding to protons of the alkoxide ligands and coordinated THF molecules. Unlike the proton NMR spectrum of the initial carbinol [34], all signals in the spectrum of complex **I** are rather narrow indicating the absence of dynamic processes. The diastereotopic protons of the CH_2NMe_2 methylene group give two characteristic well resolved doublets with chemical shifts of 3.26 and 3.96 ppm (spin–spin coupling constants are $^2J_{\text{H,H}}$ = 13.9 and 14.8 Hz, respectively). Although only one of three NMe_2 groups is coordinated to the potassium ion in the crystalline state, all the three NMe_2 groups of each ligand are equivalent and appear as a singlet with a chemical shift of 2.03 ppm in the proton and carbon NMR spectra. Probably, a very fast dynamic coordination–decoordination of the NMe_2 groups to the metal occurs in the solution at 25°C. The signals corresponding to the α-CH_2 and β-CH_2 protons of the coordinated THF molecule appear as the triplet (3.61 ppm) and multiplet (1.48–1.66 ppm).

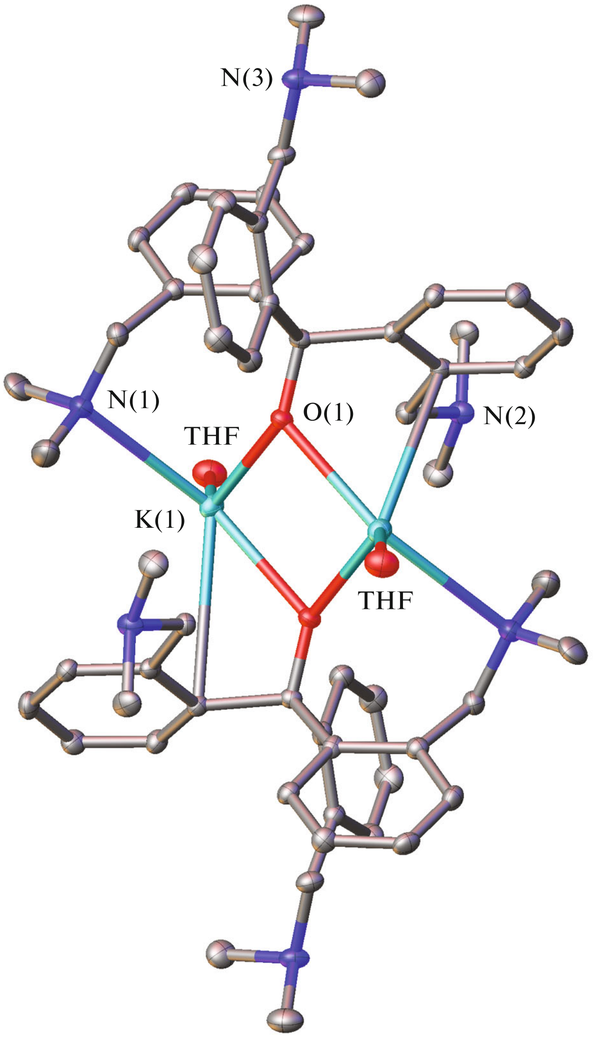


Fig. 1. General view of complex **I**. Hereinafter the atoms are presented by thermal vibration ellipsoids (p = 30%), the hydrogen atoms and CH_2 groups of the THF molecules are omitted for clarity, and the numeration is given only for symmetrically independent heteroatoms. The O(1S) oxygen atoms of the THF molecules are marked as THF. The molecule of the complex in the crystal occupies the partial position: the inversion center is localized in the geometric center of the K_2O_2 cycle.

The alkoxyiodide complex $\{[(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_3\text{CO}]\text{Yb}(\mu\text{-I})(\text{THF})_2\}_2$ (**II**) was synthesized by the reaction of equimolar amounts of $\text{YbI}_2(\text{THF})_2$ and **I** in THF at 25°C (Scheme 1) and was isolated as orange crystals upon recrystallization from a THF–hexane mixture in a yield of 57%. Complex **II** is highly soluble in THF and insoluble in hexane. When complex **II** is dissolved in aromatic solvents, a finely crystalline yellow-orange precipitate not suitable for XRD is formed. However, the microanalysis and IR spectroscopy data indicate the loss of one molecule of coordinated THF and formation of a complex with the presumable composition $\{[(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_3\text{CO}]\text{Yb}(\mu\text{-I})(\text{THF})\}_2$. No ligand redistribution and formation of symmetric products are observed.

Complex **II** was characterized by elemental analysis, NMR and IR spectroscopy, and XRD. According to the XRD data, complex **II** crystallizes in the triclinic space group (symmetry $P\bar{1}$), and its molecular structure is shown in Fig. 2. The complex is dimeric, and the ytterbium atoms are bound to each other by

Table 2. Selected bond lengths (*d*) and bond angles (ω) in complexes **I**–**III***

Bond	*d*, Å	Angle	ω, deg
		I	
K(1)–O(1)	2.531(3)	O(1)K(1)O(1)$^{\#}$	84.46(9)
K(1)–O(1)$^{\#}$	2.621(3)	K(1)O(1)K(1)$^{\#}$	95.55(7)
K(1)–N(1)	2.884(4)		
K(1)–O(1S)	2.759(7)		
K(1)–C(12)	3.390(4)		
		II	
Yb(1)–I(1)	3.2282(6)	I(1)Yb(1)I(1)$^{\#}$	83.189(14)
Yb(1)–I(1)$^{\#}$	3.2490(5)	Yb(1)I(1)Yb(1)$^{\#}$	96.810(13)
Yb(1)–O(1)	2.147(4)		
Yb(1)–O(1S)	2.482(4)		
Yb(1)–O(2S)	2.443(4)		
Yb(1)–N(1)	2.581(5)		
		III	
Sm(1)–I(1)	3.1737(4)	O(1)Sm(1)O(2)	100.39(11)
Sm(1)–O(1)	2.128(3)	O(1)Sm(1)I(1)	105.00(7)
Sm(1)–O(2)	2.149(3)	O(2)Sm(1)I(1)	154.60(8)
Sm(1)–N(1)	2.608(4)		
Sm(1)–N(2)	2.670(3)		
Sm(1)–N(4)	2.759(4)		

* Symmetry code: $^{\#}$ $1 - x$, $1 - y$, $2 - z$.

two μ^2-bridging iodide ligands. The geometry of the coordination environment of each of the ytterbium atoms is a distorted octahedron. Two oxygen atoms of the coordinated THF molecules, iodide ligand, and NMe_2 group lie in the equatorial plane, whereas the alkoxide oxygen and the second bridging iodide ligand I^- occupy the axial positions. The coordination number of the ytterbium atom is 6. The Yb–O covalent bond lengths are the same and equal to 2.145(4) Å. These values are close to the bond lengths in the earlier published ytterbium alkoxide complexes with the $^t Bu_3CO^-$ (2.092(14) Å) [43] and 2,4,6-$Me_3C_6H_2O^-$ (2.178(5) Å) ligands [44]. The Yb–O bonds in complex **II** are predictably shorter noticeably than those in the ytterbium complexes with the bridging alkoxide ligands: $[(Me_3Si)_3CYb(Et_2O)OEt]_2$

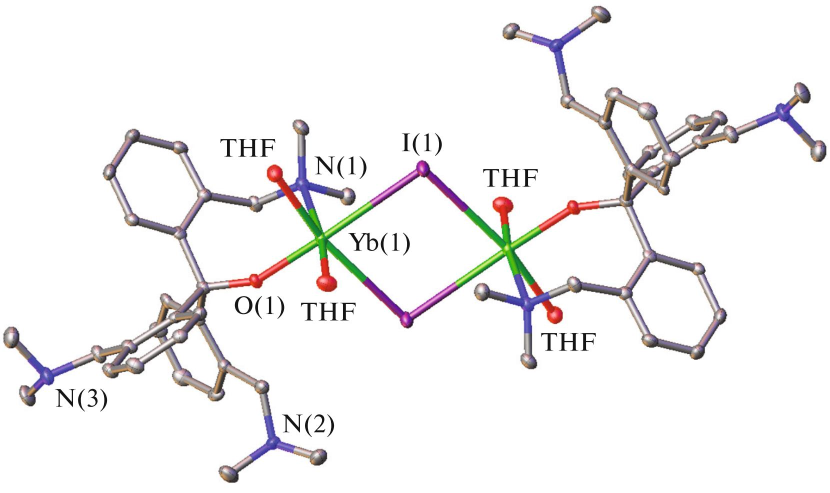
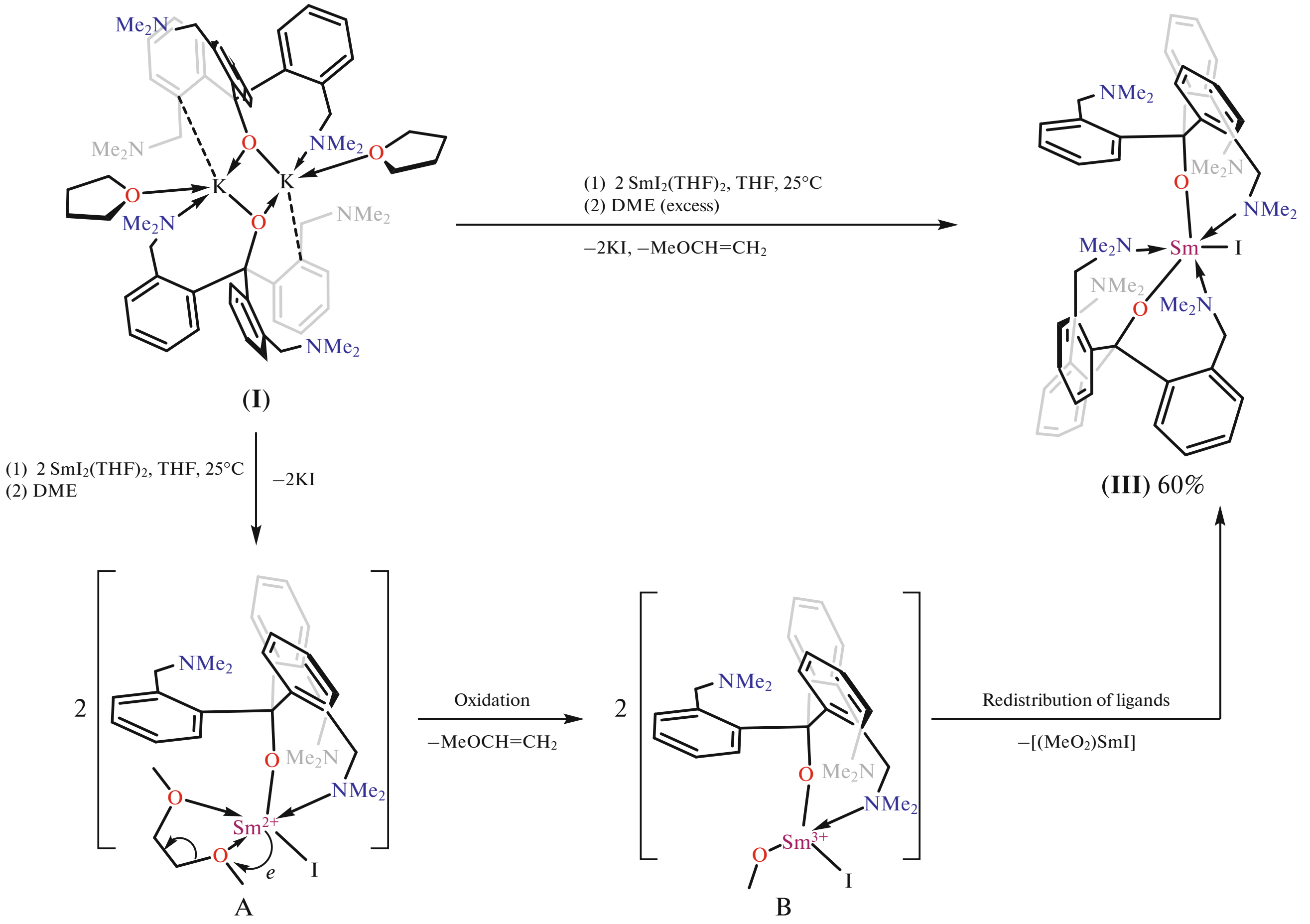


Fig. 2. General view of complex **II**. The O(1S) and O(2S) oxygen atoms of the THF molecules are marked as THF. The molecule of the complex in the crystal occupies the partial position: the inversion center is localized in the geometric center of the Yb_2I_2 cycle.

(2.276(10) Å) [45] and $[Ph_3COYb(DME)I]_2$ (2.302(10) Å) [46]. Unlike complex **II**, the dimeric structure is accomplished in the related mixed-ligand ytterbium complex $[(Ph_3CO)Yb(DME)I]_2$ due to the bridging Ph_3CO^- anions [46]. The four-membered metallocycle $Yb(\mu^2\text{-}I)Yb$ is planar: the I(1)Yb(1)I(1) bond angle is appreciably smaller (83.186(14)°) that those in the half-sandwich cyclopentadienyl–iodide $[Cp^{Bn5}Yb(DME)(\mu\text{-}I)]_2$ (85.707(8)°) [47], $[C_5Me_5\text{-}Yb(THF)_2(\mu\text{-}I)]_2$ (88.28(5)°) [48], and $[C_5H_3tBu_2Yb(Et_2O)(\mu\text{-}I)]_2$ (88.78(1)°) [49] and formamidinate–iodide $[(DippForm)Yb(THF)_2(\mu\text{-}I)]_2$ (90.486(14)°) [50] Yb(II) complexes. The Yb–I bonds in complex **II** (3.2282(6) and 3.2490(6) Å) are somewhat longer than those in the previously published complexes with the bridging iodide ligands [49, 51]. Nevertheless, they are comparable with the Yb–I bond lengths in the half-sandwich ytterbium cyclopentadienyl complex, where the metal ions are additionally coordinated by the NMe_2 donating groups $(1,2\text{-}Do_2Cp)YbI(THF)_2$ (3.2529(8) Å) [52]. Similarly to complex **I**, in complex **II** only one NMe_2 group is coordinated to the metal, and the Yb(1)–N(1) bond length is 2.581(5) Å. The coordination sphere of ytterbium also contains two THF molecules, and the Yb–O bond lengths (2.482(4) and 2.443(4) Å) fall on the range of values typical of similar complexes [53].

Complex **II** is stable in a C_6D_6–THF-d_8 (90 : 10, %/%) mixture, and no properties of ligand redistribution and symmetrization were observed even when a solution of the complex was hold at elevated temperature (70°C) for 24 h. In the absence of THF-d_8, a solution of the complex in C_6D_6 becomes turbid rather rapidly and an insoluble orange precipitate is formed (see above). In this case, the proton NMR spectrum exhibits signals of unbound THF only. In the proton NMR spectrum, all signals belonging to three aromatic substituents of the carbinolate ligand are equivalent, which is likely related to the absence of rigid κ^1-O-, κ^2-N coordination of the ligand to the metal in the solution. The spectrum of complex **II** differs from the spectrum of the earlier published scandium alkoxide–dialkyl complex $[(2\text{-}Me_2NCH_2C_6H_4)_3CO]Sc(CH_2SiMe_3)_2$, where all signals belonging to the carbinolate ligand are nonequivalent because of the rigid κ^1-O-, κ^2-N coordination. The signals belonging to the diastereotopic protons of the CH_2NMe_2 methylene group appear as well resolved doublets with chemical shifts of 2.89 and 4.37 ppm (spin–spin coupling constants are $^2J_{H,H}$ = 12.9 and 12.3 Hz, respectively). Nevertheless, the signals belonging to the protons of the coordinated THF groups are rather strongly broadened (1.41 and 3.58 ppm), which possibly indicates the occurrence of dynamic processes related, most probably, to the coordination–decoordination of the THF molecules. It is likely just this explains the loss of the coordinated solvent upon an attempt of dissolving the complex in aromatic solvents.

In the case of the reaction of complex **I** with $SmI_2(THF)_2$ (THF–DME, 25°C), the bis(alkoxide)–iodide complex of trivalent samarium $[(2\text{-}Me_2NCH_2C_6H_4)_3CO]_2SmI$ (**III**) was synthesized. The compound was isolated as yellow crystals in a yield of 60% based on the initial potassium alkoxide **I** (Scheme 2).



Scheme 2.

The reaction was carried out in a THF medium and accompanied by a change in the solution color from dark blue to almost black and precipitation of KI. Attempts to crystallize the product from THF were unsuccessful. The addition of DME to the reaction mixture led to a gradual change in its color to yellow, which is related to the oxidation of Sm(II) to Sm(III) (Scheme 2). It is most likely that the exchange reaction results in the target mixed-ligand Sm(II) alkoxide–iodide complex (Scheme 2, A), which undergoes intramolecular one-electron oxidation leading to the cleavage of the C–O bond of DME and formation of methyl vinyl ether and Sm(III) methoxide (Scheme 2, B). In turn, compound B undergoes symmetrization, the products of which are compounds **III** and [$(MeO)_2SmI$]. The GC/MS detection of $MeOCH=CH_2$ in the reaction mixture unambiguously indicates the occurrence of the redox process involving the DME molecule. The oxidation of Ln(II) to Ln(III) (Ln = Sm, Yb) under the action of DME with the formation of the methoxide complex is the well-known process [54–56], which was observed for both the samarium and ytterbium compounds with a lower reduction potential. Unfortunately, we failed to isolate [$(MeO)_2SmI$] in the individual form from the reaction mixture.

Light yellow crystals of complex **III** suitable for XRD were prepared by the slow diffusion of hexane to a concentrated solution of the complex in a DME–THF (1 : 3, mL/mL) mixture. The complex crystallizes in the monoclinic space group (symmetry $P2_1/c$) and has the monomeric structure, unlike complexes **I** and **II**. The Sm^{3+} cation has the octahedral environment, and the alkoxide ligands are nearly perpendicular to each other with an O(1)Sm(1)O(2) angle of 100.39(11)° (Fig. 3). The Sm–O bond lengths are 2.128(3) and 2.149(3) Å. In spite of the high oxophilicity of the Sm^{3+} ion, the coordination sphere of the metal contains no coordinated DME molecules. However, the intramolecular coordination of the NMe_2 fragments occurs preferably in this case, and the Sm–N distances differ substantially from each other being 2.608(4), 2.670(3), and 2.759(4) Å. The iodide ligand is terminal with a Sm(1)–I(1) bond length of 3.1737(4) Å, which correlates well with the values in the earlier described Sm(III) iodide complexes (coordination number 6) [57–59].

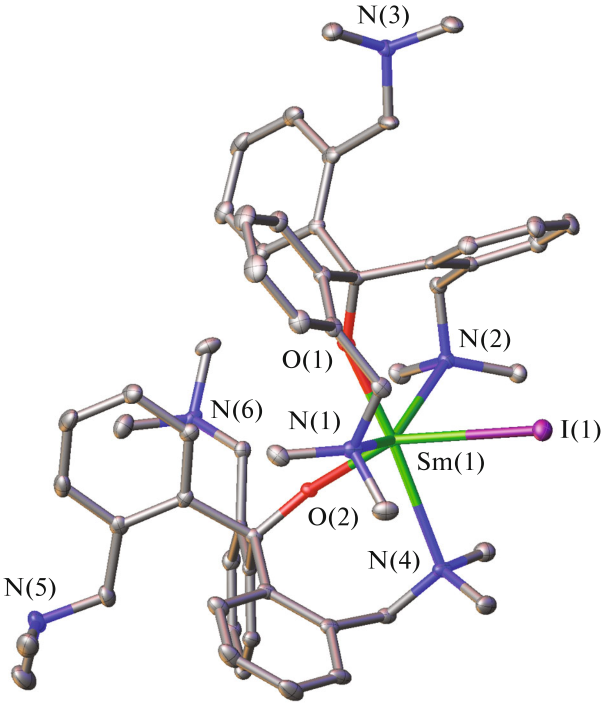


Fig. 3. General view of complex **III**.

To conclude, the specific features of the coordination of the new tetrapodal alkoxide ligand $(2\text{-}Me_2NCH_2C_6H_4)_3CO^-$ with Yb^{2+} and Sm^{3+} ions were studied. The ytterbium and potassium complexes were found to be dimeric, and in complex **I** the dimeric structure takes place due to the bridging alkoxide anions, whereas the I^- iodide ligands are bridging in complex **II**. An attempt to synthesize the mixed-ligand Sm(II) alkoxide–iodide complex resulted in the oxidation of the metal by the DME molecule with the simultaneous redistribution of the ligands and formation of the Sm(III) bis(alkoxide)–iodide complex.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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