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Study of the Possibility of Using Salt Metathesis Reactions for the Synthesis of the Neodymium and Samarium β-Diketiminate Chalcogenide Complexes. Unexpected Reduction of Sm(III) to Sm(II)

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Abstract—The possibilities of the ion exchange reactions between the neodymium(III) and samarium(III) diiodo-β-diketiminate complexes [Ln(Nacnac)I_2(Thf)$_2$] (Ln = Nd (**I**), Sm (**II**); Nacnac is $\mathrm{HC}\left\{\mathrm{C(Me)N}\left(2,6-\mathrm{C_6H_4^{\mathit{i}}Pr_2}\right)\right\}_2^-$; Thf is tetrahydrofuran) and potassium mono- and dichalcogenides K_2Q_n (Q = S, Se, Te; n = 1, 2) in Thf are studied. The ion exchange of iodide ligands by dichalcogenide ligands does not occur under these conditions. The reaction of complex **I** with K_2Se affords the divalent samarium complex [Sm(Nacnac)I(Thf)$_2$] (**III**). The sequence of the steps leading to the formation of this complex, including the reduction of the sterically hindered bis(diketiminate) complex, is proposed.

Keywords: neodymium, samarium, β-diketiminate complexes, chalcogenide complexes, sterically induced reduction

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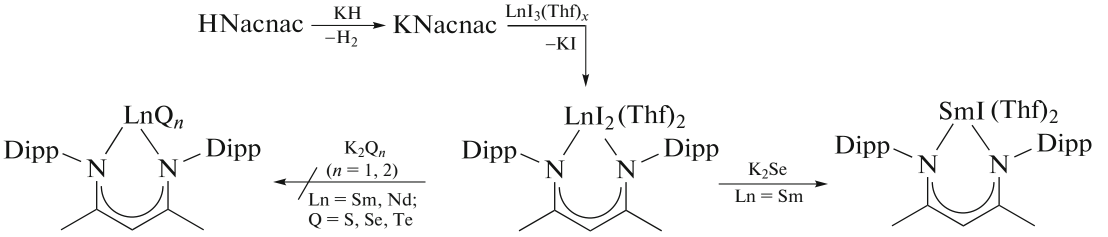
INTRODUCTION

Lanthanide cations are hard Lewis acids and predominantly form complexes with O- and N-donor ligands. The lanthanide complexes with the ligands coordinated by the heavy chalcogen atom (for example, mono- and polychalcogenides or chalcogenolate anions, where chalcogen is Q = S, Se, or Te) are less resistant, as a rule, toward hydrolysis and oxidation [1]. Attention to these compounds is caused by their physicochemical properties interesting for practical applications, first of all, efficient IR luminescence [2]. In addition, the molecular complexes can be used as precursors for the thermal syntheses of lanthanide chalcogenide (nano)materials with magnetic [3–5] and photoelectric [6] properties. According to the Cambridge Structural Database (CSD) data [7], chalcogenolates (QR^-) and complexes with diverse chalcogen-substituted oxo anions significantly prevail among the known lanthanide complexes with chalcogen-donor ligands. The predominant number of the complexes with diverse chalcogen-substituted oxo anions contains sulfur donor atoms, for example, dithiocarbamates and dithiophosphinates [8]. Molecular complexes containing chalcogenide or polychalcogenide fragments in the coordination sphere of one or several lanthanide cations are very rare. Various bulky polydentate ligands are used for the kinetic stabilization of these (poly)chalcogenide complexes. A series of the complexes with the bridging or chelating ligands Q_n^{2-} (Q = S, Se, Te) stabilized by the substituted cyclopentadienide (n = 1–3 [9–12]) or formamidinate ligands (n = 1, 2, 4 [13–15]) is known. The single examples of the complexes with tris(pyrazolyl borate) (n = 1, 2, 4, 5 [16, 17]), β-diketiminate (n = 1 [18, 19]), silylamide (n = 1, 2 [20]), or amine (n = 1, 2 [21, 22]) ligands are also known. Mononuclear chalcogenide complexes are presented by pentachalcogenides (Q = S, Se; n = 5) stabilized by tris(pyrazolylborate) [17] or iminoquinone [23] ligands and by the complex $[\mathrm{DyI_2(Thf)_5}]^+[\mathrm{DyI_2S_5(Thf)_2}]^-$ (Thf is tetrahydrofuran) containing no bulky organic ligands in the coordination sphere of dysprosium [24]. Many polynuclear ("cluster") chalcogenide complexes bearing internal mono- and dichalcogenide ligands were studied [2]. All these complexes were synthesized using the redox reactions in which the lanthanide complex (reducing agent) reacts with a chalcogen source (oxidant), such as elemental chalcogen, phosphinechalcogenide (Ph_3PS, $^n Bu_3PTe$), or a transition metal polychalcogenide complex [25]. The use of other reactions, which are not related to the reduction of the chalcogenide precursors, for the synthesis of lanthanide polychalcogenide complexes was not described. The only exception is the substitution of chloride ions in neodymium and samarium cyclopentadienyl dichlorides $LnCp^xCl_2$ in the reactions with Na_2Se_5 leading to the formation of the unique hexanuclear complexes $[Cp^x_6Ln_6(\mu_6\text{-}Se)(\mu\text{-}Se_2)_6]^{2-}$ (Cp^x = η^5-C_5H_5, η^5-${}^tBuC_5H_4$; Ln = Nd, Sm) containing the inner-cavity hexacoordinated selenium atom [26, 27].

The possibility for the synthesis of the samarium and neodymium mono- and dichalcogenide complexes stabilized by the bulky *N*,*N*'-bis(2,6-diisopropylphenyl)-β-diketiminate ligand ($Nacnac^-$, Scheme 1) using the ion exchange reactions was studied in this work.



$[Ln(Nacnac)I_2(Thf)_2]$
Ln = Nd (**I**); Sm (**II**)

$[Sm(Nacnac)I(Thf)_2]$ (**III**)

Scheme 1.

The diketiminate ligands (L) allow one to modify the substituents both at the donor nitrogen atoms and in the carbon skeleton to achieve the necessary steric and electronic effects. In addition, these ligands can act as antennas for the sensitization of luminescence of lanthanide ions due to a system of conjugated bonds.

EXPERIMENTAL

All procedures with easily oxidized and hydrolyzed substances were carried out in purified argon or in vacuo using the standard Schlenk technique and sealed ampules. The compounds were treated and analyses were prepared in an argon glove box. Solvents were distilled in argon over sodium or sodium–potassium alloy in the presence of benzophenone ketyl, kept over Na–K alloy before use, and transferred by recondensation in vacuo. The initial complexes $[Ln(Nacnac)I_2(Thf)_2]$ (Ln = Nd (**I**), Sm (**II**)) were synthesized in solutions *in situ* without isolation by the interaction of equimolar amounts of lanthanide iodide ($NdI_3 \cdot 3.5Thf$ or SmI_3) and K(Nacnac) and in the crystalline state using a described procedure [28]. SmI_2 was obtained according to the method from [29]. Other reagents (not worse than analytical grade) were used in the commercially available form.

IR spectra (ν, cm^{-1}) were recorded on an FT-801 spectrometer (Simex) in KBr pellets. Elemental analyses (C, H, and N) were performed on a Vario Micro Cube analyzer (Elementar). Elemental analysis on Se was carried out using back iodometric titration [30]. Analysis by energy dispersive X-ray (EDX) spectroscopy was carried out using a Hitachi TM 3000 microscope equipped with a Bruker Nano analyzer.

The syntheses of K_2Q_n (Q = S, Se, Te; n = 1, 2) were carried out using a described procedure [31] from the elements in Thf in the presence of naphthalene. The solvent and naphthalene were removed by heating in vacuo. The procedure was modified for the thorough purification of K_2Se from impurities of K_2Se_2 and metallic potassium. A mixture of elements (K: 0.766 g, 19.6 mmol; Se powder: 0.725 g, 9.18 mmol) and naphthalene (0.117 g, 0.913 mmol) in Thf was stirred in an evacuated vessel consisting of two sections connected at a right angle and equipped with a vacuum stopcock with a Teflon valve. An excess of potassium was taken for the deliberately complete reduction of selenium, and the mixture was stirred for 48 h (6 h are usually enough for the reaction completion [31]). A solution containing potassium naphthalide was decanted to the second section to remove a potassium excess. Without opening the vessel, the solvent and naphthalene were recondensed to the first section by cooling. The suspension was stirred, the precipitate of K_2Se was let to settle, and the solution was poured to the second section. The washing procedure was repeated until the green color of the washing solution disappeared (determined by potassium naphthalenide). The precipitate of K_2Se was dried in vacuo on heating to 70°C. The yield was 1.09 g (75%). The analysis showed a sufficient purity of the product (found: 49.5% Se, calculated: 50.24% Se).

An alternative synthesis of K_2Se was carried out from the elements in liquid ammonia [32]. The product was dried in vacuo without heating. The analysis indicated the presence of one ammonia molecule (exp. 46.3% Se, for $K_2Se \cdot NH_3$ calcd. 45.33% Se), which is consistent with the mentioned procedure. The product was not dried in vacuo at 250°C to

Table 1. Reagents used for the exchange reactions, mg/mmol

Reagents	Q = S		Q = Se		Q = Te	
	$n = 1$	$n = 2$	$n = 1$	$n = 2$	$n = 1$	$n = 2$
SmI_3 (or $[Sm(Nacnac)I_2(Thf)_2]$)	191/0.360	105/0.198	276/0.519	(354/0.366)	101/0.190	(114/0.118)
KL	165/0.360	91/0.20	237/0.519		87/0.19	
K_2Q_n	40/0.36	29/0.20	82/0.52	87/0.37	39/0.19	43/0.13
$NdI_3 \cdot 3.5Thf$ (or $[Nd(Nacnac)I_2(Thf)_2]$)	164/0.211	84/0.11	121/0.155	94/0.12	(201/0.209)	92/0.12
KL	97/0.21	50/0.11	71/0.16	56/0.12		54/0.12
K_2Q_n	23/0.21	16/0.11	25/0.16	29/0.12	43/0.21	40/0.12

remove ammonia, because ammonia does not affect the course of further reactions.

Reaction of $[Ln(Nacnac)I_2(Thf)_2]$ with potassium chalcogenides. To a mixture of SmI_3 (276 mg, 0.519 mmol) and K(Nacnac) (237 mg, 0.52 mmol) was added Thf (5 mL), the resulting mixture was stirred for 12 h, and K_2Se (82 mg, 0.52 mmol) was added to the formed red solution of compound **II** with the KI precipitate. The reaction mixture was stirred with heating (75°C) for 3 days. The dark solution was separated from the orange precipitate by centrifugation. According to the EDX data, the ratio of the contents of heavy elements in the precipitate was K : I : Sm : Se = 31.8(6) : 16.8(10) : 5.0(4) : 18.6(11) at %. The solution was concentrated in vacuo to a volume of 1 mL. The formed oil was diluted with hexane (3 mL), and the mixture was sealed in an evacuated two-section L-like ampule. The ampule was placed in such a way that the bottom section with the solution was at 40°C, and the upper section with a mixture of the reaction products was kept at room temperature. The solvent was transferred to the upper part due to the temperature gradient, and soluble compounds were extracted during several days and collected in the bottom part of the ampule. The resulting solution was concentrated to a small volume to form a mixture of gray-brown needle-like crystals of complex $[Sm(Nacnac)I(Thf)_2]$ (**III**), red crystals of complex **II**, and a small amount of crystals of $SmI_2(Thf)_5 \cdot 1.25Thf$ (**IV** · 1.25Thf according to the X-ray structure analysis data). The formed crystalline product was decanted and dried in vacuo. A minor amount of the dark finely crystalline precipitate of samarium(II) iodide (Sm : I = 11.4(9) : 22.6(15) at % according to the EDX data) remained in the upper part of the ampule. The interaction of equimolar amounts of the beforehand isolated complex **II** with K_2Se gave the same results.

The reactions with other potassium chalcogenides and with the neodymium complexes were carried out similarly (the reagents and their amounts are indicated in Table 1). No change in the color of the solution was observed after heating for 3 days. After the precipitate was separated by centrifugation, the solutions were evaporated in vacuo. The IR spectra of the solid residues were identical for each lanthanide and corresponded to the spectra of complexes $[Ln(Nacnac)I_2(Thf)_2]$ [28].

IR (ν, cm^{-1}; Sm complexes): 3055 w, 2960 s, 2927 m, 2891 m, 2868 m, 1528 br.s, 1459 m, 1429 m, 1394 br.s, 1359 m, 1338 w, 1313 s, 1262 s, 1167 m, 1109 m, 1096 m, 1033 w.sh, 1012 s, 925 s, 875 m, 853 br.m, 838 m, 794 w.sh, 790 s, 757 m, 693 w, 667 w, 636 w. IR (ν, cm^{-1}; Nd complexes): 3063 w, 2961 s, 2929 m, 2868 s, 1515 br.s, 1462 m, 1435 s, 1382 br.s, 1314 m, 1256 m, 1169 m, 1105 m, 1039 w.sh, 1015 s, 930 s, 844 br.m, 797 s, 787 w.sh, 760 w, 754 m, 720 w, 701 w, 631 m.

Direct synthesis of complex $[Sm(Nacnac)I(Thf)_2]$ (III). To a mixture of SmI_2 (171 mg, 0.423 mmol) and K(Nacnac) (202 mg, 0.442 mmol) was added Thf (7 mL), and the resulting suspension was stirred at room temperature for 2 h. The formed precipitate of KI was separated by centrifugation. The solution was slowly concentrated in vacuo to a volume of 0.5 mL, which was accompanied by the crystallization of the product as fine dark needle-like crystals. The solvent was removed, and the crystals were washed with ether (two portions 1 mL each), and dried in vacuo. The yield of complex **III** was 204 mg (60%).

For $C_{37}H_{57}N_2ISm$

Anal. calcd., %	C, 52.95	H, 6.85	N, 3.34
Found, %	C, 53.8	H, 7.05	N, 3.5

According to the elemental analysis data, the compound contains about 5% of a KNacnac impurity. According to the EDX data, the ratio was Sm : I = 4.4(8) : 3.6(5) at %.

IR (ν, cm^{-1}): 3058 w, 2960 s, 2928 m, 2869 m, 1624 m, 1551 s, 1489 w, 1463 m, 1436 m, 1381 m, 1363 m, 1323 m, 1274 m, 1254 m, 1174 m, 1099 w, 1059 w, 1022 w, 934 w, 838 w, 787 m, 759 m, 731 m, 701 m.

Reaction of SmI_3 with K_2Se. A mixture of SmI_3 (57 mg, 0.11 mol), K_2Se (25 mg, 0.16 mol), and Thf

(2 mL) was sealed in an evacuated ampule. The ampule was kept at 45°C for 24 h (no occurrence of the reaction was observed). Then the temperature was increased to 70°C, and the mixture was kept for 15 h more. The color of the solution changed from yellow to colorless, and an orange precipitate was formed. No further changes were induced by the prolonger storage of the mixture at the same temperature for 20 days.

Reaction of SmI_2 with K_2Se_2. A mixture of SmI_3 (49 mg, 0.12 mol), K_2Se_2 (16 mg, 0.07 mol), and Thf (2 mL) was sealed in an evacuated ampule. The ampule was kept at 70°C for 20 days. No changes were observed after 40 h of the reaction. Single yellow crystals were formed after 5 days. Their cell parameters were identical to those for $SmI_3(Thf)_{3.5}$ (according to the X-ray diffraction data on several single crystals, they were compared with the TOVZAF structure in the CSD). The amount of the yellow crystals increased within the next 15 days along with the gradual bleaching of the dark blue solution (this color is characteristic of SmI_2). The brown precipitate of K_2Se_2 retained to the end of the experiment and the solution was not decolorated indicating that the reaction occurred incompletely.

The X-ray structure analyses of compounds **III** (two modifications) and **IV** were carried out using a standard procedure on a Bruker Apex DUO automated four-circle diffractometer equipped with a CCD two-coordinate detector (MoK_α radiation, λ = 0.71073 Å, graphite monochromator) at 150 K. Reflection intensities were measured using φ- and ω-scanning of narrow (0.5°) frames. An absorption correction was applied using the SADABS program [33]. All selected crystals of compound **IV** are nonmerohedral twins and, therefore, the array of the data obtained for one of them was processed taking into account two domains with the twinning matrix (1 0.031 –0.123 0 –1 0 0 0 –1), BASF 0.471. An adsorption correction was applied using the TWINABS program (Version 2012/1). The structures of compounds **III** and **IV** were solved by a direct method and refined by full-matrix least squares in the anisotropic (for non-hydrogen atoms) approximation using a package of the SHELXT [34] and SHEXL [35] programs in the Olex2 program shell [36]. At the last stages of the structure refinement of compound **IV**, the data in the HKLF 5 format were used. The solvate Thf molecules in this structure were refined in the isotropic approximation. Hydrogen atoms in all structures were localized geometrically and refined in the rigid body approximation. The crystallographic data and the experimental and structure refinement details are presented in Table 2.

The X-ray structure analysis data were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1951605 (**II**), 1951606 (**IIIa**), and 1951607 (**IIIb**); http://www.ccdc.cam.ac.uk/conts/retrieving.html).

RESULTS AND DISCUSSION

The “softest” Lewis base, iodide anion, should be the best leaving halide in the exchange of halide ligands by chalcogenides in the coordination sphere of lanthanide ions. Therefore, we checked the possibility of exchange reactions of iodide ions in the $[Nd(Nacnac)I_2(Thf)_2]$ (**I**) and $[Sm(Nacnac)I_2(Thf)_2]$ (**II**) complexes, whose synthesis was described earlier [28]. As a rule, the formation of the KI precipitate insoluble in an organic solvent results in the shift of the ion exchange equilibrium, which can lead to the formation of the chalcogenide complexes (Eq. (1), Solv denotes solvent molecules, e.g., Thf, as ligands).

$$\begin{gathered}\mathrm{LnLI_2(Solv)}_m + \mathrm{K_2Q}_n\mathrm{(s)} \\ \rightarrow \mathrm{LnL(Q}_n\mathrm{)(Solv)}_x + 2\mathrm{KI}\downarrow\mathrm{(s)}.\end{gathered} \tag{1}$$

An aprotic solvent of medium polarity is the most optimum medium for the reaction. A weakly polar or nonsolvating solvent would result in a very low reaction rate because of an insignificant concentration of ions in the solution. A high-polarity solvent (dimethyl sulfoxide, dimethylformamide) or a solvent capable of chelating (e.g., dimethoxyethane or tetramethylethylenediamine) can lead to the isolation of lanthanide cations as solvate complexes $[Ln(Solv)_x]^{3+}$ followed by the complete dissociation of the initial complexes and the redistribution of the stabilizing ligand and chalcogenide ligands between the cations. Protic solvents (e.g., alcohols) can be fairly strong acids for the protonation of the stabilizing anionic ligand, resulting in its leaving in the form of a neutral molecule. Therefore, Thf was chosen as a solvent capable of solvating, to some extent, alkaline metal ions. At the same time, Thf is a fairly labile ligand capable of leaving the coordination sphere of lanthanides [28, 37, 38]. Side processes are possible in the reactions of iodide ligand exchange by chalcogenide ligands, such as a deeper redistribution of ions rather than the exchange of two iodide ions by chalcogenide. In this case, insoluble lanthanide chalcogenides can be formed, for example, according to Eq. (2) (here and in other reaction equations, solvate Thf molecules are omitted).

$$\begin{gathered}3\mathrm{LnLI_2} + 3\mathrm{K_2Q}_n \rightarrow \mathrm{Ln_2(Q}_n\mathrm{)_3}\downarrow \\ + \mathrm{LnL_2I} + 5\mathrm{KI}\downarrow + \mathrm{KL}.\end{gathered} \tag{2}$$

This side process should form complex species with a higher content of diketiminate ligands, for example, $[LnL_2]^+$ or $[LnL_3]$. The possibility of their formation can be excluded using bulky ligands L, which make the formation of bis- or tris(diketiminate) complexes unfavorable for steric reasons. The Nacnac ligand is appropriate from the viewpoint of steric effects. In fact, the $[Ln(Nacnac)_2]$ homoleptic complexes are known only for divalent lanthanide ions (Ln = Sm^{2+}, Eu^{2+}, and Yb^{2+} [38–40]), whereas these complexes of trivalent lanthanide ions with noticeably smaller ionic radii (by ~0.2 Å [41]) are poorly stable because of steric

Table 2. Crystallographic data and structure refinement results for compounds **III** and **IV**

Parameter	Value		
	IIIa	**IIIb**	**IV** · 1.25Thf
Empirical formula	$C_{37}H_{57}N_2O_2ISm$	$C_{37}H_{57}N_2O_2ISm$	$C_{25}H_{50}O_{6.25}I_2Sm$
FW	839.09	839.09	854.80
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a, Å	8.8354(6)	8.5558(7)	13.0752(10)
b, Å	39.068(2)	18.8555(16)	22.7268(17)
c, Å	22.3398(14)	23.909(2)	23.9186(18)
α, deg	90	88.869(3)	69.185(3)
β, deg	98.594(2)	80.891(3)	84.109(3)
γ, deg	90	86.627(3)	89.264(3)
V, Å^3	7624.7(8)	3801.7(6)	6606.5(9)
Z	8	4	8
ρ_{calc}, g/cm^3	1.462	1.466	1.719
μ, mm^{-1}	2.381	2.388	3.679
F(000)	3392.0	1696.0	3344.0
Crystal size, mm	0.26 × 0.13 × 0.05	0.33 × 0.05 × 0.05	0.31 × 0.28 × 0.12
Range of data collection over 2θ, deg	2.118–51.478	1.726–49.426	1.83–51.462
Ranges *h, k, l*	$-10 \le h \le 10$, $-37 \le k \le 47$, $-27 \le l \le 26$	$-10 \le h \le 7$, $-22 \le k \le 22$, $-28 \le l \le 28$	$-15 \le h \le 15$, $-27 \le k \le 27$, $-29 \le l \le 29$
Number of measured reflections	68526	28301	40003
Number of independent reflections (R_{int}, R_σ)	14478 (0.0578, 0.0593)	12767 (0.0641, 0.1119)	40003 (0.0523, 0.0745)
Number of refined parameters	947	884	1086
Number of restraints	594	242	665
GOOF for F^2	1.039	0.946	1.099
R factor ($I > 2\sigma(I)$)	$R_1 = 0.0441$, $wR_2 = 0.0775$	$R_1 = 0.0464$, $wR_2 = 0.0688$	$R_1 = 0.0593$, $wR_2 = 0.1184$
R factor (all data)	$R_1 = 0.0751$, $wR_2 = 0.0855$	$R_1 = 0.0981$, $wR_2 = 0.0822$	$R_1 = 0.1076$, $wR_2 = 0.1455$
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	1.36/–0.81	0.72/–0.73	3.15/–2.18

factors. The only known complex $[Tm^{III}(Nacnac)_2]^+$ was isolated only in the presence of the noncoordinating anion $[B(C_6F_5)_4]^-$ [42].

An additional hindrance for the ion exchange reaction is the low solubility of the initial chalcogenides K_2Q_n in moderately polar organic solvents, which can level down the driving force of the ion exchange reaction. Nevertheless, it can be estimated that the formation of two moles of KI ($\Delta_f G^\circ_{298} = -324.9$ kJ/mol) from one mole of K_2S ($\Delta_f G^\circ_{298} = -364.0$ kJ/mol [43]) provides a substantial thermodynamic gain of 285.8 kJ. This can be enough for the substitution reaction to occur if the Gibbs energies of formation of the lanthanide iodide and chalcogenide complexes in solutions differ by a lower value. No data on the Gibbs energies of formation are available for other potassium (di)chalcogenides K_2Q_n ($n = 1, 2$; Q = S, Se, Te) and, hence, this gain cannot be estimated directly. However, the gain can be expected to be even higher due to the expectedly lower enthalpies of formation of other K_2Q_n compared to that of K_2S.

The reagents were stirred in Thf at room temperature in order to study the possibility of substitution reactions to occur. The concentration of the starting lanthanide complex in solution was about 0.02 mol/L.

In all cases, no reaction was observed within 8 h of stirring. Then the temperature was increased to 60°C, and after 72-h stirring the solution was separated and evaporated in vacuo. The IR spectrum of the solute was compared with the known spectrum of β-diketiminate diiodide complex **I** or **II**. It has previously been shown [28] that the absorption bands corresponding to vibrations of the conjugated system of the β-diketiminate ligand are very sensitive to the ligand environment in the complex. By analogy to the known scandium β-diketiminate chalcogenide complexes [18, 19], we believe that the reaction products of the exchange of iodide ions by (di)chalcogenides should be fairly soluble in Thf, and the presence of them would change the vibration frequencies in the IR spectrum. However, in all cases except for the reaction of complex **II** with K_2Se, the IR spectra of the compounds isolated from solutions did not differ from that for the initial complex **I** or **II**. Thus, even a prolonged contact of the reactants at elevated temperature does not result in the formation of molecular chalcogenide complexes.

The color of the reaction mixture changed from light yellow to brown in the only case of the reaction of complex **I** with K_2Se for 24 h (60°C). Black needle-like crystals of the complex $[Sm^{II}(Nacnac)I(Thf)_2]$ (**III**) were isolated from the solution in 72 h. This compound is formed in a yield of ~15% and crystallizes along with the unreacted initial complex **II**. A longer reaction time results in the gradual disappearance of complex **II** from the solution. However, the crystallization of **III** is accompanied, in this case, by the formation of an insoluble by-product of undetermined structure from can be removed by recrystallization from a Thf-hexane (1 : 5 vol/vol) mixture. We failed to attain a noticeable increase in the yield of compound **III**. The formation of **III** in the bulk was proved by the X-ray diffraction analysis of the single crystal, and the same cell parameters were confirmed for several crystals taken from the mixture of visually homogeneous crystalline precipitates obtained in independent experiments. The ratio of the amounts of the heavy atoms Sm : I = 1 : 1 was confirmed by the EDX method. For a more complete characterization, complex **III** was synthesized via the direct reaction of samarium diiodide $SmI_2(Thf)_2$ with one equivalent of K(Nacnac).

Two polymorphic modifications **IIIa** and **IIIb** were obtained by the crystallization of complex **III** obtained in the reaction of **II** with K_2Se and by direct reaction. The crystallization conditions differed so that **IIIa** was crystallized by the evaporation of a Thf solution, whereas **IIIb** was crystallized from a Thf–hexane (1 : 5 vol/vol) mixture. Nevertheless, both modifications contain no solvate molecules. Each structure contains two crystallographically independent molecules, and the molecular structures of the complexes are nearly identical in both modifications (Table 3). The coordination environment of the samarium atom represents a tetragonal pyramid with a base formed by two nitrogen atoms of the $Nacnac^-$ ligand and two oxygen atoms of the Thf molecules (Fig. 1a), and the iodine atom is located at the pyramid vertex. The coordination number is equal to five, which is unusually low compared to that of complex **II** (coordination number 6), in spite of the larger size of the Sm^{2+} cation compared to that of Sm^{3+}. Only one similar ytterbium complex $[Yb^{II}(Nacnac)(\mu\text{-}I)(Thf)]_2$ (coordination number 5) is known among the lanthanide(II) compounds [44]. The Yb^{2+} ion is coordinated by two iodide ions and only one Thf molecule, although the complex crystallizes from this solvent. Since the ionic radius of Yb^{2+} is noticeably smaller than that for Sm^{2+} (1.08 and 1.22 Å, respectively, for coordination number 7 [41]), it can be concluded that the Thf molecule occupies a larger volume in the coordination sphere than the iodide anion. In both crystalline modifications **IIIa** and **IIIb**, the molecules are oriented similarly relative to the nearest neighbors and the iodine atom of one complex is arranged between the cycles of two Thf molecules of the adjacent complex (Fig. 1b). The stacks are thus formed which propargate along the [100] direction. The adjacent molecules in the stacks are shifted by the translation vector, which determines the minimal lattice parameter *a* (in both cases, see Table 3). Two modifications differ by the relative turn of the adjacent stacks. The diketiminate ligand in the complex adopts the characteristic “boat” geometry, and the C(1), C(3), N(1), and N(2) atoms lie almost in one plane. The C(2) atom deviates from the least-squares plane of these atoms by 0.120–0.144 Å, and the samarium atom deviates in the same direction by 0.958 and 0.961 Å or by 1.084 and 1.114 Å, depending on the modification (atom numbering given in Fig. 1a). The Sm–I, Sm–N, and Sm–O bond lengths are nearly the same for two modifications, and the bonds are substantially elongated compared to similar bonds in complex **II** (Table 2), which unambiguously confirms the oxidation state of samarium +2 in complex **III**. A comparison of the IR spectra of complexes **II** and **III** is also remarkable. The characteristic frequencies of vibrations of the conjugated system of bonds in β-diketiminate are sensitive to a different ligand environment. According to the earlier studies [28], the spectrum of the Sm(III) β-diketiminate complex exhibits the characteristic bands corresponding to stretching vibrations of the C=C, C=N, and $C-CH_3$ bonds in the ligand (1528, 1398, 1314, 1166, and 924 cm^{-1}) and to the C–O bond vibrations in coordinated Thf (853 cm^{-1}). The spectrum of complex **III** demonstrates appreciable shifts of the bands of the diketiminate ligand to the high-energy range, except for the peak at 1398 cm^{-1} (1551, 1381, 1324, 1174, and 934 cm^{-1}), and the peak of coordinated Thf is observed at 840 cm^{-1}. The spectrum also exhibits the medium-intensity band at

Table 3. Selected bond lengths (Å) in complexes **II** [28] and **III**[a]

Bond	**II**[b]	**IIIa (IIIb)**
Sm–N(1)	2.400(3)	2.514(4), 2.507(4)[c] (2.523(5), 2.514(5)[c])
Sm–N(2)		2.515(4), 2.519(4)[c] (2.522(5), 2.521(5)[c])
Sm–O(1)	2.536(3)	2.552(4), 2.546(4)[c] (2.571(4), 2.544(4)[c])
Sm–O(2)		2.559(1), 2.557(4)[c] (2.570(4), 2.587(5)[c])
Sm–I	3.0823(5), 3.0072(4)	3.1536(5), 3.1582(5)[c] (3.1554(6), 3.1577(7)[c])

[a] Atoms are enumerated according to Fig. 1.
[b] The molecule of the complex lies on the crystallographic symmetry plane passing through the Sm and I atoms.
[c] Data for the second independent molecule.

1622 cm^{-1} corresponding to the formation of small amounts of HNacnac due to hydrolysis during spectrum recording.

The formation of the Sm(II) complex from Sm(III) in the reaction that occurs in the absence of evident strong reducing agents is a fairly unusual fact, since all Sm(II) compounds are strong reducing agents (for example, $E°$ for the $\mathrm{SmI}_2^+/\mathrm{SmI}_2$ pair in Thf is 1.41 V vs. Fc$^+$/Fc [45]). It can be assumed that the reducing agent in the reaction is metallic potassium, which could remain in the K_2Se sample after its synthesis from the elements. To exclude this possibility, K_2Se was synthesized by different methods using liquid ammonia as a reaction medium or Thf with naphthalene as an electron carrier. In both cases, the absence of coloration of the final solutions was thoroughly monitored that would indicate an admixture of excess potassium. The selenium content in the obtained K_2Se samples well corresponded to the theoretical value, and the admissible residual amounts of free potassium could not result in the formation of noticeable amounts of the reduction product of **III**. Therefore, the influence of an elemental potassium impurity can be excluded.

The transformation of Sm^{3+} into Sm^{2+} can also take place as a result of so-called sterically induced reduction [46]. In these processes, one of the anionic ligands donates an electron and leaves as a neutral particle (e.g., $\mathrm{Cp}^{*-} - e \rightarrow \mathrm{Cp}^{*\cdot} \rightarrow 0.5\mathrm{Cp}_2^*$, Cp* is pentamethylcyclopentadiene). The leaving ligand is substituted by a less bulky one, or the lanthanide ion is reduced accompanied by an increase in the ionic radius ($\mathrm{Ln}^{3+} \rightarrow \mathrm{Ln}^{2+}$). Any variant leads to a decrease in the steric hindrance in the coordination sphere. A higher steric hindrance of the coordination

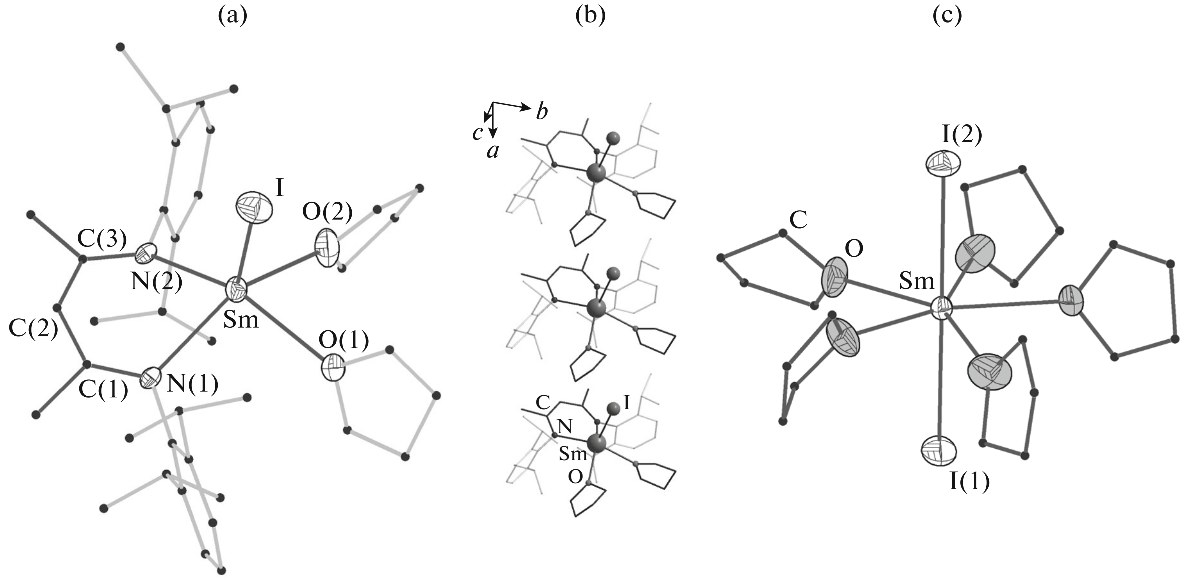


Fig. 1. (a) Molecular structure of complex **III** according to the X-ray structure data, (b) crystal packing of molecules of complex **III**, and (c) molecular structure of complex **IV** according to the X-ray structure data. Thermal ellipsoids are given with 50% probability, hydrogen atoms are omitted, and organic fragments are presented in the simplified form.

sphere results in the situation where the reduction process becomes more favorable. For the complexes with β-diketiminate ligands, a similar reduction effect of the ligand was described for complexes of europium, which is characterized by the highest potential of Ln^{3+}/Ln^{2+} among all lanthanides [37, 47]. The reaction of $EuCl_3$ with a less bulky anion $(L^{Me})^-$ affords complex $[Eu^{III}L_3^{Me}]$ (L^{Me} = {N(2-MeC_6H_4)C(Me)}$_2$CH), whereas the presence of a more bulky anion $(L^{Me2})^-$ leads to the sterically induced reduction of europium and formation of $[Eu^{II}(L^{Me2})_2(Thf)]$ (L^{Me2} = {N(2,6-$Me_2C_6H_3$)C-(Me)}$_2$CH). It should be mentioned that only one example of sterically induced reduction of Sm^{3+} to Sm^{2+} is known. This reduction occurred upon an attempt to insert three very bulky and rigid pentaphenylcyclopentadienyl ligands (Cp^{BIG} = η^5-$C_5(4\text{-}^tBuC_6H_4)$) into the coordination sphere of Sm^{3+} [48]. As a result, the stable sandwich complex $[Sm^{II}Cp_2^{BIG}]$ is formed, stabilized by interaction of the phenyl rings of the adjacent cycles. A similar reduction process in the studied reaction would require the intermediate formation of a sterically hindered complex. This complex can be $[Sm(Nacnac)_2]^+$, which could be formed in the ligand disproportionation process (Eq. (3)). The latter can be driven by the simultaneous formation of insoluble samarium selenide (Eq. (4)). In fact, it is shown in a separate experiment that the reaction of SmI_3 with K_2Se in Thf gradually leads to the complete precipitation of samarium in the form of Sm_2Se_3.

$$2Sm(Nacnac)I_2 \rightarrow [Sm(Nacnac)_2]I + SmI_3, \quad (3)$$

$$\begin{gathered}4Sm(Nacnac)I_2 + 3K_2Se \\ \rightarrow Sm_2Se_3 + 2[Sm(Nacnac)_2]I + 6KI.\end{gathered} \quad (4)$$

A similar thulium complex $[Tm(Nacnac)_2]^+$ was shown [42] to be very unstable, and one of the ligands readily loses the proton of the methyl group of the main chain in the presence of bases to form the heteroligand complex [Tm(Nacnac)(Nacnac')] (Nacnac' is $CH(C(CH_3)NDipp)(C(=CH_2)NDipp)^{2-}$). Since K_2Se can play the role of a base, a similar transformation in the studied reaction can be expected. However, the deprotonation of the ligand should result in the retention of the Sm(III) complex rather than in metal reduction. In addition, [Sm(Nacnac)(Nacnac')] was not found in the reaction mixture. Another probable route of $[Sm(Nacnac)_2]^+$ transformation can be the reduction to the neutral complex $[Sm^{II}(Nacnac)_2]$ (Eq. (5), Red is reducing agent), which is stable under the reaction conditions [39]. It can be assumed that the initial complex **III** is formed due to one more process of ligand exchange under the reaction conditions (Eq. (6)). Thus, the overall process (Eqs. (4)–(6)) can be represented as the reduction of the Sm(III) complex to Sm(II) accompanied by leaving of one iodide ligand and samarium(III) selenide formation. The formation in the reaction the solid phase containing samarium and selenium in significant and comparable amounts was shown by the EDX method. This overall process (possible reaction is described by Eq. (7)) will also result in the formation of the $[Sm(Nacnac)_2]$ complex, assuming that the diketiminate ligands are stable under the reaction conditions.

$$\begin{gathered}[Sm(Nacnac)_2]I + Red \\ \rightarrow [Sm(Nacnac)_2] + Red{-}I,\end{gathered} \quad (5)$$

$$\begin{gathered}[Sm(Nacnac)_2] + Sm(Nacnac)I_2 \\ \rightarrow Sm(Nacnac)I + [Sm(Nacnac)_2]I,\end{gathered} \quad (6)$$

$$\begin{gathered}6Sm(Nacnac)I_2 + 7K_2Se \\ \rightarrow Sm_2Se_3 + 2Sm(Nacnac)I \\ + 2[Sm(Nacnac)_2] + 10KI + 2K_2Se_2.\end{gathered} \quad (7)$$

The possibility of the ligand redistribution between the Sm(II) complexes is indicated by the fact that minor amounts of samarium diiodide (insoluble under these conditions) were formed upon the recrystallization of separately obtained complex **III** from hexane. In some cases, individual crystals of this compound were also isolated from a Thf solution after the reaction of complex **II** with K_2Se. Probably, the solubility of the $[Sm(Nacnac)_2]$ complex is much higher, which prevents its crystallization.

Two reducing agents are possible in the studied system: selenide and diketiminate anions. Under the discussed reaction conditions, their reduction potentials are unknown, but the possibility of the redox process to occur can be evaluated using the known reactions as references. For example, the possibility of the reduction of elemental selenium by samarium(II) iodide with the formation of Se_2^{2-} or Se^{2-}, depending on the stoichiometry of the reducing agent, was demonstrated [49]. A SmI_2 excess is needed for the complete reduction to Se^{2-}, but the reaction does not proceed to the end even in this case. The completeness of the reaction can be provided only by the addition of hexamethylphosphatriamide, which increases the reduction potential of SmI_2 in a Thf solution. Our experiment showed that the reaction of SmI_2 with K_2Se_2 in Thf occurred very slowly at elevated temperatures (at 70°C the incomplete occurrence of the reaction becomes noticeable within ~15 days). Thus, we may conclude that the redox potential of K_2Se_2/K_2Se is close to that of SmI_2^+/SmI_2 in Thf and K_2Se can be the reducing agent in this reaction. On the contrary, we believe that the $Nacnac^-$ anion cannot act as a reducing agent in this process, since otherwise the initial $[Sm(Nacnac)I_2(Thf)_2]$ complex can undergo the intramolecular redox process leading to the formation of Sm(II) compounds, which is not observed even on prolonged heating of solutions of this complex during recrystallization [28]. In addition, the one-electron oxidation of the Nacnac$^-$ anion should afford the dimeric product $(Nacnac)_2$ [50], but the characteristic signals of this compound are absent in the NMR spectra of the reaction solution. It is most likely that the role of the diketiminate ligand is to provide the necessary steric hindrance of the Sm^{3+} ion, because SmI_3 is not reduced in the absence of the diketiminate ligand under other equivalent conditions.

The scheme proposed for the process agrees with the absence of the reaction for the neodymium complexes, since the reduction potential of neodymium is much higher than that of samarium [51]. It is not quite clear why complex **II** does not react with other potassium (di)chalcogenides except for K_2Se. In these cases, the observed absence of redox processes can be explained by (a) a low solubility of potassium chalcogenides under the experimental conditions, which decreases the driving force and reaction rate, and (b) an insufficiently high reduction potential of some chalcogenides compared to that of Se^{2-} (e.g., S^{2-} or Se_2^{2-}). Nevertheless, it cannot be excluded that the reduction reactions can also occur with other chalcogenides but with a lower rate.

Crystals of samarium(II) iodide formed in minor amounts were studied by X-ray structure analysis. The structure contains molecular complexes $[SmI_2(Thf)_5]$ and 1.25 molecules of solvate Thf per samarium atom. The complex is characterized by a nearly regular pentagonal bipyramidal structure in which the Thf molecules are arranged in the equatorial plane (Fig. 1c). The unit cell contains four independent molecules of the complex with similar geometric parameters (the bond lengths are Sm–I 3.227(2)–3.266(2) and Sm–O 2.546(11)–2.630(10) Å). Note that attempts to determine the structure of $SmI_2(Thf)_5 \cdot n$Thf were made previously [52], but the authors succeeded to localize only the heavy Sm and I atoms and to determine the geometry of the complex because of the low quality of the obtained structural data. The R factor was 15%, space group $P2_1/n$, unit cell parameters $a = 23.154(12)$, $b = 26.033(6)$, $c = 23.866(10)$ Å, $\beta = 111.69(4)°$, $V = 13367(11)$ Å^3, $Z = 16$. The exact number of solvate molecules were not determined earlier either. The structure of the obtained crystals of $SmI_2(Thf)_5 \cdot 1.25$Thf was solved in the cell with a halved volume as a nonmerohedral twin in the space group $P\overline{1}$ ($Z = 8$). Both the coordinated and solvate Thf molecules were reliably localized. Unfortunately, the coordinates of the atoms are not presented in the previous article [52] and in the corresponding CSD file (ZEKXIW) and, hence, it remains unclear whether these compounds are identical in fact or they represent different phases.

Thus, the ion exchange reactions cannot be applied to the synthesis of the lanthanide β-diketiminates complexes with (poly)chalcogenide anions in the coordination sphere. It is most likely that the best synthetic method for these complexes is provided by the reactions involving redox transformations [18, 19]. According to the proposed scheme of the reaction of complex **II** with K_2Se, the samarium complexes with N-donor ligands can also participate in the sterically induced reduction processes, which have been known so far mainly for the cyclopentadienyl derivatives. The possibility of the variation of the steric influence of the N-donor ligands in the coordination sphere of samarium can potentially lead to the further development of the chemistry of the redox processes involving the complexes of this element.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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