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Lanthanide Iodide Nitride Sulfide Clusters

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Abstract—The reaction of $[(NdI)_3N_2]$ (**I**) with Cp_3Er in the presence of sulfur in THF gave $CpNdI_2(THF)$, $NdI(S_2N_2)(THF)$, and an unidentified erbium compound. A similar reaction of $[(DyI)_3N_2]$ yielded $CpDyI_2(THF)$ and $ErI(S_2N_2)(THF)$. When **I** reacted with $ErCl_3$, the clusters $[Nd_2ErClI_4(S_2)(S_2N_2)(THF)_7]$ and $[Nd_2ErCl_2I_3(S_2)(S_2N_2)(THF)_7]$ were formed in 33–34% yield. From the mixture of reaction products of $[(DyI)_3N_2]$ with sulfur and NdI_3, only $[Nd_2DyI_5(S_2)(S_2N_2)(THF)_7]$ was isolated in a minor yield and identified. Europium diiodide EuI_2 almost did not react with complex **I** and sulfur under the chosen conditions. The starting EuI_2 (50%) and previously characterized cluster $[Nd_3I_5(S_2)(S_2N_2)(THF)_9]$ were isolated from the reaction mixture.

Keywords: clusters, lanthanides, reactivity, X-ray diffraction analysis

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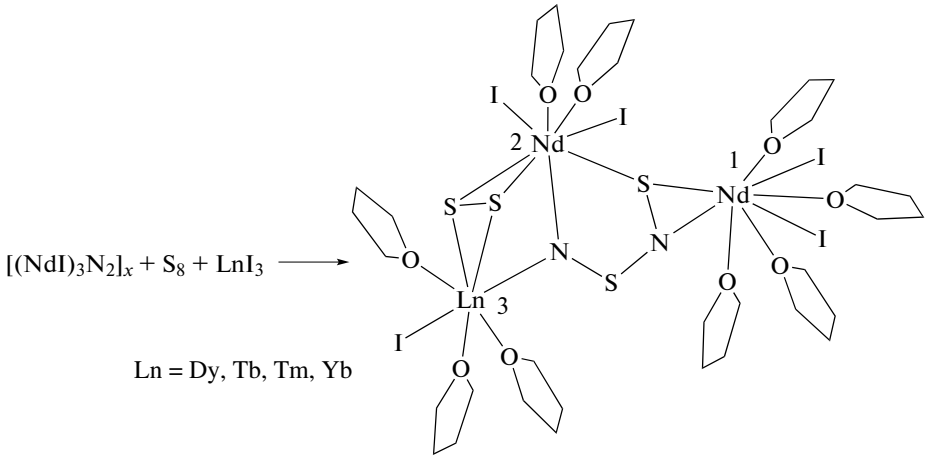
INTRODUCTION

Owing to the variety of their molecular structures and luminescent and magnetic properties, lanthanide nitride chalcogenide halide clusters attract a lot of attention of physicists and chemists as objects for studying the structural features of compounds of 4*f* elements, promising materials for optoelectronics and biomedicine, and single-molecule magnets [1–5]. However, the number of these compounds, especially four-element ones, is moderate, which is due to difficulty of their synthesis. Recently, using reactions of the iodide nitrides [(LnI)3N2]x with sulfur, we prepared and structurally characterized trinuclear neodymium and dysprosium clusters [Ln3I5(N2S2)(S2)(THF)10] (Ln = Nd, Dy) [6, 7]. A similar synthesis with other lanthanides cannot be accomplished, due to insufficiently high reactivity of the starting diiodides LnI2. However, a detailed study of the cluster formation process showed that this reaction is reversible. The reversible stage involves three components: [(LnI)3N2], sulfur, and the triiodide NdI3 or DyI3 formed in the first stage. The use of terbium, thulium, ytterbium, or dysprosium triiodide in the back reaction of neodymium iodide nitride (I) with sulfur resulted in the synthesis of isostructural heterometallic clusters [Nd2LnI5(S2)(S2N2)(THF)9] (Ln = Dy, Tb, Tm, Yb) (Scheme 1) [8, 9].



Scheme 1.

It was shown that the Ln atom of the triiodide always occupies position 3 in the resulting trinuclear cage, irrespective of the nature of the metal. In the complexes containing Dy and Tb, excitation with UV light was shown to induce intense luminescence of the corresponding Ln^{3+} ion. While searching for the ways to expand the range of iodide nitride sulfide clusters and to gain more in-depth understanding of the mechanism of synthesis, we carried out reactions of **I** with sulfur in the presence of $ErCl_3$, EuI_2, and Cp_3Er and dysprosium iodide nitride $[(DyI)_3N_2]$ with NdI_3.

EXPERIMENTAL

The reactions were carried out without access of oxygen and air moisture using the standard Schlenk technique. THF was purified with sodium benzophenone ketyl, hexane was distilled from sodium, and acetonitrile was dried over P_2O_5 and kept above K_2CO_3. Elemental analysis for C, H, N, S was performed on a Vario El cube analyzer (Germany); lanthanides were quantified by complexometric titration, and iodine was determined by argentometric titration. Magnetic measurements were done at room temperature as described previously [10].

Reactions of $[(NdI)_3N_2(THF)_6]$ with $ErCl_3$ and sulfur. $ErCl_3$ (0.050 g, 0.183 mmol) and a solution of sulfur (0.023 g, 0.735 mmol) in THF (20 mL) were added to $[(NdI)_3N_2(THF)_6]$ (0.234 g, 0.184 mmol). The mixture was stirred for 6 h at 55°C. The solution turned yellow-brown. After centrifugation of the mixture, the precipitate was separated by decanting the solution. The mother liquor was concentrated to 10 mL and cooled down to 0°C. The fine yellow crystals of $[Nd_2ErClI_4(S_2)(N_2S_2)(THF)_7]$ formed after 12 h was separated by decantation and dried in vacuo at room temperature. The product yield was 0.080 g (34%). The effective magnetic moment (μ_{eff}) was 5.9 μ_B. IR: (ν, cm^{-1}): 1345 ν(C–H), 1010 ν(C–O), 960 ν(C–O), 860 ν(C–O).

For $C_{28}H_{56}N_2O_7S_4ClI_4Nd_2Er$

Anal. calcd., %	C, 20.26	H, 3.40	Cl, 2.14	I, 30.58
	N, 1.69	Nd, 17.38	Er, 10.08	S, 7.73
Found, %	C, 20.70	H, 3.34	Cl, 2.36	I, 30.12
	N, 1.40	Nd, 17.29	Er, 9.71	S, 7.45

After separation of the crystals of $[Nd_2ErClI_4(S_2)(N_2S_2)(THF)_7]$, the mother liquor was slowly concentrated at room temperature. Fine yellow crystals of $[Nd_2ErCl_2I_3(S_2)(N_2S_2)(THF)_9]$ precipitated within 12 h; they were washed with cold THF and dried under reduced pressure. The yield of the crystals was 0.105 g (32.8%).

For $C_{36}H_{72}N_2O_9S_4Cl_2I_3Nd_2Er$

Anal. calcd., %	C, 25.25	H, 4.24	Cl, 4.14	I, 22.23
	N, 1.64	Nd, 16.84	Er, 9.77	S, 7.49
Found, %	C, 24.86	H, 4.03	Cl, 4.40	I, 22.51
	N, 1.49	Nd, 16.76	Er, 10.12	S, 7.33

Reaction of $[(DyI)_3N_2(THF)_6]$ with Cp_3Er and sulfur. Cp_3Er (0.056 g, 0.153 mmol) and a solution of sulfur (0.020 g, 0.620 mmol) in THF (15 mL) were added to $[(DyI)_3N_2(THF)_6]$ (0.203 g, 0.153 mmol). The mixture was stirred for 3 h at 45°C on an ultrasonic bath. After centrifugation of the mixture, the precipitate was separated by decanting the solution. After separation of the precipitate, the mother liquor was concentrated to 7 mL. Colorless crystals of $CpDyI_2(THF)$ precipitated within 8 h; they were washed with THF and dried under reduced pressure. The yield was 0.021 g (24%).

For $C_9H_{13}OI_2Dy$

Anal. calcd., %	C, 19.53	H, 2.37	I, 45.85	Dy, 29.36
Found, %	C, 19.5	H, 2.42	I, 46.11	Dy, 29.24

One of the crystals was used for X-ray diffraction.

The dark brown mother liquor was slowly concentrated at room temperature, fine pink crystals of the iodide $[Er(N_2S_2)I(THF)_4]$ precipitated; they were washed with THF and dried under reduced pressure. The yield was 0.031 g (30%). μ_{eff} = 9.5 μ_B (for Er^{3+}, 9.6 μ_B [11]).

For $C_9H_{13}OI_2Er$

Anal. calcd., %	C, 28.48	H, 4.78	I, 18.81	Er, 25.01	S, 9.50
Found, %	C, 27.99	H, 4.46	I, 18.66	Er, 29.24	S, 9.16

The reaction of $[(NdI)_3N_2(THF)_6]$ with Cp_3Er and sulfur was carried out similarly to the reaction of $[(DyI)_3N_2(THF)_6]$ with Cp_3Er and sulfur. The reaction of $[(NdI)_3N_2(THF)_6]$ (0.124 g, 0.097 mmol), Cp_3Er (0.035 g, 0.097 mmol), and a solution of sulfur (0.08 g, 0.222 mmol) in THF (13 mL) gave $CpNdI_2(THF)$ as light blue crystals. The yield was 0.010 g (19.3%).

For $C_9H_{13}OI_2Nd$

Anal. calcd., %	C, 20.20	H, 2.45	I, 47.42	Nd, 26.95
Found, %	C, 20.45	H, 2.66	I, 47.85	Nd, 26.58

One of the crystals was used for X-ray diffraction.

The brown mother liquor was slowly concentrated at room temperature; fine pink crystals of

$[Nd(N_2S_2)I(THF)_4]$ precipitated; they were washed with THF and dried under reduced pressure. The yield was 0.016 g (25.8%). μ_{eff} = 3.8 μ_B (for Nd^{3+}, 3.68 μ_B [11]).

For $C_{16}H_{32}N_2O_4S_2INd$

Anal. calcd., %	C, 29.49	H, 4.95	I, 19.47	Nd, 22.13	S, 9.84
Found, %	C, 29.34	H, 4.87	I, 20.03	Nd, 22.12	S, 9.52

The mother liquor that remained after isolation of $CpNdI_2(THF)$ and $[Nd(N_2S_2)I(THF)_4]$ was slowly concentrated at 4°C to give a brown precipitate of $[(CpErI)_2(N_2S_2)(THF)_2]$, which was washed with THF and dried under reduced pressure. The yield was 0.0162 g (17.7%). μ_{eff} = 9.2 μ_B.

For $C_{18}H_{26}N_2O_2S_2I_2Er_2$

Anal. calcd., %	C, 22.64	H, 2.74	I, 26.58	Er, 35.03	N, 2.93	S, 6.72
Found, %	C, 22.50	H, 2.42	I, 26.90	Er, 35.41	N, 2.58	S, 6.81

The gray precipitate formed in the reaction was dried under reduced pressure after separation of the brown solution. The weight of the dry precipitate was 0.022 g. μ_{eff} = 9.7 μ_B.

Reaction of $[(DyI)_3N_2(THF)_6]$ with $NdI_3(THF)_3$ and sulfur. $NdI_3(THF)_3$ (0.226 g, 0.304 mmol) and a solution of sulfur (0.22 g, 0.69 mmol) in THF (20 mL) were added to $[(DyI)_3N_2(THF)_6]$ (0.428 g, 0.322 mmol). The mixture was stirred for 6 h at 60°C. After centrifugation of the mixture, the precipitate was separated by decanting the solution, washed with THF, and dried at room temperature. The product isolated as yellowish-brown crystals (0.023 g, 8%) corresponded, in the elemental composition and the IR spectrum, to the previously obtained complex $[(Nd_2DyI_5(S_2)(N_2S_2)(THF)_9]$ [8]. The yield was 0.023 g (8%).

Reaction of $[(NdI)_3N_2(THF)_6]$ with $EuI_2(THF)_4$ and sulfur. $EuI_2(THF)_4$ (0.069 g, 0.110 mmol) and a solution of sulfur (0.043 g, 1.340 mmol) in THF (20 mL) were added to $[(NdI)_3N_2(THF)_6]$ (0.420 g, 0.330 mmol). The mixture was stirred for 4 h at 60°C. After centrifugation of the mixture, the precipitate was separated by decanting the solution. After separation of the precipitate, the mother liquor was concentrated to 15 mL and cooled to 0°C. Fine yellow and colorless crystals precipitated within 12 h. The mixture of crystals was washed with cold THF until the colorless crystals completely dissolved. The yellow crystals remaining in the solution were dried under reduced pressure and identified as $[Nd_3I_5(S_2)(N_2S_2)(THF)_9]$ on the basis of elemental analysis and IR spectrum. The yield was 0.105 g (51%).

X-ray diffraction study of $CpNdI_2(THF)$ and $CpDyI_2(THF)$ was carried out on a Bruker D8 Quest automated diffractometer (graphite monochromator, MoK_α-radiation, φ- and ω-scan mode, λ = 0.71073 Å). The experimental sets of intensities were integrated using the SAINT software program [12]. The TWINABS software program [13] was used to apply absorption corrections. The structures were solved by the dual-space method using the SHELXT program package [14]. All non-hydrogen atoms in $CpNdI_2(THF)$ and $CpDyI_2(THF)$ were refined by the full-matrix least-squares method in the anisotropic approximation on F^2_{hkl} using the SHELXTL software package [15]. Hydrogen atoms were placed in geometrically calculated positions and refined in the riding model ($U_{iso}(H) = 1.2U_{equiv}(C)$). The main crystallographic data and X-ray experiment details for $CpNdI_2(THF)$ and $CpDyI_2(THF)$ are summarized in Table 1. Both the $CpNdI_2(THF)$ and $CpDyI_2(THF)$ crystals were non-merohedral twins. Numerous attempts to select a single crystal from the mass were not a success in both cases. The final structure refinement for $CpNdI_2(THF)$ and $CpDyI_2(THF)$ was carried out using an HKLF5 data file. The ratios of the domains were 0.498 : 0.502 and 0.460 : 0.540 For $CpNdI_2(THF)$ and $CpDyI_2(THF)$, respectively. The EADP and ISOR instructions were used in the refinement to constrain the anisotropic parameters of some carbon and oxygen atoms.

The structures were deposited with the Cambridge Crystallographic Data Centre (no. 2082930 ($CpNdI_2(THF)$ and 2082931 ($CpDyI_2(THF)$); http://www.ccdc.cam.ac.uk/structures/).

RESULTS AND DISCUSSION

Previously, a cluster with the Nd-Nd-Dy cage was obtained by the reaction of neodymium iodide nitride (**I**) with sulfur in the presence of DyI_3 [8]. It was expected that a similar reaction of $[(DyI)_3N_2(THF)_6]$ with sulfur in the presence of NdI_3 would afford a compound with the Dy-Dy-Nd cage. However, the already known bis-neodymium cluster $[(Nd_2DyI_5(S_2N_2)(S_2)(THF)_9]$ was unexpectedly isolated from the reaction mixture [8]; the composition of this product was established by X-ray diffraction and magnetic measurements. In this case, the Dy^{3+} ion in the heterometallic cage also occupied position 3. Unfortunately, the remaining mixture of reaction products could not be separated, which did not allow us to propose an adequate reaction pathway.

In order to establish the possibility of obtaining chlorine-containing clusters similar to the previously prepared iodide complexes $[Ln_3I_5(N_2S_2)(S_2)(THF)_{10}]$ (Ln = Nd, Dy) [6], we allowed **I** to react with sulfur in the presence of chloride $ErCl_3$. The erbium compound with high μ_{eff} was chosen with the goal to facil-

Table 1. Main crystallographic data and structure refinement details for $CpNdI_2(THF)$ and $CpDyI_2(THF)$

Parameter	Value	
	$CpNdI_2(THF)$	$CpDyI_2(THF)$
Molecular formula	$C_{17}H_{29}O_3I_2Nd$	$C_{17}H_{29}O_3I_2Dy$
M	679.44	697.70
Temperature, K	100(2)	100(2)
System	Monoclinic	Monoclinic
Space group	*Pc*	*Pc*
a, Å	8.2184(5)	8.1750(3)
b, Å	13.5722(8)	13.4699(4)
c, Å	19.0712(10)	18.9473(6)
α, deg	90	90
β, deg	92.2101(16)	91.8946(11)
γ, deg	90	90
V, Å^3	2125.7(2)	2085.27(12)
Z	4	4
ρ (calcd.), mg/m^3	2.123	2.222
μ, mm^{-1}	5.358	6.555
Crystal size, mm	0.21 × 0.09 × 0.05	0.22 × 0.12 × 0.05
F(000)	1284	1308
θ, deg	2.480–28.360	2.493–30.631
Number of reflections collected/unique	5288/5288	6336/6336
R_{int}	0.0850	0.0962
R_1, wR_2 ($I > 2\sigma(I)$)	0.0367, 0.0910	0.0462, 0.1265
R_1, wR_2 (for all data)	0.0407, 0.0930	0.0539, 0.1324
Absolute structure parameter	0.051(19)	0.065(15)
S	1.043	1.060
Residual electron density (max/min), e/Å^3	1.498/–1.282	2.117/–2.121

itate the subsequent product identification using magnetic measurements. After the mixture was heated for 6 h at 55°C, two crystalline dihalide clusters were isolated from the resulting solution by fractional crystallization in 34 and 32% yields. The quality of crystals precluded X-ray diffraction study, but the data of elemental analysis provided the conclusion that one compound contained chlorine and iodine in 1 : 4 ratio: $[Nd_2ErI_4Cl(N_2S_2)(S_2)(THF)_7]$, while in the other product, the chlorine to iodine ratio was 2 : 3: $[Nd_2ErI_3Cl_2(N_2S_2)(S_2)(THF)_9]$. The ratio of metals in the complexes was confirmed by magnetic measurements: in both cases, a magnetic moment of 5.9 μ_B was found, which corresponded to the $2Nd^{3+}/Er^{3+}$ mixture: $\mu_{eff} = 5.6\ \mu_B$).

When the cyclopentadienyl complex Cp_3Er was used in the synthesis instead of the chloride, no polynuclear products were formed. In THF solution at 45°C, the reaction was completed within several hours giving the cyclopentadienyl neodymium complex $CpNdI_2(THF)$ in 19% yield and neodymium iodide dithiadinitride $[Nd(N_2S_2)I(THF)_4]$ in 26% yield. A similar reaction of dysprosium iodonitride with Cp_3Er and sulfur afforded the cyclopentadienyl dysprosium complex $CpDyI_2(THF)$ in 24% yield and erbium iodide dithiadinitride $[Er(N_2S_2)I(THF)_4]$ in 30% yield. X-ray diffraction analysis demonstrated that the complexes $CpNdI_2(THF)$ and $CpDyI_2(THF)$ were isostructural. It is noteworthy that thulium [16] and samarium [17] complexes with a similar molecular structure, but crystallizing in the orthorhombic system (space group $Pna2_1$) were reported previously. The β angle in $CpNdI_2(THF)$ and $CpDyI_2(THF)$ was considerably different from 90°. An attempt to solve the

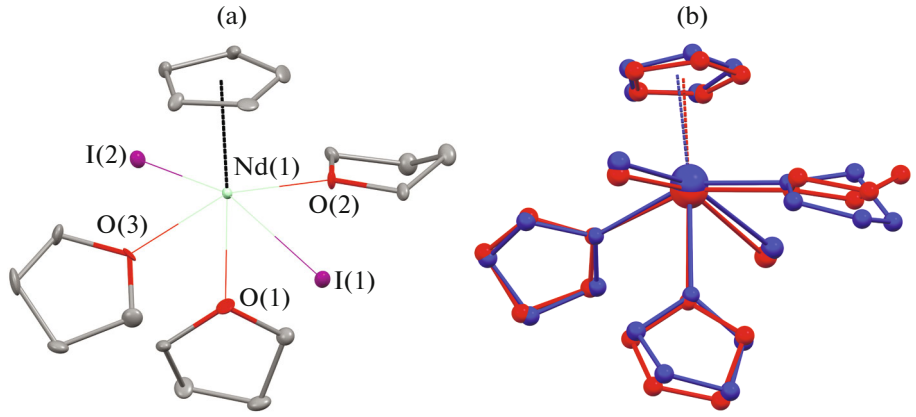


Fig. 1. (a) Molecular structure of independent molecule A of $CpNdI_2(THF)$, (b) superposition of two independent molecules A (red) and B (blue) of $CpNdI_2(THF)$. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity.

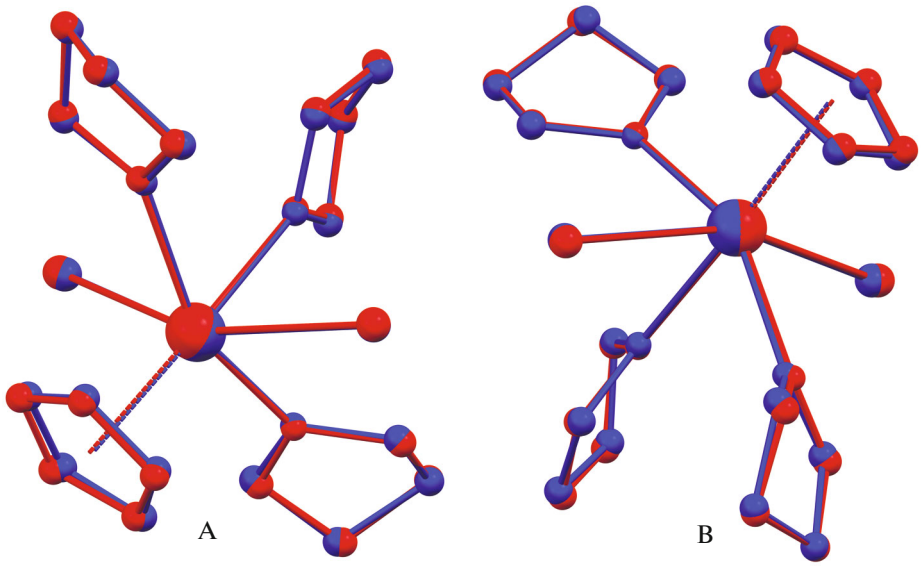


Fig. 2. Superposition of two independent molecules A and B of $CpNdI_2(THF)$ (red) and $CpDyI_2(THF)$ (blue). Hydrogen atoms are omitted for clarity.

structure in space group $Pna2_1$ led to pronounced deterioration of the key refinement parameters.

The crystal structure of both complexes contains two independent molecules A and B. Each lanthanide ion is linked to one cyclopentadienyl anion (Cp), two iodine atoms, and three THF molecules. The molecular structure of independent molecule A of $CpNdI_2(THF)$ is shown in Fig. 1a. Except for the carbon atoms of one coordinated THF molecule, the structures of independent molecules A and B are in excellent agreement (Fig. 1b). The average deviation of non-hydrogen atoms in these molecules after applying the inversion to one of the molecules is 0.367 Å. The structures of molecules A and B of $CpDyI_2(THF)$ are in excellent agreement with those of $CpNdI_2(THF)$ (Fig. 2). All distances in the lanthanide coordination sphere of $CpDyI_2(THF)$ are systematically shorter than those in $CpNdI_2(THF)$ (Table 2), which is the strict correspondence with the relationship of ionic radii of dysprosium and neodymium [18].

Low quality of erbium iodide dithiadiazine $[Er(N_2S_2)I(THF)_4]$ crystals precluded an X-ray diffraction study, but the data of elemental analysis, IR spectroscopy and magnetic measurements confirmed the proposed formula. The reaction of Cp_3Er with $[(DyI)_3N_2(THF)_6]$ proceeded in a similar way to give $CpDyI_2(THF)$ and $[Er(N_2S_2)I(THF)_4]$. The forma-

Table 2. Selected distances (Å) and angles (deg) in the complexes $CpNdI_2(THF)$ and $CpDyI_2(THF)$

Distance (Å)	$CpNdI_2(THF)$; Ln = Nd		$CpDyI_2(THF)$; Ln = Dy	
	A	B	A	B
Ln(1)–I(1)	3.1306(11)	3.1419(12)	3.0757(14)	3.0928(14)
Ln(1)–I(2)	3.1688(11)	3.1670(12)	3.1215(14)	3.1192(14)
Ln(1)–O(1)	2.493(11)	2.491(10)	2.420(14)	2.413(12)
Ln(1)–O(2)	2.474(10)	2.433(10)	2.417(13)	2.370(13)
Ln(1)–O(3)	2.400(10)	2.433(10)	2.350(12)	2.403(13)
$Ln(1)–Cp_{center}$	2.428	2.440	2.360	2.386
Angle	$CpNdI_2(THF)$; Ln = Nd		$CpDyI_2(THF)$; Ln = Dy	
	A	B	A	B
	ω, deg			
I(1)Ln(1)I(2)	158.06(3)	160.03(4)	157.58(4)	159.81(4)
O(1)Ln(1)I(1)	81.3(3)	81.2(3)	80.6(3)	80.8(3)
O(2)Ln(1)I(1)	86.6(2)	85.7(3)	86.5(3)	85.3(3)
O(3)Ln(1)I(1)	87.5(3)	88.3(3)	87.9(3)	88.4(3)
O(1)Ln(1)I(2)	76.9(3)	79.5(2)	77.1(3)	79.5(3)
O(2)Ln(1)I(2)	86.9(2)	85.3(3)	86.6(3)	85.8(3)
O(3)Ln(1)I(2)	89.7(2)	91.5(3)	89.0(3)	91.0(3)
O(1)Ln(1)O(2)	79.6(4)	78.5(4)	78.0(5)	77.0(4)
O(1)Ln(1)O(3)	75.7(4)	74.1(3)	75.9(4)	74.8(4)
O(2)Ln(1)O(3)	155.2(4)	152.5(4)	154.0(5)	151.7(5)

tion of these products attests to a complex mechanism of reactions with Cp_3Er, which is significantly different from the mechanism of reactions with lanthanide triiodides LnI_3.

All the above and previously reported syntheses of trinuclear clusters were carried out with compounds of trivalent lanthanides. In this study, we used europium diiodide $EuI_2(THF)_4$ as the lanthanide halide to react with **I** and sulfur. The reaction proceeded under comparable conditions to give the neodymium cluster $[Nd_3I_5(S_2)(S_2N_2)(THF)_9]$ in a more than 50% yield. In addition, crystals of the starting europium diiodide were isolated from the reaction mixture, indicating that the reaction followed the previously established scheme of direct synthesis [6], not involving the europium salt.

The performed extended study of reactions of lanthanide iodide nitrides $[(LnI)_3N_2]$ (Ln = Nd, Dy) with lanthanide halides and erbium cyclopentadienide in the presence of sulfur showed that these reactions differ substantially from those involving NdI_3 and DyI_3 (Scheme 2).

$$[(NdI)_3N_2] + S_8 \xrightarrow{THF} \begin{cases} \xrightarrow{ErCl_3} Nd_2ErI_{5-x}Cl_x(S_8)(N_2S_2)(THF)_9 \ (x = 1, 2) \\ \xrightarrow{EuI_2} Nd_2I_5(S_8)(N_2S_2)(THF)_9 \\ \xrightarrow{Cp_3Er} CpNdI_2(THF) + Er(N_2S_2)I(THF)_4 \end{cases}$$

Scheme 2.

The new trinuclear heterometallic clusters $[Nd_2ErI_{5-x}Cl_x(S_2)(N_2S_2)(THF)_7]$ (x = 1, 2) were obtained only in reactions with $ErCl_3$. The iodine and chlorine ratio in the products was random and was determined by the conditions of their isolation. It was found that the reaction of $[(DyI)_3N_2(THF)_6]$ with an equimolar amount of NdI_3 gave a cluster with the Nd-Nd-Dy cage, similar to the cluster synthesized previously by the reaction of iodide nitride **I** with DyI_3.

This result may be attributed to higher reactivity of neodymium intermediates. The use of the Cp_3Er complex with organic ligands in reactions with nitride **I** and sulfur showed that, in this case, no polynuclear groups are formed, but ligand exchange takes place to give dithiadinitride coordinated to the erbium ion.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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