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On the Reactivity and Stability of Iodide–Nitride–Sulfide Clusters of Neodymium and Dysprosium

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Abstract—The thermal decomposition of cluster $Nd_3I_5(S_2)(S_2N_2)(THF)_{10}$ (**I**) at 50–400°C affords a mixture of products among which tetrahydrofuran (THF), sulfur, diiodine, HI, H_2S, CS_2, S_3N_6, S_3N_5, MeI, thiophene, tetrahydrothiophene, diiodobutane, iodobutene, and NdI_3 are identified. The treatment of $Ln_3I_5(S_2)(S_2N_2)(THF)_{10}$ (Ln = Nd (**I**), Dy (**II**)) with phenanthroline (Phen) in THF at room temperature results in the partial substitution of THF to form new complexes $Ln_3I_5(S_2)(S_2N_2)(THF)_4(Phen)_3$. The dissolution of compound **I** in pyridine gives a pyridine (Py) complex $Ln_3I_5(S_2)(S_2N_2)(THF)_3(Py)_7$. The dissolution of compounds **I** and **II** in acetonitrile at 20°C is accompanied by the fast rearrangement and fragmentation of the complexes to form $LnI_3(MeCN)_6$, $[LnI(S_2)(MeCN)]$, and $[LnI(S_2N_2)(MeCN)]$. Complex **I** in THF does not react with white phosphorus, carbon monoxide, fullerene C_{60}, and chromium hexacarbonyl.

Keywords: clusters, neodymium, dysprosium, reactivity, iodide–sulfide, iodide–dithiadinitride, phenanthroline

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INTRODUCTION

It is much more difficult to study the reactivity of clusters than the properties of mononuclear compounds, because polynuclear compounds contain, as a rule, several potential centers for the attack of the substrate [1]. Classical quantum dots consisting of an inorganic core (in the majority of cases, cadmium or zinc chalcogenide) coated with an organic shell (most frequently trioctylphosphine oxide or oleic acid) [2] can also be attributed to the class of clusters. As far as we know, the reactivity of these substances has not been studied previously, and this study is a more complicated problem. Recently, when searching for new lanthanide semiconductor materials, we have synthesized unusual trinuclear neodymium and dysprosium clusters $Ln_3I_5(S_2)(S_2N_2)(THF)_{10}$ (Ln = Nd (**I**), Dy (**II**)) [3]. The molecular structure of these compounds (inorganic core $Ln_3I_5(S_2)(S_2N_2)$ coated with an organic shell of THF and *iso*-propylamine molecules) allows one to consider them as quantum dots in spite of a substantial distinction in the geometries of the cores (three planar orthogonal fragments) from the spherical shape of classical quantum dots. It should be mentioned that the zinc(cadmium) chalcogenide quantum dots can also be nonspherical [2]. The study of the chemical behavior of these compounds is especially interesting, because the molecules of compounds **I** and **II** contain several different reaction centers and fragments. However, the determination of the reaction directions, isolation of the products, and calculation of the yields become more difficult for the same reason.

In order to determine the main chemical properties of complexes **I** and **II**, we studied their reactivity toward several substrates with various coordination and redox properties. In the most part of cases, cluster **I** was used as a model, since the synthesis of this cluster is easier and gives higher yields of the products than the synthesis of compound **II**. The chemical behavior of both clusters is identical.

EXPERIMENTAL

The reactions were carried out using the standard Schlenk technique under the conditions excluding contact with air oxygen and moisture. Tetrahydrofuran was purified with sodium benzophenone ketyl, hexane was distilled over sodium, acetonitrile was dried with P_2O_5 and kept over K_2CO_3, 1,10-phenanthroline (Phen) was multiply sublimed after keeping an ethereal solution over molecular sieves, and *iso*-

$PrNH_2$ was used as received (Sigma–Aldrich). Complexes $Ln_3I_5S_4N_2(C_4H_8O)_{10}$ (Ln = Nd, Dy) were synthesized using a previously developed method [3]. The IR spectra of the samples as suspensions in Nujol were recorded between KBr windows on a Vertex 70 FT-IR spectrometer (Bruker, Germany) in a range of 4000–450 cm^{-1}. A Vario El analyzer (Germany) was used for C, H, N, S elemental analyses. The content of lanthanides was determined complexonometrically. The iodine content was determined by argenometry. The GC/MS (gas chromatography coupled with mass spectrometry) analysis was conducted on a Trace GC Ultra/Polaris Q instrument (Thermo Electron Corporation, USA). The temperature of a TR-35MC capillary column (60 m) was varied from 60 to 300°C with a rate of 10°C/min. The temperature of an ion source was 230°C, and the energy of ionizing electrons was 70 eV. Mass spectra of positive ions were detected in a mass range of 20–1000. The components of mixtures were identified using the NIST 2005 electronic library of mass spectra. Thermogravimetric (TG) measurements were carried out on a PYRIS6TGA instrument (Perkin Elmer, USA) in a nitrogen atmosphere in the temperature range from 50 to 800°C with a heating rate of 5°C/min.

Reaction of compound II with 1,10-phenanthroline. A solution of Phen (0.048 g, 0.27 mmol) in THF (2 mL) was added to a solution of complex **II** (0.155 g, 0.078 mmol) in THF (5 mL). The mixture was stirred for 1 h at room temperature. The formed precipitate was separated by decantation from the solution after the centrifugation of the mixture, washed with THF, and dried under reduced pressure. The yield of $[Dy_3I_5(S_2N_2)(S_2)(THF)_2(Phen)_3]$ as yellowish-brown crystals was 0.132 g (96%).

IR (ν, cm^{-1}): 3045 $\nu(C_{Ar}{-}H)$, 1625 $\nu(C_{Ar}{=}C_{Ar})$, 1586 $\nu(C_{Ar}{=}C_{Ar})$, 1502 $\nu(C_{Ar}{=}C_{Ar})$, 1090 $\delta(C_{Ar}{-}H)$, 1006 $\nu(C{-}O)$, 854 $\nu(C{-}O)$, $\delta(C_{Ar}{-}H)$, 739 $\delta(C_{Ar}{-}H)$.

For $C_{44}H_{40}N_8O_2S_4I_5Dy_3$

Anal. calcd., %	C, 26.92	H, 2.05	N, 5.71	S, 6.53
Found, %	C, 26.78	H, 2.04	N, 5.68	S, 6.50

The reaction of compound **I** (0.056 g, 0.028 mmol) with Phen (0.011 g, 0.06 mmol) gave $[Nd_3I_5(S_2N_2)$-$(S_2)(THF)_2(Phen)_3]$ in a yield of 0.011 g (42%).

The IR spectrum of the product is similar to that of complex $[Dy_3I_5(S_2N_2)(S_2)(THF)_2(Phen)_3]$.

For $C_{44}H_{40}N_8O_2S_4I_5Nd_3$

Anal. calcd., %	C, 27.69	H, 2.11	N, 5.87	S, 6.72
Found, %	C, 27.55	H, 2.10	N, 5.84	S, 6.69

Reaction of compound I with pyridine. Pyridine (10 mL) was added to complex $Nd_3I_5(S_2)(S_2N_2)(THF)_{10}$ (0.198 g, 0.10 mmol). The complex was dissolved to form an orange solution. A white precipitate was formed in 30 min, and the color of the solution changed from orange to yellow. The mixture was stirred for 15 h at room temperature. The precipitate was separated by decantation from the solution after the centrifugation of the mixture, washed with pyridine, and dried under reduced pressure. The yield of compound $Nd_3I_5(S_2)(S_2N_2)(Py)_7(THF)_3$ was 0.057 g (28%).

IR (ν, cm^{-1}): 3054 $\nu(C_{Ar}{-}H)$, 1628 $\nu(C_{Ar}{=}C_{Ar})$, 1596 $\nu(C_{Ar}{=}C_{Ar})$, 1484 $\nu(C_{Ar}{=}C_{Ar})$, 1217 $\delta(C_{Ar}{-}H)$, 1158 $\delta(C_{Ar}{-}H)$, 1064 $\delta(C_{Ar}{-}H)$, 1035 $\delta(C_{Ar}{-}H)$, 1006 $\nu(C{-}O)$, $\delta(C_{Ar}{-}H)$, 854 $\nu(C{-}O)$, $\delta(C_{Ar}{-}H)$, 703 δ $(C_{Ar}{-}H)$.

For $C_{47}H_{59}I_5N_9O_3S_4Nd_3$

Anal. calcd., %	C, 28.32	H, 2.98	N, 6.32	S, 6.43	Nd, 21.71
Found, %	C, 28.80	H, 2.904	N, 6.42	S, 6.21	Nd, 21.97

Reaction of compound I with acetonitrile. Acetonitrile (7 mL) was added to the crystals of complex **I** (0.190 g, 0.098 mmol) at room temperature. A precipitate was dissolved completely in 5 min, and the solution gained a yellow-brown color. In 10 min, a yellow-brown precipitate was formed in the solution. To complete the reaction, the mixture was stirred for 4 h at 50°C and left overnight at room temperature. A formed precipitate of $[NdIS_2(MeCN)]$ was separated by decantation, washed with acetonitrile (7 mL), and dried in vacuo. The yield was 0.029 g (85%).

IR (ν, cm^{-1}): 2303, 2273 $\nu(C{\equiv}N)$, 1030 $\delta(C{-}H)$, 776 $\nu(C{-}CN)$.

For $C_2H_3NS_2INd$

Anal. calcd., %	C, 6.38	H, 0.80	N, 3.72
	S, 17.04	I, 33.73	Nd, 38.32
Found, %	C, 6.35	H, 0.802	N, 3.69
	S, 17.12	I, 33.56	Nd, 8.13

After the precipitate was separated, the mother liquor was concentrated to 3 mL and cooled to –20°C. The formed light blue crystals were identified as triiodide $[NdI_3(MeCN)_8]$. The yield was 0.073 g (96%).

IR (ν, cm^{-1}): 2303, 2273 $\nu(C{\equiv}N)$, 1030 $\delta(C{-}H)$, 776 $\nu(C{-}CN)$.

For $C_{16}H_{24}I_3N_8Nd$

Anal. calcd., %	I, 49.36	Nd, 18.70
Found, %	I, 49.01	Nd, 18.57

After $[NdI_3(MeCN)_8]$ was separated, the solution was concentrated to 1 mL and cooled to –20°C. A finely crystalline colorless precipitate of $[NdIN_2S_2(MeCN)_2]$ was washed with cold MeCN

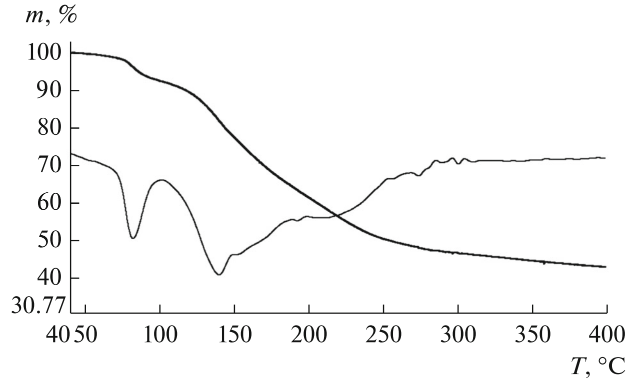


Fig. 1. TG curves of complex **I**.

and dried under reduced pressure. The yield was 0.022 g (55%).

IR (ν, cm^{-1}): 2303, 2273 ν(C≡N), 1030 δ(C–H), 776 ν(C–CN).

For $C_4H_6IN_4NdS_2$

Anal. calcd., %	C, 11.50	H, 1.16	N, 5.68
	S, 14.81	I, 28.32	Nd, 32.50
Found, %	C, 11.42	H, 1.15	N, 5.64
	S, 14.71	I, 28.18	Nd, 32.33

Thermal decomposition of compound I. Complex **I** (0.205 g, 0.107 mmol) was placed in an ampule with two branches. The ampule was evacuated to 0.02 mmHg and heated to 500°C, increasing the temperature with a rate of 1°C/min. The elimination of THF (0.045 g, 0.65 mmol), which was condensed into the first branch, was observed in a range of 50–100°C. Other volatiles were condensed into the second branch cooled with liquid nitrogen. The following substances were determined by GC/MS in the volatiles: sulfur, diiodine, HI, H_2S, CS_2, S_3N_6, S_3N_5, MeI, thiophene, tetrahydrothiophene, diiodobutane, and iodobutene. The nonvolatile residue (0.083 g) contained the following elements (%): C, 2.12; N, 0.18; S, 7.65; I, 41.8; Nd, 44.95.

RESULTS AND DISCUSSION

Thermogravimetric analysis (TG) was conducted in order to establish temperature ranges that can be used in the reactions of compounds **I** and **II** (Fig. 1). The TG study showed that the compounds started to decompose at 60°C and finished at 360°C. The intense mass loss in a range of 6–80°C corresponds to the elimination of coordinated THF, which was found by thermal decomposition in a dynamic vacuum with the GC/MS identification of the products. Complicated and undetermined processes occur at higher temperatures and result in the formation of sulfur, hydrogen sulfide, iodobutene, diiodobutane, thiophene, tetrahydrothiophene, and species with the mass corresponding to S_2N_2 and SN_3. Neodymium and diiodine were identified in the nonvolatile products.

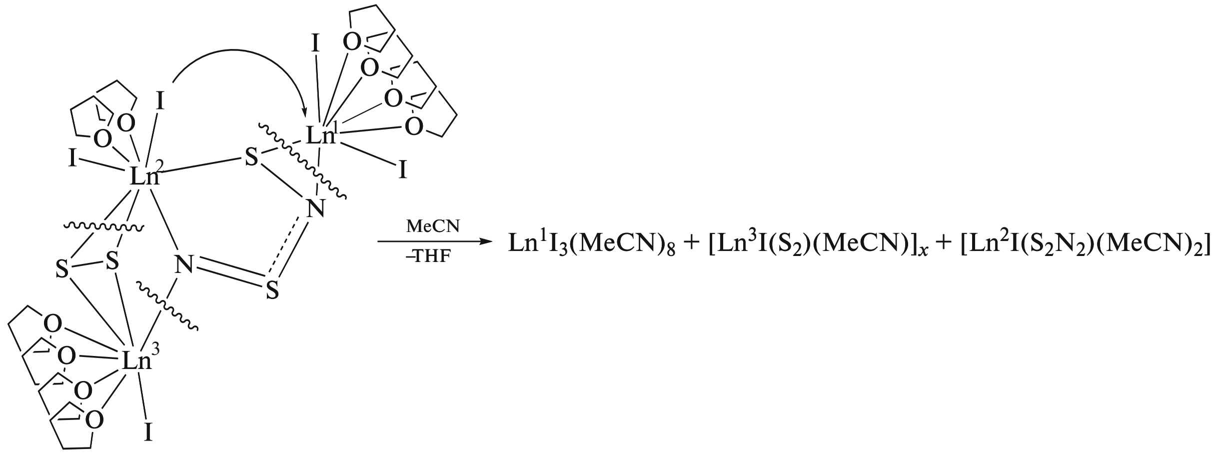
The synthesis of clusters **I** and **II** includes several steps, each being the direct reaction of the free element with the product obtained in the previous step [3, 4].

$$\mathrm{Ln} \xrightarrow{+I_2} \mathrm{LnI_2} \xrightarrow{+N_2} \mathrm{(LnI_2)_3N} \xrightarrow[\mathrm{THF}]{+S_8} \mathrm{Ln_3I_5(S_2)(S_2N_2)(THF)_{10}}$$

It seemed interesting to extend this series of direct reactions by the addition of new simple substrates. For this purpose, compound **I** was tested in the reactions with white phosphorus, carbon monoxide, fullerene C_{60}, and $Cr(CO)_6$. The insertion of the substrate at the Nd–S or Nd–N bonds could be expected in the reactions with P_4 and CO. In the case of fullerene, which is known to be an electron-withdrawing agent, its addition to the inorganic core of the molecule seems to be highly probable. The reaction with $Cr(CO)_6$ was carried out as an attempt to obtain an arene complex similar to the known arene carbonyls (arene)$Cr(CO)_3$ [5], which would confirm an assumption about the conjugation in the inorganic core assumed earlier [3]. However, the complex turned out to be inert to all listed substrates even on the prolonged heating of reaction mixtures in THF at 70°C, which can be considered as an evidence for the low reactivity of the cluster. In fact, the obtained result indicates only the specific chemical behavior, since the reactions of this compound with 1,10-phenanthroline, pyridine, acetonitrile, acrylonitrile, and CO_2 (these data will be published elsewhere) occur readily under mild conditions.

The stirring of a solution of compound **I** or **II** with Phen in THF for 1 h at room temperature leads to the partial substitution of THF by Phen and the formation of new complexes $Ln_3I_5(S_2N_2)(S_2)(THF)_2(Phen)_3$ in high yields. The complexes are formed as noncrystalline yellow precipitates. The formation of the products was confirmed by the data of elemental analysis and IR spectroscopy. A yellow finely crystalline product $Nd_3I_5(S_2)(S_2N_2)(THF)(Py)$ was obtained similarly by the dissolution of compound **I** in pyridine.

An unexpected result was obtained in the reactions of the clusters with acetonitrile. The dissolution of the complexes in MeCN at 20°C results in their fast fragmentation to form triiodide $LnI_3(MeCN)_8$, iodide–sulfide $[LnI(S_2)(MeCN)]_x$, and iodide–dithiadinitride $[LnI(S_2N_2)(MeCN)_2]$ in high yields. Similar products were isolated from the reaction with acrylonitrile. Unfortunately, attempts to obtain all products, except for triiodide, as crystals suitable for X-ray diffraction analysis were unsuccessful, but their compositions were reliably determined on the basis of full elemental analysis and IR spectroscopy. It can be assumed that molecules of iodide–sulfides $[LnI(S_2)(MeCN)]_x$ contain a bi- or polynuclear core with tetradentate =S–S= bridging dianions, since all known lanthanide compounds with the $LnX(S_2)$ groups have such a structure [4, 6, 7]. The molecular structure of $[LnI(S_2N_2)(MeCN)_2]$ is less evident, because other lanthanide complexes with dithiadinitride ligands, except for the starting compounds **I** and **II**, are unknown. The molecular structures of similar Co [8–10], Rh [9], Ir [11], Pt [12, 13], Sn [14], and Sb [15] complexes show that the LnS_2N_2 fragment is a planar cycle. Taking into account the steric and electronic structures of a molecule of compound **I**, we can assume that the indicated products are formed via the scheme presented below. Similar transformations were observed when complex **I** was placed in an acrylonitrile solution and also when complex **II** was dissolved in acetonitrile.



Scheme 1

The deep transformations of complexes **I** and **II** upon the simple substitution of coordinated THF by MeCN or acrylonitrile indicate that the stability of these complexes depends strongly on the type of coordination ligands. Previously we assumed the existence of some conjugation in the heterocyclic groups of the clusters involving the 5*d*-sublevels of lanthanides [3]. It should be mentioned that the 5*d*-orbitals are energetically close to the 4*f*-sublevels and are relatively diffuse due to which can accept electrons during the reduction of the complexes [16]. In the case of compounds **I** and **II**, the low-lying $5d_z^2$-orbitals of neodymium and dysprosium can be populated owing to unpaired electrons of the adjacent O and N atoms. In accordance with this approach, it is reasonable to assume that coordinated THF (as well as Phen and Py) stabilizes complex **I** due to the donation of the electron density to the Nd^{3+} cations involved in the conjugation system in the $Nd(2)S_2N_2$ and/or Nd(1)SNd(2)NSN heterocycles (Scheme 1). The substitution of donating THF (donor number (DN) 20.0 [17]) by less donating MeCN (DN 14.2 [17]) results in a decrease in the electron density on the metal atoms and, correspondingly, in the conjugation system, leading to the destruction of the inorganic core of the molecule. The calculated charge on the Nd(1) (0.208) and Nd(2) (0.142) atoms, the population of the Nd(1)–I (0.95, 092) and Nd(2)–I (0.81, 0.88) bonds, and the determined lengths of these bonds (3.1045, 3.1106 and 3.2067, 3.1812 Å) [3] suggest that the substitution of THF by MeCN in a molecule of compound **I** is accompanied by the transfer of the iodine anion from the Nd(2) atom to the Nd(1) atom with the formation of triiodide $Nd(1)I_3(MeCN)$. The latter is detached to leave an unstable system $[Nd(3)I(S_2)Nd(2)(S_2N_2)(MeCN)_x]$, which decomposes to two products: $[Nd(3)I(S_2)(MeCN)]_x$ and $[Nd(2)I(S_2N_2)(MeCN)_2]$. It is most likely that all indicated processes occur simultaneously and the transformations observed represent one general unusual reaction that can be designated as a multivector reaction (but not multistep one).

The quantum-chemical simulation of the changes in the inorganic core of the molecule of complex **I** upon the replacement of THF by acetonitrile confirmed a decrease in the stability of the compound. The calculations were performed by the PBE density functional method [18] using the scalar relativistic approach for the description of the system [19] and the extended four-component basis set. All calculations were performed by the PRIRODA program package [20] using computational possibilities of the Interdepartmental Supercomputer Center of the Russian Academy of Sciences.

When all THF ligands are replaced by MeCN in complex **I**, the geometries of the S_2N_2 and S_2 groups remain almost unchanged but the bond lengths

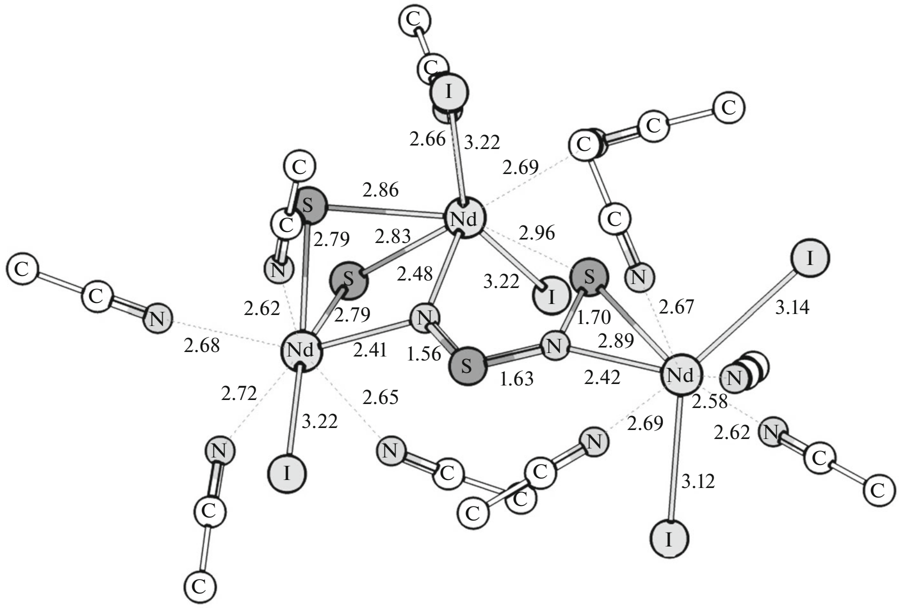


Fig. 2. Calculated structure of complex **I**. Hydrogen atoms are omitted.

change systematically: the Nd(1)–I bonds elongate by 0.01, Nd(2,3)–I elongate by 0.04 Å, and the Nd–S and Nd–N distances shorten by 0.02–0.04 Å (Fig. 2). The average energy of the Nd–THF and Nd–MeCN bonds of the ligands with respect to the optimized core of the cluster is 20.3 and 18.1 kcal/mol, respectively; i.e., the complete substitution of THF by MeCN is thermodynamically unfavorable. Therefore, the reactions of ligand substitution and transformation of the core occur in parallel.

Thus, the study shows that the sensitized recently $Ln_3I_5(S_2)(S_2N_2)(THF)_{10}$ (Ln = Nd, Dy) complexes are unique not only because of their molecular structure but as well due to chemical behavior. The clusters exhibit a low reactivity toward soft oxidants and reducing agents but undergo deep transformations under mild conditions, when the donating coordination ligands are replaced by less donating ones. The fragmentation of the nonanuclear core of the molecules during the replacement of coordinative THF by MeCN is multivector, i.e. occurs simultaneously via several routes according to the charge density on the metal atoms and population of the Ln–X bonds. The data obtained can be considered as an indirect confirmation of conjugation in the polycyclic ring of the studied clusters.

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