



Research paper

Iodide-sulfides of dysprosium: Elucidation of the pathway to lanthanide iodide-sulfide-nitride clusters

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ABSTRACT

In an attempt to get more insight into the way of formation of recently obtained unusual iodide-sulfide-nitride clusters $\text{Ln}_3\text{I}_5(\text{S}_2)(\text{S}_2\text{N}_2)(\text{THF})_{10}$ ($\text{Ln} = \text{Nd}$ (**1**), Dy (**2**)) and modify this synthesis reactions of dysprosium iodide-nitride with sulfur were carried out in various conditions. It was found that the reaction of as prepared dysprosium iodide-nitride $[(\text{DyI}_2)_3\text{N}]_x$ with sulfur in THF yields ionic complex $\{[\text{DyI}_2(\text{THF})_5]^+[\text{DyI}_2\text{S}_5(\text{THF})_2]^{-}\}$ (**3**) anionic part of which contains six-membered cycle DyS_5 . The same reaction in *iso*-propylamine medium affords ionic iodide-sulfide $\{[(\text{PrNH}_2)_4\text{Dy}(\mu\text{-}\eta^2\text{-}\eta^2\text{-}\text{S}_2)]_2^+[\text{I}^-]_2\}$ (**4**) containing bipyramide core formed by two apical Dy^{3+} cations and two equatorial S_2 fragments. The nitride $[(\text{DyI})_3\text{N}_2]$ in THF does not interact with sulfur but upon addition of triiodide DyI_3 the reaction affords cluster **2** in moderate yield.

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1. Introduction

Binary and ternary systems based on sulfides and nitrides of transition and non-transition metals are well known semiconductor materials, which attract the attention of researchers and engineers [1]. Similar lanthanide compounds are no less attractive as semiconductors and emissive materials but they are much less studied due to their complicated availability [2].

Recently, in the search for new lanthanide luminophores, we investigated the reactions of neodymium and dysprosium iodide-nitrides with sulfur in THF and have found that these processes give unusual clusters of the general formulas $\text{Ln}_3\text{I}_5(\text{S}_2)(\text{S}_2\text{N}_2)(\text{THF})_{10}$ ($\text{Ln} = \text{Nd}$ (**1**), Dy (**2**)) [3]. The X-ray analysis showed that both compounds have identical molecular structure (Fig. 1).

The neodymium complex **1** turned out to be luminescent silent while product **2** displayed a metal-centered emission characteristic for Dy^{3+} cation. In molecule of compound **2** there are three Dy atoms with different coordination surrounding but emits only one of them since time-resolved emission spectrum of **2** has mono-modal character as it was established in this work. The scheme of formation of exciting complexes **1** and **2**, which includes several stages, remained unclear and is challenging task. In an attempt

to elucidate this problem, we investigated the final stages of these syntheses with the example of dysprosium derivatives. The reactions of neodymium analogues proceed quite similarly but the products formed are more soluble that hampers their separation and isolation.

2. Experimental procedures

All operations were performed in evacuated tubes using standard Schlenk techniques, thus excluding traces of air and water. Solvents were purified by distillation from sodium/benzophenone ketyl (THF). The iodide-nitride $[(\text{DyI}_2)_3\text{N}]$ was synthesized by the reaction of DyI_2 with nitrogen as described earlier [4]. The C, H, N elemental analyses were performed by the Vario El cube CHNS elemental analyzer (Nizhny Novgorod State University). Lanthanides content was analyzed by complexometric titration.

2.1. Synthesis

3: The suspension of $[(\text{DyI}_2)_3\text{N}]$ (588 mg, 0.466 mmol), sulfur (58 mg, 1.8 mmol) in 17 ml THF was stirred in an ultrasonic bath for 4 h at 60 °C. The formed mixture was centrifuged, the yellow solution was separated from precipitate by decantation, evaporated to 5 ml and cooled to –20 °C for two days. The formed yellow crystalline precipitate of **3** was separated by decantation and

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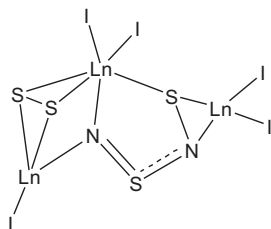


Fig. 1. Inorganic core of molecules of **1** and **2**.

washed with cold THF. Yield 39 mg (3%, calculated for dysprosium taken into the reaction). Calcd. for $C_{28}H_{56}Dy_2I_4S_5$ (1497.68 $g\ mol^{-1}$): C 21.70, H 3.77, S 10.70, Dy 21.70, I 33.89; found C 21.81, H 3.64, S 10.87, Dy 21.81, I 33.95. One of the crystals was used for X-ray crystallographic analysis.

4: $[(DyI_2)_3N]$ (690 mg, 0.546 mmol) was washed with *iso*-propylamine (8 ml \times 3) at 50 °C. To the remaining gray precipitate *iso*-propylamine (7 ml) and sulfur (52 mg, 1.62 mmol) were added. The mixture was stirred in an ultrasonic bath for 4 h at 50 °C. The reaction solution was separated from the formed pale yellow precipitate by decantation, concentrated to 3 ml, cooled to –20 °C and left for a night. The formed yellow crystals of **4** were separated and dried in vacuo. Yield 215 mg (36%). calcd. for $C_{24}H_{72}Dy_2I_2N_8S_4$ (1179.93 $g\ mol^{-1}$): C 24.43, H 6.15, N 9.50, S 10.87, Dy 27.54, I 21.51; found C 24.31, H 6.12, N 9.45, S 10.82, Dy 27.40, I 21.40. One of the crystals was used for X-ray analysis.

2.2. Reaction of $[(DyI)_3N_2(i-PrNH_2)_9]$ with sulfur

To 151 mg (0.106 mmol) of $[(DyI)_3N_2(i-PrNH_2)_9]$ was added 13 mg (0.405 mmol) of sulfur and condensed THF (15 ml). The mixture was stirred in an ultrasonic bath for 4 h at 60 °C. The solution acquired a pale yellow color but formation of crystals of the complex **2** was not observed. $DyI_3(i-PrNH_2)_4$ (84 mg, 0.108 mmol) was added to the reaction mixture. The mixture was stirred in an ultrasonic bath for 4 h at 60 °C. The solution turned yellow-brown. The formed mixture was centrifuged, the solution was separated from precipitate by decantation, evaporated to 3 ml and cooled to 0 °C for 10 h. The yellow crystals were formed. The crystals were washed with cold THF and dried in vacuo to give 45 mg (22%) of **2**.

2.3. X-ray crystallography

The X-ray data for **3** and **4** were collected on *Bruker D8 Quest* diffractometer (*MoK α* radiation, ω -scans technique, $\lambda = 0.71073\ \text{\AA}$, $T = 100(2)\ K$) using *APEX2* [5] software package. The structures were solved by dual-space methods [6] and were refined by full-matrix least squares on F^2 for all data using *SHELX* [7]. *SADABS* [8] was used to perform area-detector scaling and absorption corrections. All non-hydrogen atoms were found from Fourier syntheses of electron density and were refined anisotropically. All hydrogen atoms were placed to calculated positions and were refined in the “riding” model with $U_{iso}(H) = 1.2U_{eq}$ of their parent atoms ($U_{iso}(H) = 1.5U_{eq}$ for methyl groups). The structure of complex **3** was refined as two-component inversion twin with Flack parameter equal to 0.16(2). CCDC–1519019 (**3**) and 1519020 (**4**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre: ccdc.cam.ac.uk/getstructures. The crystallographic data and structure refinement details are given in Table 1.

Table 1
Crystallographic data and structure refinement details for complexes **3** and **4**.

	3	4
Empirical formula	$C_{28}H_{56}Dy_2I_4S_5$	$C_{24}H_{72}Dy_2I_2N_8S_4$
Formula weight	1497.68	1179.93
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12$	$I2/a$
<i>a</i> , Å	8.3679(4)	17.5382(13)
<i>b</i> , Å	15.9037(8)	12.6606(10)
<i>c</i> , Å	16.3210(9)	19.357(2)
α , °	90	90
β , °	90	91.3480(10)
γ , °	90	90
<i>Z</i>	2	4
Volume, Å ³	2172.0(2)	4296.9(7)
Crystal size, mm	0.19 \times 0.07 \times 0.03	0.38 \times 0.20 \times 0.19
<i>d</i> _{calc} , Mg/m ³	2.290	1.824
Absorption coefficient, mm ^{–1}	6.534	5.107
<i>F</i> (0 0 0)	1408	2296
θ range for data collection, °	2.56–30.00	2.87–30.00
Index ranges	–11 $\leq h \leq$ 11 –22 $\leq k \leq$ 22 –22 $\leq l \leq$ 22	–24 $\leq h \leq$ 24 –17 $\leq k \leq$ 17 –27 $\leq l \leq$ 27
Reflection collected	30,163	20,987
Unique reflections	6329	6275
<i>R</i> _{int}	0.0384	0.0310
Completeness to 2 θ , %	99.6	99.8
Data/restraints/parameters	6329/0/211	6275/0/190
<i>Goof</i>	1.044	0.998
<i>R</i> ₁ and <i>wR</i> ₂ ($I > 2\sigma(I)$)	0.0235/0.0506	0.0232/0.0492
<i>R</i> ₁ and <i>wR</i> ₂ (all data)	0.0264/0.0513	0.0395/0.0525
Largest diff. peak and hole, e/Å ³	1.984/–0.619	1.024/–1.112

3. Results and discussion

In our previous study we found that the yield of clusters **1**, **2**, which are formed in a multistage synthesis (the reaction of lanthanide with iodine, the reaction of the resulted LnI_2 with nitrogen and the reaction of the obtained lanthanide iodide-nitride with sulfur), deviates from 0 to 65% depending on the way of isolation of the intermediate lanthanide iodide-nitride [3]. Therefore we investigated in detail the products formed after treatment of as prepared dysprosium iodide-nitride by THF and their reactions with sulfur. The iodide-nitride obtained by burning the Dy/I_2 mixture and subsequent reaction of the formed product with nitrogen at 600 °C was isolated as a pale brown solid insoluble in THF. Its elemental composition corresponds to the formula $[(I_2Dy)_3N]$ [4]. Treatment of this nitride by THF at 20–60 °C leads to the formation of $DyI_3(THF)_3$ (75%) and a new nitride, which can be formulated on the basis of the metal and iodine content and IR spectrum as $\{[(DyI_2)_3N]\}[(DyI_3N_2)(THF)_x]$. Reaction of the latter with sulfur in ultrasonic bath at 60 °C gives cluster **2** in 60% yield. Sixfold extraction of nitride $[(DyI_2)_3N]$ with THF led to its deep disproportionation with the formation of triiodide $DyI_3(THF)_3$ and nitride $[(DyI_3N_2)]$. The latter did not change upon further treatment with THF. Its reaction with sulfur after separation of DyI_3 gave a very low yield of **2** which is formed probably because the presence of negligible amount of triiodide remaining in the nitride $[(DyI_3N_2)]$. To confirm the assumption an equimolar amount of DyI_3 was added to the reaction mixture. The yield of **2** in this case increased to 22%.

It was found that the reaction of as prepared $[(DyI_2)_3N]$ with sulfur in THF results in formation of ionic iodide-sulfide **3**, which consists of cation $[DyI_2(THF)_5]^+$ and anion $[DyI_2S_5(THF)_2]^-$ (Fig. 2). The product yield after 4 h of heating at 60 °C was about 3% and did not increase with further heating, apparently due to encapsulation of the reaction centers by poorly soluble DyI_3 and other side products. The reaction of sulfur with neodymium iodide-nitride without previous treatment by THF gave intractable mixture of products from which the cluster **1** was isolated in negligible yield.

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