Dalton Transactions

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ARTICLE

$Ln_3I_5(S_2N_2)(S_2)(THF)_{10}$– a new type of molecular compounds

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Unprecedented complexes of composition $Ln_3I_5(S_2N_2)(S_2)(THF)_{10}$ were obtained in the reactions of neodymium and dysprosium iodide-nitrides with sulfur. Inorganic core of the molecules contains the cyclic fragments Ln(μ-S_2)Ln, LnSNSN and LnSN. Ten of fourteen atoms of the core are coplanar, the remaining four S_2 and I_2 atoms lie in other two orthogonal planes. Dysprosium complex upon excitation with UV light exhibits the metal-centered luminescence characteristic for Dy^{3+} ion. Geometric parameters of the molecules, computational data, electron spectroscopy and fluorescence suggest the existence of some conjugation in the mentioned heterocycles.

Chalcogenide clusters of lanthanides are of considerable interest from both fundamental point of view and potential application as catalysts, magnetic materials and materials for optoelectronics. The simplest ways to lanthanide chalcogenides, in particular sulfides, are the direct reactions of free sulfur with lanthanide metal at high temperature[1] or with organolanthanide complexes under mild conditions[2], as well as sulfurization of inorganic substrates such as oxides, sulfides or nitrates with CS_2[3] or H_2S[4]. In the cases of organolanthanide derivatives, the reactions lead to insertion of sulfur into lanthanide-carbon bonds. Subsequent transformations of the products result in formation of clusters containing Ln-SR, Ln-S-Ln or Ln(μ-η^2:η^2-S_2)Ln fragments[5, 6]. The synthesis of lanthanide chalcogenides with usage of lanthanide metals and oxides as starting reagents proceed at temperature 850-1300 °C and give binary compounds LnX or Ln_2X_3 depending on lanthanide, chalcogen and conditions[7, 8]. The lanthanide sulfides of the same composition were obtained by thermal decomposition of dithiocarbamates[9, 10]. Interaction of YbI_2 with sulfur affords the polynuclear clusters containing Ln_4(μ^4-S) and the mentioned disulfur groupings[11]. Neither organic nor inorganic compounds with Ln-N bonds were used as substrates for preparation of lanthanide chalcogenides until recently when Evans and coworkers have shown that yttrium nitride {[($Me_3Si)_2N]_2Y(THF)$}(μ-η^2:η^2-N_2) reacts with elemental sulfur to give the binuclear complexes with S, S_2 bridges and the compounds with $[S_3N(SiMe_3)_2]^-$ anion[12]. Here we describe the reactions of sulfur with neodymium and dysprosium iodide-nitride complexes and unprecedented products formed in these processes.

Results and discussion

Recently it has been found that Nd(II) and Dy(II) iodides react with dinitrogen at ambient pressure and temperature 270-500°C to give iodide-nitrides $(I_2Ln)_3N$, treatment of which with THF or isopropylamine causes their disproportionation to LnI_3 and lanthanide iodide-nitrides of indefinite structure[13]. The products do not form the single crystals suitable for X-ray structural investigation but on the basis of elemental analysis they were formulated as $[(ILn)_3N_2]_x$. Note that the iodides of all other divalent lanthanides (Sm, Eu, Tm, Yb) do not react with dinitrogen under the same conditions or give negligible amount of unidentified products. In order to gain more insight into the arrangement of Nd and Dy nitrides and in attempt to synthesize new advanced optoelectronic materials we carried out the reactions of these products with sulfur in THF solution. The reactions have not clarified the structure of the nitrides but unexpectedly led to the formation of complexes unprecedented not only for lanthanide derivatives but also for the compounds of all other metals. The products were isolated as pale brown (Nd) or yellow (Dy) crystals moderately stable in air, readily soluble in THF, poorly soluble in toluene and insoluble in hexane. Upon heating in sealed capillary, the products split THF at 120 °C and decomposed (darkened) above 170 °C.

X-ray analysis revealed that the products formulated as $Ln_3I_5(S_2N_2)(S_2)(THF)_{10}$ (Ln = Nd (**1**), Dy (**2**)) are isomorphous. In Fig. 1 the molecular structure of neodymium complex **1** is shown. The same structure of cluster core was found in the Nd analogue **3**, in which one of coordinating THF molecules is substituted with *iso*-propylamine (Fig. S2). In the inorganic framework of the molecule **1** one can distinguish three central fragments: the bicycle Nd(3)S(3)S(4)Nd(2), the cycle

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Nd(2)S(1)N(1)S(2)N(2) and three-membered cycle Nd(1)N(1)S(1) (total number of cycles is 13). All non-carbon and non-hydrogen atoms of the molecule lie in three planes that are orthogonal to each other (Fig. S3). Majority of atoms (10 of 14) are located in the plane of Nd(1)Nd(2)Nd(3) which is substantially a plane of symmetry of the whole molecule. The largest deviation from the plane is observed for I(1) (0.255(1) Å), I(2) (0.376(1) Å) and I(3) (0.299(1) Å) atoms which are out of the cycle. Deviation of atoms from the planes I(5)Nd(3)S(3)S(4) and S(3)S(4)Nd(2)I(3)I(4) does not exceed 0.05 Å. The Nd(1)-Nd(2) and Nd(2)-Nd(3) distances are 5.707(1) Å and 3.9497(8) Å.

Coordination number of each Nd atom is eight but their coordination spheres are filled differently. The Nd(1) atom is coordinated by four THF molecules, two iodine anions, atoms of sulfur and nitrogen. In the coordination surrounding of Nd(2) atom there are two THF molecules, three sulfur atoms and one nitrogen atom. The Nd(3) cation is bonded to oxygen atoms of four THF molecules, two sulfur atoms, one iodine anion and terminal nitrogen atom of S_2N_2 fragment. Since the molecule is neutral as a whole, S_2 and S_2N_2 groups should be considered as bearing charges 2-. However, the charge distribution on the atoms of the framework is not obvious. In the fragment Nd(μ-η^2:η^2-S-S)Nd the Nd(2)-S(4) and Nd(3)-S(4) bond lengths are virtually the same 2.798(3) and 2.794(2) Å, which is less than respective distances in the complexes $Cp^{Me}{}_2Nd(THF)(\mu\text{-}SPh)_2NdCp^{Me}{}_2$ (THF) (2.922(1) and 2.937(1) Å)[14] and $Nd(SC_6F_5)_3(DME)_2$ (2.840(1), 2.844(1) Å)[15]. The lengths of Nd(2)-S(3) (2.839(3) Å) and Nd(3)-S(3) (2.771(2) Å) bonds noticeably differ from each other and from those in the first couple of Nd-S bonds. Bond lengths Nd(3)-N(2) (2.469(8) Å) and Nd(2)-N(2) (2.460(8) Å) are equal, so the situation with Nd-S bonds in this fragment remains unclear. All these contacts are short (Table S1) what makes difficult determination of character of the bonds and the S_2 group does not add clarity because S(3)-S(4) distance (2.084(3) Å) is close to the lengths of interatomic bonds in a molecule of sulfur S_8 (2.064 Å) and significantly exceeds analogous bond length in solvate S_2 molecule in copper complex [16].. It should be noted that the Ln(μ-η^2:η^2-S-S)Ln grouping is known for derivatives of Yb[5][11][6][17] and Er[5] but in all these cases the compounds have quite different structure and the S-S distances vary in the range of 2.079-2.146 Å.

Probably the most interesting and unexpected result of the studied reactions is formation of S_2N_2 ligands, which form five-membered and three-membered cycles with LnI_2^+ cations.

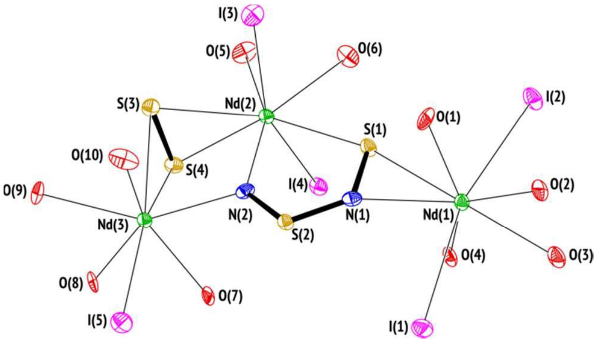

Fig. 1 Molecular structure of $Nd_3I_5(S_2N_2)(S_2)(THF)_{10}$ (**1**) with the probability ellipsoids drawn at the 30% level. Carbon and hydrogen atoms of THF ligands are omitted for clarity.

The disulfur dinitride S_2N_2 is known since 1953[18] but extensive studies of this compound began in the seventies when it was discovered that the polymer $(SN)_x$, which is formed upon heating of S_2N_2, has metallic conductivity at room temperature[19] and low-temperature superconductivity[20]. Despite great number of theoretical and experimental studies, which continue until the present day [21], nature of this amazing substance remains unclear to the end. Nevertheless, more than 20 complexes of S_2N_2 with various metals (K[22] , Sn[23] , Ni[24], Ti[25], Co[25-27], Rh[26], Au[28], Pt[29], Ir[30]) and elements (As[30], Sb[31]) were synthesized and structurally characterized. From the Fig. S5, where molecular types of these complexes are depicted, one can see that the compounds **1**, **2** and **3** have quite different arrangement. Analysis of the geometrical characteristics of organometallic complexes, containing S_2N_2 ligands[22–31], shows that the length of S–N bonds lie in the wide range (S(1)–N(1) 1.621(7)–1.709(9) Å, N(1)–S(2) 1.531(6)–1.621(7) Å, S(2)–N(2) 1.510(8)–1.607(8) Å) and bond distances S–N in **1** (S(1)–N(1) 1.684(8) Å, N(1)–S(2) 1.573(8) Å, S(2)–N(2) 1.531(8) Å) and **2**, **3** (Table S1) are in good argeement with previous published data.

The results of DFT calculations of molecular structures (Fig. S6) reproduce well the experimental data with a mean error of 0.03 Å for bond lengths of inorganic framework. The energies of lowest unoccupied (LUMO) and highest occupied (HOMO) orbitals of **3** were found to be -2.26 and -3.91 eV respectively. The electron affinity and the first ionization potential were calculated as 1.84 and 5.67 eV. The computed population of the bonds in the inorganic fragment of **1** presented in Fig. 2 agrees well with the found interatomic distances.

Analysis of the bonds populations and lengths in the inorganic core of **1** leads to the conclusion that (i) the bonds Nd(1)-S(1), Nd(1)-N(1), Nd(2)-S(4), Nd(3)-S(4) cannot be interpreted as strictly valence or coordination and (ii) in the ligand S_2N_2 the bond S(1)-N(1) is formally single, S(2)-N(2) is double but the order of N(1)-S(2) bond is 1.5. It should be pointed out also that the charge density on the Nd(2) atom noticeably lower than those on the Nd(1) and Nd(3) centers (Table S2). Calculated populations of the bonds in isolated ligands $(SS)^{2-}$ and $(SNSN)^{2-}$ S(3)-S(4), 1.11, and S(2)-N(2), 2.13, N(1)-S(2), 1.52, S(1)-N(1), 1.03, are similar to their values in the complexes 1-3 . This certainly indicates that the SS and SNSN ligands have a formal charge -2 in the complexes and their lone pairs are responsible for binding to metal ions. The possible Isomeric structure of **3** with coordination Nd(1) to N(2)-S(2) bond (Nd(1)-N(2)= 2.599 Å and Nd(1)-S(2)=3.027 Å) has significantly more energy on 21 kcal/mol and coordination to S(2)-N(1) bond is not realized. The reason evidently is poor donor properties of S(2) atom due to its positive charge. From it follows that the central S atom in the ligand [N=S =N-S] is formally tetravalent. Thus, observed structure of the complexes has no alternatives. Considering the possible reasons of the formation of the unusual inorganic skeletons of complexes **1**, **2** and **3,** that faithfully replicate each other (Fig. S4), we came to conclusion that the only explanation could be the existence of some conjugation in these systems, which makes them energetically favourable. We are aware that the assumption of the participation of lanthanide electrons (apparently 5d (p) electrons) in conjugation contradicts to generally accepted notions, but it results in a consensus of all the above inconsistencies and explains the remarkable reproducibility of the formation of just such frameworks under various conditions and with different metals. An indirect confirmation of the supposition is the delocalization of π-electrons resulted in aromaticity which was established earlier in the cobalt complex CpCo(S_2N_2) containing five-membered CoSNSN cycle[32].

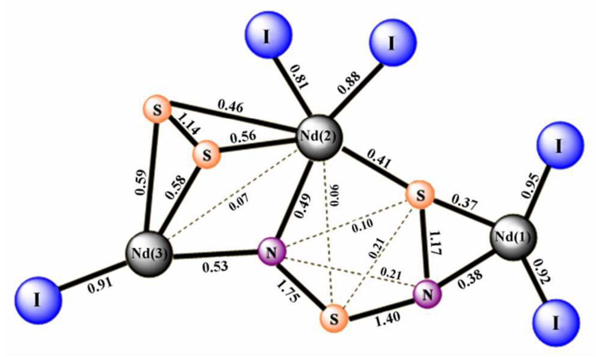

Fig. 2 Computed bonds population in the inorganic framework of **1**.

In search of confirmation of this suggestion we studied the vibrational, electronic and photoluminescence spectra of the obtained substances. Note that the spectral study of all previously obtained complexes with S_2N_2 ligands were limited to IR spectroscopy. UV-visible absorption spectrum (one broad band at 250 nm) was published only for free S_2N_2[33].

The IR spectra of **1**, **2** and **3** in the region 1000 – 400 cm^{-1} (Fig. S7a are identical and similar to those of disulfur dinitride of Co, Rh, Ir[26, 32] and other metals containing five-membered M(S_2N_2) ring. The calculated IR spectrum for the complex **3** (Fig S7b) is in good agreement with the experimental one (Fig S7a) taking into account masking bands at 724, 1200, 1377 and 1462 cm^{-1} of nujol.

In the UV-visible absorption spectra of obtained products in THF solution there is a band at about 235-240 nm (Fig. S8) attributed apparently to disulfur dinitride fragments because in the studied compounds there are no other ligands or groups, which can absorb in the region 200-300 nm. Besides, as noted above the band with close wavelength was observed in the spectrum of free S_2N_2. Study of luminescence properties of the obtained clusters has shown that neodymium derivatives **1** and **3** are not luminescent while dysprosium analogue **2** upon excitation with UV light (λ_{ex} 260 nm) exhibits characteristic emission of Dy^{3+} cations as two narrow bands at 482 and 575 nm corresponding to $^4F_{9/2}$ – $^6H_{15/2}$, $^6H_{13/2}$ transitions (Fig. 3). We believe that the main contribution to the luminescence of the complex brings Dy(2) atom forming a five-membered ring with disulfur dinitrogen ligand, which absorbs in the region where the excitation band was registered. Atom Dy(1), included in three-membered ring DySN, apparently also fluoresces due to excitation via S-N group. The luminescence of Dy(3)atom is less probable because its coordination sphere is filled with non-sensitizing atoms (I, N) and group S_2.

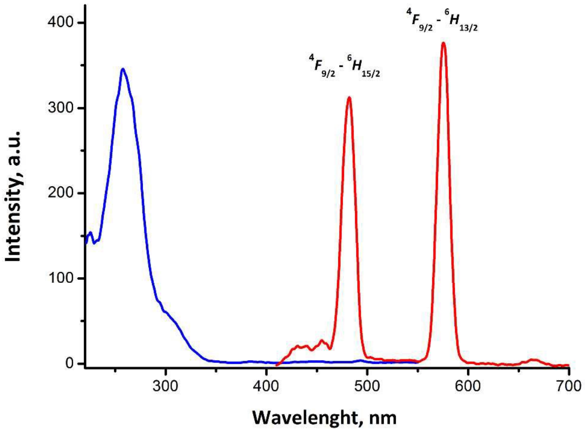

Fig. 3 Excitation (blue) and photoluminescence (red) spectra of **2** in THF solution upon excitation at λ_{ex} 260 nm.

For exact definition of luminescence centers in the molecule additional studies are needed.

Synthetic procedures

Preparation of $Nd_3I_5(S_2N_2)(S_2)(THF)_{10}$ (1). To an evacuated Schlenk tube containing 0.78 g (0.48 mmol) of neodymium iodide-nitride prepared as described earlier[13] and THF (8 ml) 0.017 g (0.52 mmol) of sulfur was added. The tube was sealed and kept in ultrasonic bath at 50 °C for 4 h. Most of the precipitate of neodymium nitride dissolved and the solution became yellow-brown. The mixture was centrifuged, the solution was separated by decantation and left at -5°C for a night. The formed light yellow-brown crystals of 1 (one of which was used for X-ray analysis) was separated, washed with cold THF and dried in vacuum. Yield 0.52 g (56%); upon heating up to 120 °C the substance released THF, at 160°C it darkened. Infrared (Nujol, cm^{-1}): ν 960 (s), 675 (m), 420 (m). Analysis. Found: C, 24.47; H, 4.08; N, 0.92; S, 5.30. $C_{40}H_{80}I_5N_2Nd_3O_{10}S_4$ requires C, 24.71; H, 4.15; N, 1.44; S, 6.60.

Note that the starting neodymium iodide-nitride after its preparation by the reaction of NdI_2 with dinitrogen was washed with THF at 60°C (10 ml × 2). Changing the washing mode leads to formation of another products in the subsequent reaction with sulfur. These transformations now are under study.

The dysprosium complex **$Dy_3I_5(S_2N_2)(S_2)(THF)_{10}$** (**2**) was synthesized in a similar manner. From 0.67 g (0.395 mmol) of dysprosium iodide-nitride and 0.015 g (0.47 mmol) of sulfur 0.29 g (37 %) of compound **2** was obtained as yellow crystalline solid. IR spectrum was analogous to that of **1**. Analysis. Found: C, 24.33; H, 4.78; N, 0.98; S, 6.87. $C_{40}H_{80}Dy_3I_5N_2O_{10}S_4$ requires C, 24.03; H, 4.03; N, 1.40; S, 6.42.

The amine containing product **$Nd_3I_5(S_2N_2)(S_2)$ $(THF)_{9.6}$(*i*-$PrNH_2)_{0.4}$ (3)** was prepared as compound **1** in THF medium but in this case the starting neodymium iodide-nitride was washed with *iso*-propylamine (9 ml × 2). 0.62 g (61%) of **3** was obtained from 0.86 g (0.52 mmol) of neodymium iodide-nitride and 0.018 g (0.58 mmol) of sulfur. Analysis. Found: C, 24.66; H, 4.12; N, 1.22; S, 6.87. $C_{39.8}H_{80.4}I_5N_{2.4}Nd_3O_{9.6}S_4$ requires C, 24.52; H, 4.18; N, 1.73; S, 6.61.

Conclusions

We here report on the synthesis and characterization of neodymium and dysprosium complexes, which have no analogues among the inorganic, organometallic and coordination compounds of d and f metals. According to their molecular arrangement and sizes, the obtained complexes are closest to the quantum dots containing metal-chalcogenide core in the organic shell. But in contrast to the classical quantum dots the products are molecular substances containing in a molecule fourteen-nuclear inorganic core of quite definite structure formed by atoms of lanthanides (Nd or Dy), iodine, sulfur and nitrogen. The framework of the core consists of a number of metallacycles united into one common system. The molecular geometry of the compounds, computed bonds population, atomic charges, electronic and fluorescent spectra suggest the existence of conjugation of p-electrons of S, N atoms and, which is most unusual, 5p- or 5d-electrons of lanthanide atoms. Although the Ln^{3+} cations in the ground state have empty 5d orbitals (the electron configuration of Ln^{3+} is $4f^n5s^25p^65d^0$) upon reduction of lanthanide compounds the coming electron populates just this shell as it was established recently [34]. Partial population of 5d subshell in the studied cases can be carried out due to back donation of the electron density from the dithiadiazine and disulfure ligands formed in the synthesis. The nature of the obtained complexes is still unclear, but their composition and structure gives ground to expect from them new interesting reactions and transformations.

Acknowledgements

This work was supported by the Russian Scientific Foundation (project 14-13-01158).

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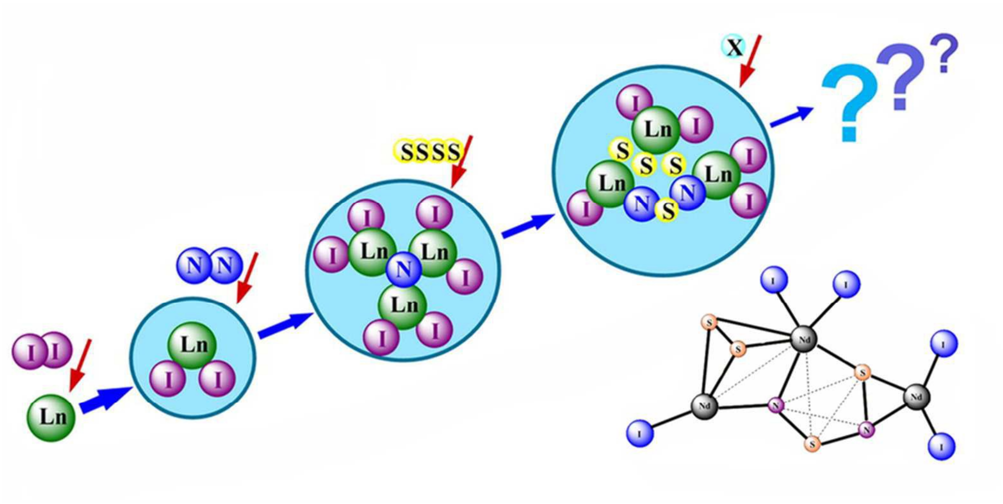

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