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Carbamide-containing complexes of lanthanides: competition of hydrogen bonding and polyiodide ion formation

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The carbamide complexes of lanthanide polyiodoiodates $[Tm(ur)_7][I_3]_3 \cdot 2I_2$, $[Yb(ur)_6][I_3]_3$ and $[Lu(ur)_6][I_3]_3$ [ur is $O{=}C(NH_2)_2$] have been synthesized and structurally characterized. The structure-forming role of the pentaiodide ions taking part in the formation of extended channels 10–12 Å in diameter with incorporated hepta(carbamide)thulium cations combined to one another into infinite columns due to H-bonding, or the triiodide ions forming lace-like net with isolated hexa(carbamide)ytterbium(III) or hexa(carbamide) lutetium(III) cations located in the net holes has been revealed.

Supramolecular polyiodoiodate compounds are of interest due to a search for new conducting materials including high-temperature superconductors and crystals with anisotropic conductivity. These compounds are characterized by the presence of extended polyiodoiodate chains (linear and branched) located in the cavities formed by complicated complex cations.[1,2] Lanthanide-containing compounds with multiple-charged cations and the central atom with a variable oxidation number are of special interest.

Carbamide as an ambidentate ligand is promising due to its ability to hydrogen bonding and the channel- and clathrate-structure formation. This ligand allows one to prepare the single crystals of lanthanide polyiodoiodates.[3] It should be noted that (i) the crystal structure formation is determined by the three types of association, namely, the cation–cation, cation–anion, and anion–anion association; (ii) cations serve as a template, which determines the polyiodide type and the anion–anion association properties; taking into account high coordination numbers and a wide variety of coordination polyhedra, the changes in growth conditions and variations in the central atom specific features make it possible to control the type of the anion–anion association; (iii) the type of the anion–anion association is the main reason for ionic conductivity.

Unfortunately, the high absorption of these complexes, on the one hand, and their low stability at room temperature, on the other, prevented the previous studies of the above compounds.

It is well known that the complexes with the proposed clathrate-coordination structure $LnI_3 \cdot 5ur \cdot 4I_2 \cdot 10H_2O$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm)[4,5] and $LuI_3 \cdot 5ur \cdot 3I_2 \cdot xH_2O$[6] are formed at 0 °C. Synthesis of polyiodoiodates of the lanthanide carbamide complexes (Ln is La, Ce, Nd, Sm, Eu, Tb, Er, Tm, Yb or Lu) at room temperature and without preliminary crystallization of lanthanide iodide complexes with carbamide yields a number of compounds with different composition.[7] The IR and Raman spectroscopic studies have proved the coordination of carbamide molecules *via* oxygen atom of a ligand, as well as the presence of $[I_3]^-$ ions.[7]

The aim of this work was to determine the structure–properties relationship for the three representative compounds of thulium, ytterbium and lutetium, in particular, in their synthesis and the single crystal X-ray structure investigation.

We have synthesized complexes $[Tm(ur)_7][I_3]_3 \cdot 2I_2$ **1**, $[Yb(ur)_6][I_3]_3$ **2** and $[Lu(ur)_6][I_3]_3$ **3** by the treatment of the corresponding oxides with concentrated hydroiodic acid (without preliminary purification) with the subsequent addition of powdered iodine and carbamide.† The molecular and crystal structures of the synthesized complexes have been studied.‡

Complex **1** (Figure 1) consists of $[Tm(ur)_7]^{3+}$ cations and two types of polyiodide ions, namely, $[I_8]^{2-}$ and $[I_5]^-$, while isostructural complexes **2** and **3** are composed by $[Ln(ur)_6]^{3+}$ cations and three $[I_3]^-$ anions (Figure 2). In all of the complexes, the mono-

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† *General procedure for the synthesis of lanthanide complexes* **1**–**3**. Sample of the respective oxide Ln_2O_3 (Ln = Tm, Yb, or Lu, 2–3 g) was treated with a 20–30% excess of concentrated hydroiodic acid taken without preliminary purification and partially contaminated with iodine (~5 wt%) with the subsequent addition of powdered crystalline iodine (the molar ratio Ln_2O_3:I_2 = 1:8). The mixture was thoroughly agitated until the complete dissolution of iodine followed by carbamide addition (the molar ratio Ln:ur = 1:5) to the homogenized solution obtained. The prepared mixtures were kept at room temperature with the subsequent cooling (down to 0 °C) for the crystallization of polyiodoiodate complexes. Crystals were separated by vacuum filtration through a funnel with a sintered glass porous bottom and dried at room temperature in a desiccator over phosphorus(V) oxide. Black needle-like crystals with metallic lustre are hygroscopic and low-melting ones and gradually loose iodine in air. They decompose in the presence of water and organic solvents.

For **1**: Found (%): Tm, 7.31; I^0, 55.52. Calc. for $C_7H_{28}N_{14}O_7I_{13}Tm$ (%): Tm, 7.55; I^0, 56.68.

For **2**: Found (%): Yb, 9.81; I^0, 45.34. Calc. for $C_6H_{24}N_{12}O_6I_9Yb$ (%): Yb, 10.33; I^0, 45.44.

For **3**: Found (%): Lu, 10.43; I^0, 45.57. Calc. for $C_6H_{24}N_{12}O_6I_9Lu$ (%): Lu, 10.43; I^0, 45.39.

The molar ratios I_2:Ln are 5.18:1, 3.52:1 and 3.02:1 for **1**, **2** and **3**, respectively. For compound **2**, an impurity of iodine was proposed.

‡ *Crystal data for* **1**–**3**.

At 100 K crystal of **1** is monoclinic, space group $P2_1/n_1$, a = 8.4315(18), b = 27.314(7) and c = 19.606(4) Å, β = 93.510(5)°, V = 4506.8(17) Å^3, Z = 4 (Z' = 1), M = 2239.06, d_{calc} = 3.300 g cm^{-3}, μ(MoKα) = 10.916 cm^{-1}, F(000) = 3928.

At 100 K crystal of **2** is monoclinic, space group $P2_1/n$, a = 10.0465(4), b = 18.1607(7) and c = 20.2236(8) Å, β = 101.3510(10)°, V = 3617.7(2) Å^3, Z = 4 (Z' = 1), M = 1675.51, d_{calc} = 3.076 g cm^{-3}, μ(MoKα) = 10.303 cm^{-1}, F(000) = 2956.

At 100 K crystal of **3** is monoclinic, space group $P2_1/n$, a = 10.0342(8), b = 18.1529(15) and c = 20.2100(16) Å, β = 101.426(2)°, V = 3608.3(5) Å^3, Z = 4 (Z' = 1), M = 1677.44, d_{calc} = 3.088 g cm^{-3}, μ(MoKα) = 10.474 cm^{-1}, F(000) = 2960.

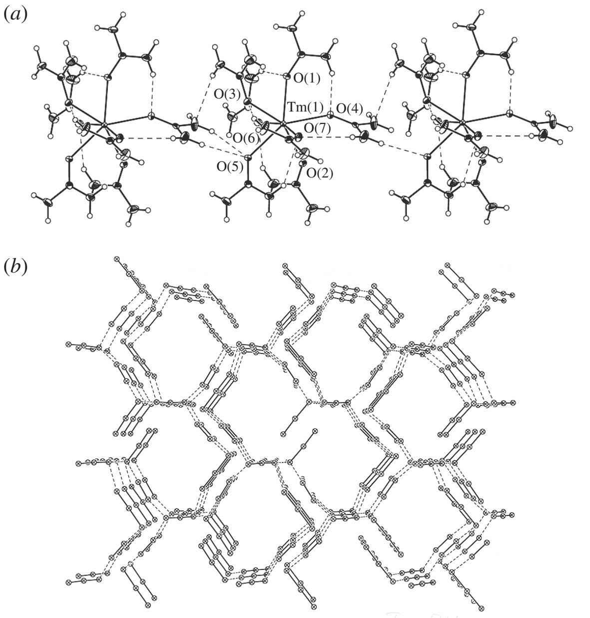

Figure 1 Crystal structure of compound **1**: (*a*) hepta(carbamide)thulium(III) cations and (*b*) channels in the polyiodide frame.

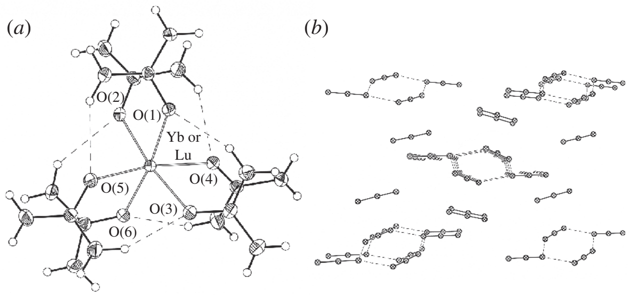

Figure 2 Crystal structure of compounds **2** and **3**: (*a*) hexa(carbamide)ytterbium(III) or hexa(carbamide)lutetium(III) cations and (*b*) polyiodide ribbons.

dendate urea molecules are coordinated by the lanthanide ions. The coordination polyhedron of Tm is the one-capped trigonal prism, while that of Yb and Lu is a slightly distorted octahedron. The geometry of cations is clearly governed by the steric requirements for the urea molecules arrangement that are reflected in the significant distortion of the Ln–O–C angles from the expected value of 120°. Indeed, in the Tm complex, the average Tm–O–C angle is 139.7°, while Yb–O–C and Lu–O–C angles are 135.5° and 136° in complexes **2** and **3**, respectively, with the octacoordinated cations. Furthermore, in addition to the steric requirements, the geometry of cations is also determined by the capability of urea molecules to form intramolecular H-bonds between the ligands. As can be seen, almost all ligands participate in the formation of intramolecular H-bonds, the N···O distances varying in the ranges 2.849(5)–3.216(5), 3.044(6)–3.250(6) and 3.029(9)–3.242(9) Å in **1**, **2** and **3**, respectively. The principal distinction of the Tm complex is the presence of intermolecular N–H···O [N···O 3.141(4)–3.267(5) Å] and N–H···N [N···N 3.389(6) Å] hydrogen bonds that assemble the cations into infinite chains. In contrast, in **2** and **3**, the cations are surrounded only by the polyiodide ions and the remaining NH groups are involved in the formation of the cation–anionic N–H···I hydrogen bonds.

The most probable reason of such a cation···cation assembly is an increase in the coordination number in **1** and, as a result, that of the steric repulsion within the coordination polyhedron. Thus, we can conclude that the formation of the cation···N–H···O hydrogen bonds is more preferable than the cation···anion (N–H···I) bonds.

The bond length distribution in the $[I_8]^{2-}$, $[I_5]^-$ and $[I_3]^-$ anions is close to the expected values. Note that the presence of $[I_8]^{2-}$ and $[I_5]^-$ anions in **1** is consistent with the Raman spectra, according to which an additional band at 172 cm^{-1} due to the polyiodide anion–iodine molecule interaction[7] is present. Bond lengths in $[I_8]^{2-}$ vary in the range of 2.811(1)–3.423(1) Å. The Z-shaped $[I_8]^{2-}$ is non-planar; the pseudotorsion angle I(2)–I(3)–I(6)–I(5) is 99.2°.

The I–I bond lengths (2.84–3.08 Å) in the nearly linear (the I–I–I angles are ~178°) triiodide ions demonstrate the asymmetry of these ions, which is in agreement with the Raman spectra.[7] All triiodide ions are oriented nearly in the same mode (angles between them are $\leq 15°$) and surround the complex cations, as well as separate them from each other. As a whole, all polyiodide ions are linked into chains clustered into the lace-like frame with cavities filled with complex cations.

The I–I distances in the outer sphere iodine molecules are ~2.77 Å (*cf.* 2.72 Å in non-coordinated I_2), while the measured values of $[I_3]^-$–$[I_2]$ contacts are 3.34–4.35 Å.

Thus, I_2 and pentaioide ions form the extended channels with diameters up to 10–12 Å, where the hepta(carbamide)thulium(III) cations integrated into infinite columns (due to hydrogen bonding formation) are located. On the other hand, hexa(carbamide)ytterbium(III) or hexa(carbamide)lutetium(III) cations are separated from each other by triiodide ions forming a lace-like frame.

In conclusion, the structures of the complexes synthesized may be considered as an example of supramolecular self-organization due to the competition of intramolecular (and/or intermolecular) H-bonding and the extended polyiodide assembly formation.

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Intensities of 109006 (**1**), 43794 (**2**) and 26876 (**3**) reflections were measured with a SmartAPEXII CCD diffractometer, λ(MoKα) = 0.71072 Å, ω-scan, $2\theta < 58°$ (**1**, **2**) and 56° (**3**) at 100 K, and 11977 (R_{int} = 0.0472) (**1**), 9629 (R_{int} = 0.0345) (**2**) and 8701 (R_{int} = 0.0472) (**3**) independent reflections were used in the further refinement. The structures were solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic–isotropic approximation. The substantial redundancy in data allows an empirical absorption correction to be applied using multiple measurements of equivalent reflections with the SADABS Bruker program.[8] The positions of hydrogen atoms were calculated and refined in the riding model.

The refinement converged to wR_2 = 0.0827 and GOF = 1.08 for all independent reflections [R_1 = 0.0364 was calculated against F for 11102 observed reflections with $I > 2\sigma(I)$] for **1**; to wR_2 = 0.0600 and GOF = 1.085 for all independent reflections [R_1 = 0.0265 was calculated against F for 8677 observed reflections with $I > 2\sigma(I)$] for **2** and to wR_2 = 0.1007 and GOF = 1.029 for all independent reflections [R_1 = 0.0402 was calculated against F for 7432 observed reflections with $I > 2\sigma(I)$] for **3**. All calculations were performed using SHELXTL PLUS 5.0.[9]

CCDC 806370–806372 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2011.