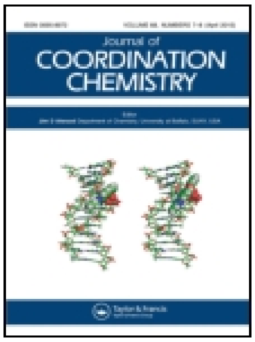

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Synthesis and structural characterization of polyiodides of rare-earth urea complexes: crystal structures of $[Ho(Ur)_7][I_3]_3$ and $[Pr(Ur)_8][I_5][I_3]_2[I_2]$

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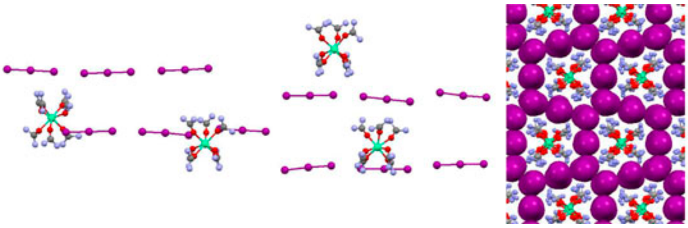

Reactions of $LnI_3 \cdot nH_2O$, I_2, and urea (Ur) produced rare-earth polyiodides $[Ln(Ur)_8][I_5][I_3]_2[I_2]$ (Ln = Pr, Nd, Sm–Tb) and $[Ln(Ur)_7][I_3]_3$ (Ln = Ho, Er); the crystal structures of the praseodymium and holmium compounds were solved. In $[Ho(Ur)_7][I_3]_3$, holmium ions are located at the centers of distorted pentagonal bipyramids (three independent complex cations) and an octahedra with a split vertex (one independent cation) of oxygens of coordinated urea. All triiodide anions are symmetric and linear; they are united in almost linear infinite chains by short contacts. The almost parallel chains of iodine atoms form infinite walls of honeycomb-like channels, and the columns of the complex cations are localized in these channels. Complex $[Pr(Ur)_8][I_5][I_3]_2[I_2]$ is isostructural to the earlier reported $[Dy(Ur)_8][I_5][I_3]_2[I_2]$.

Keywords: Polyiodides; Rare earth metals; Holmium; Praseodymium; Urea

1. Introduction

Studies on anhydrous lanthanide complexes with neutral O- and/or N-donor ligands have intensified in recent years due to their implications in homogeneous catalysis, magnetic and optical materials, as synthons for the synthesis of coordination and organometallic compounds and, for Ln(II) halide complexes, as reducing agents in organic synthesis; these complexes also hold potential as starting materials for constructing more sophisticated

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*Corresponding author. Email: e.savinkina@mail.ru heterometallic assemblies by crystal engineering [1]. However, preparing anhydrous lanthanide complexes is difficult, since lanthanide ions show high affinity to water molecules. One of the ways of excluding water molecules from the inner sphere of metal complexes with O- and/or N-donor ligands is preparing their polyiodides.

Metal-containing polyiodides have earned attention because of their structural variability [2]. Hundreds of polyiodides of transition metals, alkali metals, and earth-alkali metals are structurally characterized to date; however, rare-earth polyiodides are less studied. Series of rare-earth complexes with dibenzo-18-crown-6 [3–6], THF [7, 8], and urea (Ur) [9–11] and a single Er complex with 4,4′-bipyridine-*N*,*N*′-dioxide [12] containing various polyiodide anions are reported.

It was found earlier that isostructural $[Ln(Ur)_4(H_2O)_4]I_3$ complexes [13–15] give polyiodides with various urea and iodine content, such as $[Ln(Ur)_8][I_5][I_3]_2[I_2]$ (Ln = La, Ce, Dy) [10, 11], $[Tm(Ur)_7][I_3]_3\cdot 2I_2$, $[Ln(Ur)_6][I_3]_3$ (Ln = Yb, Lu) [9] and an Er complex of ambiguous composition [10].

In $[Ln(Ur)_8][I_5][I_3]_2[I_2]$, the V-shaped I_5^- ions are united in infinite planar twisting chains. The chains are connected by short contacts through bridging V-shaped I_5^- ions (combined of I_2 molecule and I_3^- ion) and symmetric I_3^- ions. Another I_3^- ion is isolated. The bonded iodine atoms form hexahedral channels, and the columns of the $[Ln(Ur)_8]^{3+}$ complex cations are localized in these channels and stabilized by hydrogen bonding [10, 11]. The $[Tm(Ur)_7][I_3]_3\cdot 2I_2$ compound contains pentaiodide ions taking part in the formation of extended channels with incorporated $[Tm(Ur)_7]^{3+}$ cations combined to one another into infinite columns due to H-bonding [9]. In $[Ln(Ur)_6][I_3]_3$, the triiodide ions form a lace-like net with isolated $[Yb(Ur)_6]^{3+}$ or $[Lu(Ur)_6]^{3+}$ cations located in the net holes [9]. Coordination number of the central ion decreases from La to Lu; this can be explained by decrease in the Ln radius.

However, similar compounds of Pr–Tb and Ho were not studied. The purpose of the work was to complete the series of rare-earth urea complex polyiodides and to examine their structures.

2. Experimental

2.1. *Materials and methods*

Hydroiodic acid was purified from iodine by distillation with HPH_2O_2. Rare-earth iodides were synthesized by the treatment of corresponding carbonates with hydroiodic acid (20% excess); the resulting solutions were concentrated at 110 °C and cooled. Crystals of hydrated iodides were removed with a glass filter and dried over KOH, P_4O_{10}, or H_2SO_4 in darkness. All other reagents were purchased from commercial sources and used without additional purification. IR spectra (in Nujol) were recorded with a EQUINOX 55 (Bruker) Fourier IR spectrometer from 500 to 4000 cm^{-1}. Lanthanide content was determined by titration with EDTA at pH 5.0 (acetate buffer, xylenol orange). Iodine content (in the form of I_2) was determined by titration with sodium thiosulfate. Iodide content was determined by weighing as AgI. Total iodine content was determined as I^- after reduction of iodine with sodium sulfite.

2.2. *Synthesis of polyiodides*

Polyiodides were synthesized by two procedures differing by the order of adding reagents, $LnI_3 \cdot nH_2O$ and I_2, then Ur or $LnI_3 \cdot nH_2O$ and Ur, then I_2; reagents were mixed in the molar ratio $LnI_3 \cdot nH_2O : I_2 : Ur = 1 : (4–7) : 8$. In both cases, no solvent was added; the components dissolved in crystal water of $LnI_3 \cdot nH_2O$, liberating on complexation. The resulting viscous solutions were stored in air. In 12–15 days, black crystals of polyiodides, $[Ln(Ur)_8][I_5][I_3]_2[I_2]$ (Ln = Pr, Nd, Sm, Eu, Gd, Tb), and $[Ln(Ur)_7][I_3]_3$ (Ln = Ho, Er) formed (yields 65–75%).

Calcd for $C_8H_{32}NdI_{13}N_{16}O_8$ (%): Nd, 6.34; I (in the I_2 form), 55.80; I (total), 72.53. Found (%): Nd, 6.14; I (in the I_2 form), 55.52; I (total), 71.60. Calcd for $C_8H_{32}SmI_{13}N_{16}O_8$ (%): Sm, 6.59; I (in the I_2 form), 55.65, I (total), 72.34. Found (%): Sm, 6.69; I (in the I_2 form), 55.06; I (total), 71.02. Calcd for $C_8H_{32}EuI_{13}N_{16}O_8$ (%): Eu, 6.65; I (in the I_2 form), 55.61; I (total), 72.29. Found (%): Eu, 6.43; I (in the I_2 form), 53.08; I (total), 71.05. Calcd for $C_8H_{32}GdI_{13}N_{16}O_8$ (%): Gd, 6.87; I (in the I_2 form), 55.48, I (total), 72.12. Found (%): Gd, 6.14; I (in the I_2 form), 56.77; I (total), 73.27. Calcd for $C_8H_{32}TbI_{13}N_{16}O_8$ (%): Tb, 6.94; I (in the I_2 form), 55.44; I (total), 72.07. Found (%): Tb, 7.03; I (in the I_2 form), 54.67; I (total), 70.95. Calcd for $C_7H_{28}HoI_9N_{14}O_7$ (%): Ho, 9.55; I (in the I_2 form), 44.08, I (total), 66.12. Found (%): Ho, 9.05; I (in the I_2 form), 43.07; I (total), 65.95. Calcd for $C_7H_{28}ErI_9N_{14}O_7$ (%): Er, 9.69; I (in the I_2 form), 44.02, I (total), 66.03. Found (%): Er, 9.11; I (in the I_2 form), 43.86; I (total), 65.56. The composition of $[Pr(Ur)_8][I_5][I_3]_2[I_2]$ was determined by X-ray diffraction analysis.

2.3. *X-ray diffraction analysis*

Details of the crystal data, data collection, and refinement parameters for $[Ho(Ur)_7][I_3]_3$ and $[Pr(Ur)_8][I_5][I_3]_2[I_2]$ are summarized in table 1. Intensity data were collected on a Bruker KAPPA APEX II auto diffractometer at 296 and 100 K, respectively.

The $[Ho(Ur)_7][I_3]_3$ and $[Pr(Ur)_8][I_5][I_3]_2[I_2]$ structures were solved by the direct method and refined by full-matrix least squares against F^2 in the anisotropic approximation for non-hydrogen atoms. The positions of hydrogens were calculated and refined in a riding model. Calculations were performed using SHELXS-97 and SHELXL-97 [16]. Thermal ellipsoids were presented with 20% probability. The $[Ho(Ur)_7][I_3]_3$ structure was solved and refined for a twin crystal. The second domain with 0.304 contribution was turned about the first one by 180° around a normal line to the (1 0 0) plane. Several distances and angles were restricted.

For other polyiodides, only unit cell parameters were measured (table 2).

2.4. *Theoretical study*

The optimization of the geometry of the complexes was performed using the Priroda 13/14 program package (Laikov [17–19]) with the pbe, mpbe, pbe1, or b3lyp functional in the L1 basis. The single-point calculations of the optimized cations were made by the rimp2 method in the Priroda 13/14 program package. The Bader charges were calculated with the use of the Multiwfn_3.3.7(dev) program [20]; the Molden2AIM Version 2.2.2 program and the pri2 mol script for file transformation were also used. Symmetry operations were refined in the SymApps program; the figures were drawn with the Chemcraft_1.6 and Mercury_3.1 programs.

Table 1. Crystal data, data collection, and refinement parameters for $[Ho(Ur)_7][I_3]_3$ and $[Pr(Ur)_8][I_5][I_3]_2[I_2]$.

Compound	$[Ho(Ur)_7][I_3]_3$	$[Pr(Ur)_8][I_5][I_3]_2[I_2]$
Empirical formula	$C_7H_{28}HoI_9N_{14}O_7$	$C_8H_{32}I_{13}N_{16}O_8Pr$
M	1727.46	2271.10
Crystal dimensions (mm)	0.27 × 0.19 × 0.17	0.30 × 0.20 × 0.16
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1/n$
a (Å)	12.4124 (8)	15.1946 (3)
b (Å)	22.2082 (14)	21.7653 (4)
c (Å)	28.8657 (16)	15.7166 (3)
β (°)	99.7610 (10)	111.9430 (10)
V (Å^3)	7841.8 (8)	4821.17 (16)
Z	8	4
D_c (g cm^{-3})	2.926	3.129
μ (cm^{-1})	9.148	9.382
F(000)	6144	4016
λ (Å)	Mo$K\alpha$ (0.71073)	Mo$K\alpha$ (0.71073)
Scan range (°)	4.08–27.50	4.104–30.000
Index ranges	$-26 \le h \le 16$, $-28 \le k \le 28$, $-37 \le l \le 37$	$-21 \le h \le 21$, $-30 \le k \le 29$, $-22 \le l \le 18$
Reflections collected	67,421	14,010
Independent reflections	36,488	10,967
Weighting scheme	$1/[s^2(F_o^2)+(0.0610P)^2+20.0000P]$, $P=(F_o^2+2F_c^2)/3$	$1/[s^2(F_o^2)+(0.0157P)^2+50.9827P]$, $P=(F_o^2+2F_c^2)/3$
No. parameters refined	1370	418
Final R, wR (obs. data)	0.0674, 0.1235	0.0433, 0.0751
GOF	1.008	1.054

Table 2. Unit cell parameters for $[Ln(Ur)_8][I_5][I_3]_2[I_2]$ (Ln = Nd, Sm, Eu, Gd, Tb) and $[Er(Ur)_7][I_3]_3$.

Ln	a (Å)	b (Å)	c (Å)	β (Å)	V (Å)
Nd	15.63 (3)	22.06 (2)	15.95 (3)	112.12 (5)	5117 (12)
Sm	15.51 (2)	21.97 (3)	15.80 (2)	112.03 (2)	4989 (13)
Eu	15.50 (2)	22.03 (2)	15.77 (2)	112.25 (2)	4982 (13)
Gd	15.44 (2)	21.90 (3)	15.67 (2)	112.19 (5)	4904 (15)
Tb	15.47 (1)	21.98 (1)	15.78 (1)	112.03 (1)	4972 (9)
Er	12.48 (2)	22.30 (1)	28.90 (2)	98.70 (3)	7850 (10)

Table 3. IR spectra of urea, $[Ln(Ur)_8][I_5][I_3]_2[I_2]$ and $[Ln(Ur)_7][I_3]_3$.

	$[Ln(Ur)_8][I_5][I_3]_3[I_2]$						$[Ln(Ur)_7][I_3]_3$		
Ur	Pr	Nd	Sm	Eu	Gd	Tb	Ho	Er	Assignment
789	767	772	775	768	769	775	774	774	δ(NCN)
1064	1015	1014	1019	1012	1035	1019	1021	1022	ν_s(CN)
1153	1153	1140	1155	1145	1147	1156	1156	1155	$\rho(NH_2)$
1606	1673	1576	1582	1568	1582	1584	1583	1582	$\delta(NH_2)+\nu(CO)$
1631	1621	1626	1625	1615	1621	–	–	–	$\delta(NH_2)$
1686	1656	1642	1652	1657	1645	1651	1652	1651	$\nu(CO)+\delta(NH_2)$
3268, 3333, 3436	3350,3469	3350, 3454	3343, 3436, 3470	3326, 3354, 3470	3351, 3457	3341, 3459	3340, 3459	3340, 3459	ν(NH)

3. Results

Reaction of $[Ln(Ur)_4(H_2O)_4]I_3$ with iodine in aqueous solution produced black crystals of $[Ln(Ur)_8][I_5][I_3]_2[I_2]$ (Ln = Pr, Nd, Sm, Eu, Gd, Tb) and $[Ln(Ur)_7][I_3]_3$ (Ln = Ho, Er). The same products were prepared by reaction of $LnI_3{\cdot}nH_2O$ and I_2, then Ur or $LnI_3{\cdot}nH_2O$ and Ur, then I_2. Coordination of urea through the carbonyl O is supported by significant shift of ν(CO) to lower frequencies as compared to free urea in the IR spectra of the compounds (table 3).

Crystal structure of $[Ho(Ur)_7][I_3]_3$ was determined by X-ray diffraction. Selected bond lengths and angles for the structure are given in table 4.

The unit cell of $[Ho(Ur)_7][I_3]_3$ contains four crystallographically independent $[Ho(Ur)_7]^{3+}$ cations and 12 crystallographically independent I_3^- anions (figure 1).

In three $[Ho(Ur)_7]^{3+}$ cations (Ho1, Ho2, and Ho4), coordination polyhedron is a distorted pentagonal bipyramid (figure 2). The pentagonal base is distorted; maximal outlet of O atoms is 0.6 Å. The axis is less distorted, and the O–Ho–O angle is 169–172°. These cations are stabilized by two (in two cations) or three (in one cation) intramolecular hydrogen bonds of the N–H···O type (O–N 2.884–2.997 Å) involving O of pentagonal bases. The fourth $[Ho(Ur)_7]^{3+}$ cation (Ho3) contains no H-bonds; its polyhedron can be described as an octahedra with a split vertex.

Urea molecules are planar; the C=O and C–N bond lengths vary from 1.13–1.31 to 1.23–1.38 Å, respectively, close to free urea [21]. Besides intramolecular H-bonds, urea molecules form intermolecular hydrogen bonds of the N–H···O type between Ho1 and Ho4 polyhedra (O···N 2.928 Å) uniting them in pairs and short contacts of the N–H···I type (I···N 3.480–3.519 Å) between Ho2 polyhedron and triiodide ions.

All triiodide anions, I_3^-, are symmetric (differences between two I–I distances are 0.0018–0.0725 Å) and linear (the I–I–I angles vary in the 176.97–179.30° range).

According to [22], a bond between two iodine atoms corresponds to the I···I distance less than ~4.0 Å (the sum of van der Waals radii for iodine is 4.30 Å). Therefore, we can state that the triiodide anions are united in almost linear infinite chains (figure 3) by short contacts (3.703–4.026 Å). The almost parallel chains of iodine atoms form infinite walls of honeycomb-like channels (distances between adjacent chains are ~4.5 Å, channel diameters are ~14 Å), and the columns of the complex cations are localized in these channels (figure 4).

$[Pr(Ur)_8][I_5][I_3]_2[I_2]$ (figure 5) is isostructural to the earlier reported $[Dy(Ur)_8][I_5][I_3]_2[I_2]$; the details of the latter structure were discussed [11].

Structures of the complexes, which were not solved by X-ray diffraction analysis (only unit cell parameters were determined), were optimized theoretically. For calculations, we have choosen the Priroda program package, since it allows to make all electron scalar-relativistic calculations with the use of the Dyall's Modified Dirac Hamitonian approximation [26]. To check validity of the method, we optimized geometry of the lanthanum complex cation; its structure was earlier solved by X-ray diffraction analysis. When the anionic part of the compound was not taken into account, the results were not completely satisfactory. Thus, the La–O bond lengths in the experimental structure were 2.435–2.563 Å, while they fell within the 2.435–2.689, 2.422–2.644, and 2.441–2.674 Å ranges with the use of the DFT method with mpbe, pbe1, or b3lyp functionals. Introduction of the polyiodide anion improved correlations between experimental and theoretical results; the maximal value of the Ln–O bond length became 2.600 Å. This fact confirms conclusion on polyiodide stabilization, which involves both N···I halogen bonding and cation–anion interactions [11, 23,

Table 4. Bond distances (Å) and angles (°) for $[\mathrm{Ho(Ur)_7}][\mathrm{I_3}]_3$.

$[\mathrm{Ho1(Ur)_7}]^{3+}$ Ho–O	O–C	C–N^1	C–N^2	Ho–O–C
2.349 (9)	1.20 (2)	1.31 (2)	1.34 (2)	141.9 (12)
2.200 (12)	1.2596 (10)	1.3296 (10)	1.3299 (10)	171.3 (16)
2.350 (10)	1.222 (19)	1.37 (2)	1.27 (2)	133.9 (12)
2.329 (12)	1.27 (2)	1.26 (3)	1.32 (2)	142.1 (11)
2.287 (10)	1.234 (17)	1.28 (2)	1.35 (2)	136.2 (12)
2.282 (11)	1.236 (18)	1.27 (2)	1.31 (2)	145.4 (12)
2.327 (11)	1.248 (17)	1.29 (2)	1.34 (2)	144.2 (12)
$[\mathrm{Ho2(Ur)_7}]^{3+}$				
Ho–O	O–C	C–N^1	C–N^2	Ho–O–C
2.348 (13)	1.26 (2)	1.32 (2)	1.30 (3)	150.2 (12)
2.296 (10)	1.254 (19)	1.34 (2)	1.27 (2)	137.8 (10)
2.291 (10)	1.21 (2)	1.36 (2)	1.36 (2)	140.7 (12)
2.292 (12)	1.297 (19)	1.31 (2)	1.34 (2)	139.9 (12)
2.315 (13)	1.22 (2)	1.23 (2)	1.36 (3)	134.8 (14)
2.253 (13)	1.255 (18)	1.30 (2)	1.28 (2)	155.7 (13)
2.286 (11)	1.25 (2)	1.35 (2)	1.28 (2)	142.1 (12)
$[\mathrm{Ho3(Ur)_7}]^{3+}$				
Ho–O	O–C	C–N^1	C–N^2	Ho–O–C
2.266 (17)	1.19 (3)	1.33 (5)	1.29 (4)	145 (2)
2.275 (15)	1.22 (2)	1.31 (2)	1.26 (2)	141.0 (16)
2.306 (16)	1.25 (2)	1.31 (2)	1.27 (2)	137.7(15)
2.329 (12)	1.14 (3)	1.24 (3)	1.41 (3)	154.0 (19)
2.312 (14)	1.13 (3)	1.29 (3)	1.34 (3)	142.9 (18)
2.146 (19)	1.2556 (9)	1.3256 (10)	1.3256 (10)	130.1 (16)
2.16 (2)	1.2555 (11)	1.3255 (10)	1.3257 (9)	145 (2)
$[\mathrm{Ho4(Ur)_7}]^{3+}$				
Ho–O	O–C	C–N^1	C–N^2	Ho–O–C
2.233 (12)	1.23 (2)	1.38 (2)	1.32 (3)	141.5 (14)
2.286 (14)	1.21 (2)	1.27 (2)	1.27 (2)	147.0 (14)
2.342 (13)	1.24 (2)	1.25 (2)	1.27 (2)	149.1 (12)
2.294 (14)	1.21 (2)	1.32 (3)	1.27 (3)	155.3 (16)
2.327 (12)	1.272 (19)	1.35 (2)	1.29 (2)	138.9 (13)
2.339 (11)	1.31 (2)	1.31 (2)	1.27 (2)	131.4 (12)
2.275 (11)	1.22 (2)	1.30 (2)	1.25 (2)	141.4 (12)
$[\mathrm{I_3}]^-$				
I^1–I^2		I^2–I^3		I^1–I^2–I^3
2.9256 (16)		2.9385 (16)		179.12 (6)
2.9261 (17)		2.9311 (18)		178.65 (6)
2.9288 (18)		2.9270 (18)		178.44 (6)
2.9573 (19)		2.919 (2)		179.27 (6)
2.9574 (18)		2.908 (2)		179.36 (6)
2.9508 (17)		2.9289 (17)		176.53 (5)
2.9169 (18)		2.928 (2)		178.94 (6)
2.886 (2)		2.9585 (19)		177.04 (7)
2.897 (2)		2.9465 (19)		179.16 (6)
2.9648 (17)		2.9111 (18)		177.02 (6)
2.9320 (18)		2.9208 (19)		178.21 (6)
2.9154 (18)		2.9599 (17)		177.00 (5)

27]. Therefore, we calculated the structures of other $[\mathrm{Ln(Ur)_8}][\mathrm{I_5}][\mathrm{I_3}]_2[\mathrm{I_2}]$ (Ln = Pr–Tb) complexes taking into account the anionic part of the compound (see figure 6 for the Eu complex as an example).

The charges on the central atoms were calculated by the Bader method [28]. They vary in the 2.74–2.79 Å range indicating ionic character of the Ln–O bond that correlates with conclusions of other authors [29, 30].

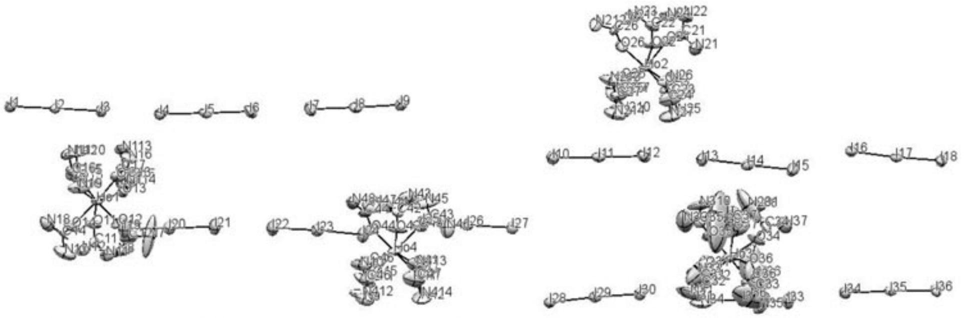

Figure 1. Independent part of the unit cell in the crystal of $[Ho(Ur)_7][I_3]_3$.

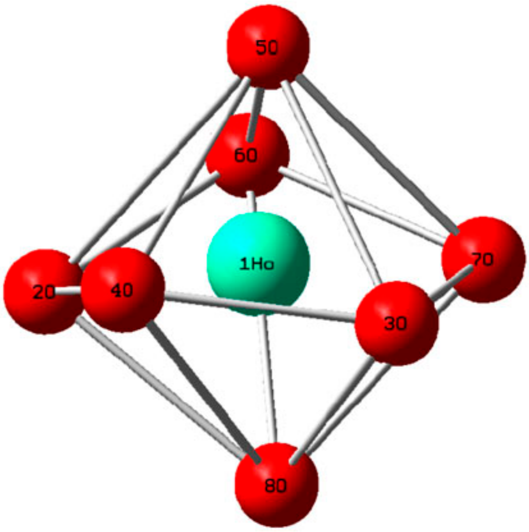

Figure 2. Coordination polyhedron of Ho1 in the crystal of $[Ho(Ur)_7][I_3]_3$.

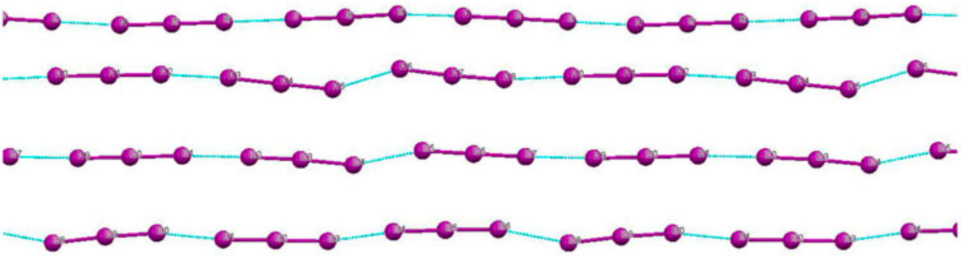

Figure 3. Polyiodide chains in the crystal of $[Ho(Ur)_7][I_3]_3$.

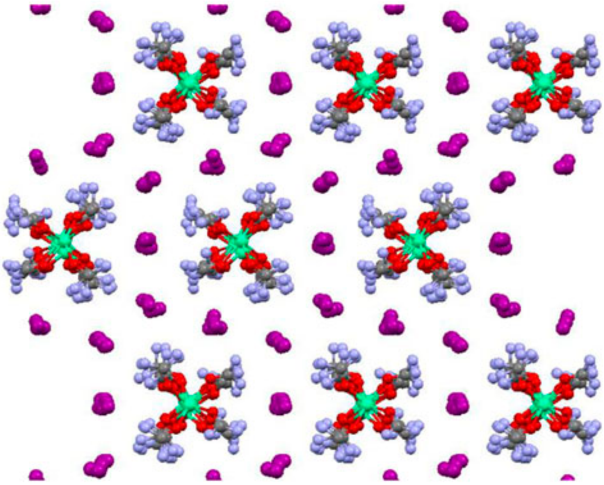

Figure 4. Packing in the crystal of $[Ho(Ur)_7][I_3]_3$.

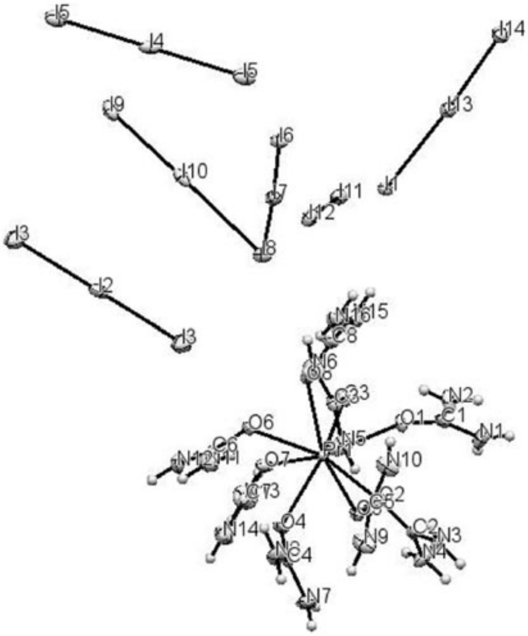

Figure 5. Independent part of the unit cell in the crystal of $[Pr(Ur)_8][I_5][I_3]_2[I_2]$.

4. Discussion

Transformation of isostructural iodides of some transition metal and lanthanide urea complexes to polyiodides with quite different structures was mentioned in our previous work [11]. The results of this work, along with the earlier reported data [9–11], allow analysis of changes in polyiodide structures for the whole lanthanide row.

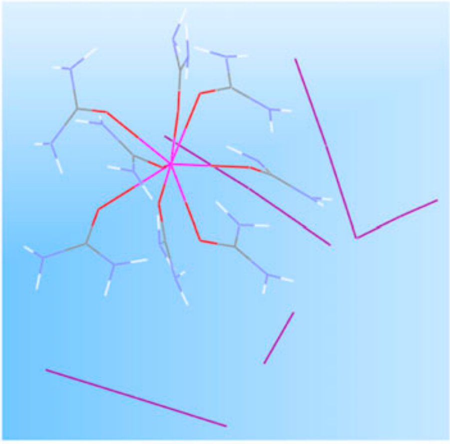

Figure 6. Optimized geometry of $[Eu(Ur)_8][I_5][I_3]_2[I_2]$.

The lanthanide urea polyiodides form a morphotropic row with three structural transformations caused by decrease in the urea quantity in inner spheres of complex cations. In the first part of the row (Ln = La–Dy), coordination number of the central ion is 8, then it decreases to 7 (Ln = Ho–Tm) and 6 (Ln = Yb, Lu).

Decrease in coordination number in the complex polyiodides in the La–Lu row correlates with the decrease in the ionic radius, although the maximal Ln–O bond length in the $[Ln(Ur)_8][I_5][I_3]_2[I_2]$ (Ln = La–Dy) row decreases unevenly (figure 7).

It is noteworthy that the same decrease in the ionic radius (by 15%) does not change the structure of the $[Ln(Ur)_4(H_2O)_4]I_3$ complexes, although the volume of the unit cell decreases by 7.8%. This can be explained by transfer of the structure-forming role from urea in iodides to iodine in polyiodides; the more rigid iodine network seems to be more sensitive to a cation size.

Anionic lattice becomes simpler when going from La to Lu. At the beginning of the row (La–Dy), polyiodide anion is complicated ($\{[I_5][I_3]_2[I_2]\}^{3-}$); at the end of the row (Ho–Lu),

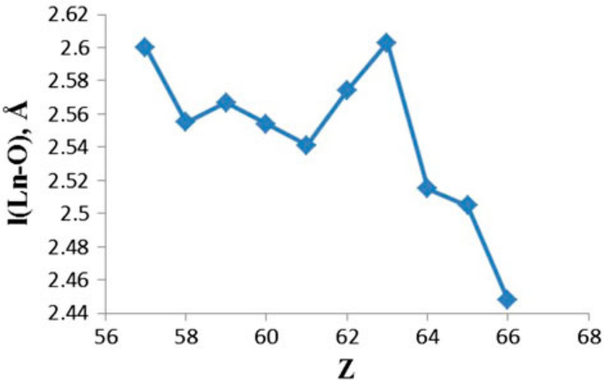

Figure 7. Maximal bond length *l* (Ln–O) in $[Ln(Ur)_8][I_5][I_3]_2[I_2]$ *vs*. Ln atomic number (*Z*).

it consists of triiodide ions, excluding Tm compound, where the $\{[I_3]_3[I_2]_2\}^{3-}$ polyiodide ions were found [9]. The iodine network changes when going from Ho to Lu. Holmium, erbium, and thulium polyiodides have the channel structure with stacks of complex cations arranged in the channels with iodine-built walls. The $[Ln(Ur)_6][I_3]_3$ structure is closer to layered; the layers are built of alternating complex cations and triiodide anions and linked in a 3-D framework by I···I (3.838–3.846 Å) and N–H···I (3.522 Å) contacts.

Complex cations in all rare-earth urea polyiodides are water-free, similar to M(II) urea complex polyiodides [23–25]. This fact can be explained by structure-forming role of iodine and impossibility of short contacts between coordinated water molecules and iodine framework for structure stabilization.

5. Conclusion

Analysis of lanthanide urea polyiodides based on the results of this work along with the data reported [9–11] shows that most lanthanides, from the beginnig of the row to Dy, form polyiodides with the same composition and similar structures. For the last five members of the row, more variability is observed. We can conclude that electronic structure has no effect on compositions and structures of polyiodides. The main reason for changing composition and structure of lanthanide urea polyiodides is the decrease in the radii of central ions. Polyiodides of transition metal or lanthanide urea complexes never include water in the inner sphere; the complex cation contains only urea ligands. Then, the coordination number of the central atom is ruled by its ability to arrange optimal quantity of bulk (as compared to water molecules) ligands. Decrease in the coordination number results in abrupt decrease in the complex cation size followed by reorganization and simplification of the anionic part of the structure.

Supplementary material

CCDC 1063543 and 1063544 contain the supplementary crystallographic data for $[Ho(Ur)_7][I_3]$ and $[Pr(Ur)_8][I_5][I_3]_2[I_2]$. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223 336 033; or E-mail: deposit@ccdc.cam.ac.uk.

Supplementary data

The supplementary material for this paper is available online at http://dx.doi.10.1080/00958972.2015.1102230.

Disclosure statement

No potential conflict of interest was reported by the authors.

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