ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2009, Vol. 35, No. 1, pp. 12–14. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © N.S. Rukk, D.V. Al'bov, A.Yu. Skryabina, R.A. Osipov, L.Yu. Alikberova, 2009, published in Koordinatsionnaya Khimiya, 2009, Vol. 35, No. 1, pp. 14–16.

Deca(hydroxo)-23-Aqua-Hexa(lanthanum(III)) Iodide Octahydrate and Deca(hydroxo)-23-Aqua-Hexa(neodymium(III)) Iodide Octahydrate: Syntheses and Structures

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Received March 26, 2008

Abstract—New hexanuclear complexes of lanthanum and neodymium iodides, $[La_6(H_2O)_{23}(OH)_{10}]I_8 \cdot 8H_2O$ (**I**) and $[Nd_6(H_2O)_{23}(OH)_{10}]I_8 \cdot 8H_2O$ (**II**), are synthesized and studied by X-ray diffraction analysis. The isostructural crystals of complexes **I** and **II** are orthorhombic: a = 13.197(4) Å, b = 15.152(3) Å, c = 15.302(4) Å and a = 13.060(4) Å, b = 14.967(5) Å, c = 15.098(4) Å, respectively; Z = 2, space group *Pnnm*. The lanthanum (neodymium) atoms coordinate the aqua and hydroxo ligands and enter the composition of the Ln_6-containing complex cations. The coordination polyhedron (ignoring the central oxygen atom) of each atom of the complexing agent is somewhat distorted square antiprism with the aqua and hydroxo ligands being in the vertices. Four bridging ligands link this atom of the complexing agent with the four adjacent atoms.

DOI: 10.1134/S1070328409010035

INTRODUCTION

Data concerning lanthanum and lanthanide iodide hydrates are few and contradictory to some extent. Based on the results of the low-temperature (153 K) X-ray diffraction analysis of single crystals of $LnI_3 \cdot nH_2O$ isolated from aqueous solutions at room temperature, two series of the hydrates were found: nonahydrates $[Ln(H_2O)_9]I_3$ (Ln = La–Ho) and decahydrates $[Ln(H_2O)_8]I_3 \cdot 2H_2O$ (Ln = Er–Lu). The nonahydrates crystallize in the orthorhombic crystal system (space group *Pnnm*, coordination polyhedron is a three-capped trigonal prism), and the decahydrates are monoclinic (space group $P2_1/c$, coordination polyhedron as a square antiprism) [1]. The formation of lanthanide iodide nonahydrates was confirmed by the study of the phase equilibria at 0°C in ternary systems involving lanthanide(III) oxide, hydroiodic acid, and water [2]. The crystal structure of heptanuclear $La_7(OH)_{18}I_3$ (**III**) (hexagonal crystal system, space group $P6_3/m$, a = 18.315(7) Å, c = 3.928(1) Å, Z = 2) was determined by the X-ray diffraction method (R = 2.9%). Structure **III** was derived from the hydroxide structure (structural type of UCl_3) by the replacement of 1/7 of positions in the anionic sublattice by iodide ions. Structure **III** is a combination of two regular and six slightly distorted trigonal $La(OH)_3$ prisms and six considerably distorted trigonal $La(OH)_2I$ prisms formed due to the incorporation of the iodide ions into unfilled channels of the initial structure. This type of incorporation retains a coordination number of nine and explains the existence of this structural type for a series of single-charged ions that substantially differ in sizes [3].

The purpose of the present work is the synthesis and crystal structure determination of two lanthanum (**I**) and neodymium (**II**) iodide polyhydrates.

EXPERIMENTAL

Synthesis. Neodymium oxide and lanthanum carbonate hexahydrate were dissolved in a minor excess of a solution of hydroiodic acid on heating. To remove solvent excess, the resulting solutions were subjected to isothermal evaporation at room temperature. The crystals of complexes **I** and **II** were formed as yellow prisms in about two months.

X-ray diffraction analysis. The experimental intensities of diffraction reflections for crystals **I** and **II** were obtained at room temperature (293(2) K) on a CAD-4 diffractometer [4] (MoK_α radiation, graphite monochromator, ω scan mode). The unit cell parameters were determined and refined by 25 reflections in the θ range θ = 13°–14° (for **I**) and θ = 14°–15° (for **II**). The main experimental parameters and crystallographic characteristics of compounds **I** and **II** are given in the table. An absorption correction was applied using the ψ scan method for particular reflections. The primary processing of the experimental data set was carried out using the WinGX program package [5], and all

subsequent calculations were performed using the SHELX-97 program package [6].

The structures of compounds **I** and **II** are shown in Figs. 1 and 2, respectively. Selected bond lengths are listed in the figure captions.

The coordinates of atoms and other parameters for the crystal structures of complexes **I** and **II** were deposited with the Karlsruhe Structural Database (Fachinformations-Zentrum Karlsruhe nos. 419186 (**I**), 419187 (**II**); e-mail: crysdata@fiz-karlsruhe.de).

RESULTS AND DISCUSSION

The X-ray diffraction data show that the lanthanum (neodymium) atoms in complex **I** (**II**) coordinate the aqua and hydroxo ligands (the water molecules and hydroxo groups are indiscernible because of the mobility of the protons and their ability to migrate, as well as due to the impeding influence of the heavy atoms) and enter the composition of the large Ln_6-containing cations (Ln = La, Nd; coordination number of nine). The polynuclear cations form three-dimensional cages due to the developed system of hydrogen bonds involving the water molecules. The iodide ions are localized in cavities between the polynuclear cations. Each lanthanum(III) (neodymium(III)) cation is bound to the central oxygen atom, four terminal aqua or hydroxo ligands, and four atoms of the complexing agent of the

Crystallographic characteristics, X-ray diffraction experimental parameters, and refinement details for structures **I** and **II**

Parameter	Value	
	I	II
FW	2504.66	2536.64
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pnnm*	*Pnnm*
a, Å	13.197(4)	13.060(4)
b, Å	15.152(3)	14.967(5)
c, Å	15.302(4)	15.098(4)
V, Å^3	3059.8(15)	2951.1(15)
Z	2	2
ρ_{calcd}, g/cm^3	2.797	2.855
μ_{Mo}, mm^{-1}	8.168	9.445
θ range, deg	1.89–25.97	1.92–27.98
Index range	$0 \le h \le 16$, $0 \le k \le 18$, $0 \le l \le 18$	$0 \le h \le 17$, $0 \le k \le 19$, $0 \le l \le 19$
Crystal sizes, mm	$0.30 \times 0.30 \times 0.30$	$0.20 \times 0.20 \times 0.20$
Independent reflections	3119	3691
Reflections with $I \ge 2\sigma(I)$	2356	3006
Refined parameters	148	147
GOOF	1.013	1.056
R_1/wR_2 ($I \ge 2\sigma(I)$)	0.0409/0.0763	0.0408/0.0821
$\Delta\rho_{max}/\Delta\rho_{min}$, *e* Å^{-3}	1.808/–1.152	2.810/–2.212

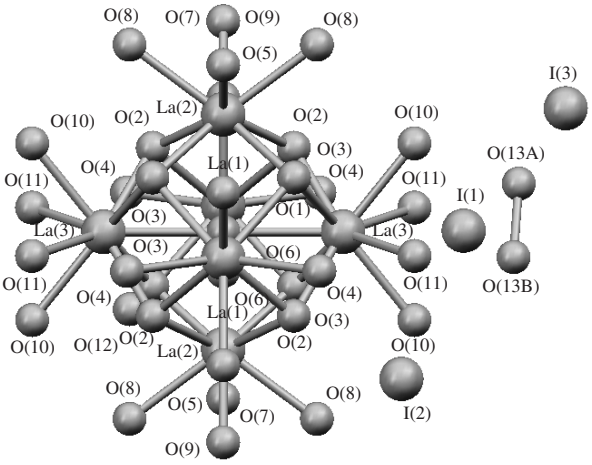

Fig. 1. Structure of compound **I**. Selected bond lengths (*d*, Å):
La(1)–O(2) = 2.492(5), La(1)–O(3) = 2.504(5), La(1)–O(6) = 2.588(8), La(1)–O(4) = 2.607(6), La(1)–O(5) = 2.616(10), La(1)–O(1) = 2.6963(10), La(2)–O(1) = 2.6872(8), La(2)–O(3) = 2.487(5), La(2)–O(2) = 2.498(5), La(2)–O(9) = 2.593(9), La(1)–O(8) = 2.627(6), La(2)–O(7) = 2.651(8), La(2)–La(3) = 3.7911(9), La(3)–O(1) = 2.6742(9), La(3)–O(2) = 2.482(5), La(3)–O(3) = 2.493(5), La(3)–O(10) = 2.575(6), La(3)–O(11) = 2.679(7).

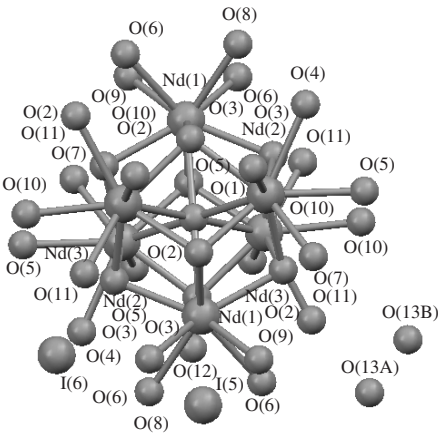

Fig. 2. Structure of compound **II**. Selected bond lengths (*d*, Å):
Nd(1)–O(3) = 2.427(5), Nd(1)–O(2) = 2.443(5), Nd(1)–O(6) = 2.535(6), Nd(1)–O(8) = 2.548(9), Nd(1)–O(9) = 2.543(8), Nd(1)–O(1) = 2.6240(9), Nd(2)–O(3) = 2.414(5), Nd(2)–O(2) = 2.428(5), Nd(2)–O(4) = 2.595(8), Nd(2)–O(1) = 2.6070(9), Nd(3)–O(3) = 2.413(4), Nd(3)–O(2) = 2.427(5), Nd(3)–O(10) = 2.515(7), Nd(3)–O(1) = 2.5953(9), Nd(3)–O(11) = 2.630(8), Nd(2)–O(7) = 2.549(9), Nd(2)–O(5) = 2.573(6).

same cation through the aqua or hydroxo bridges. Eight oxygen atoms (ignoring the central O atom) are arranged in the vertices of somewhat distorted square antiprism. Two more water molecules, one of which is disordered over two positions, link the complex cations. The La–O bonds in complex **I** are longer than the Nd–O bonds in structure **II**, which is due to a decrease in the size of the complexing atom on going from lanthanum to neodymium.

Synthesized compounds **I** and **II** represent a new example of mixed-ligand lanthanide iodides containing more than one complexing atom in the complex cation. Compounds **I** and **II** can be isolated from aqueous solutions of hydroiodic acid. The concentration of the latter substantially decreases with time due to oxidation by air oxygen.

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