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Hydrothermal Synthesis, Crystal Structures, and Fluorescence Properties of Ni(II)–Ln(III) Complexes (Ln = Sm, Pr, Eu)[1]

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Abstract—Three novel 3*d*–4*f* heterometal complexes $[Ln(NiL)_3(Btca)(NO_3)] \cdot xH_2O$ (Ln = Sm(III) (**I**), Pr(III) (**II**), Eu(III) (**III**) (H_2L = 2,3-dioxo-5,6,14,15-dibenzo-1,4,8,12-tetraazacyclo-pentadeca-7,13-dien, H_2Btca = benzotriazole-5-carboxylic acid) were solvothermally synthesized and characterized by single-crystal X-ray diffraction (CIF files CCDC nos. 1555557 (**I**), 1555555 (**II**), 1555556 (**III**)). They crystallized in the monoclinic space group $P2_1/n$ for **I** ($x = 1.5$) and $C2/c$ for (**II**) and (**III**) ($x = 1$), respectively. In these complexes, the central Ln(III) and external nickel ions are bridged by macrocyclic oxamide groups. The metal center of Ln(III) resides in a distorted bicapped square antiprism surrounding with six oxygen atoms of three oxamide groups, two oxygen atoms of $Btca^{2-}$ ion and two oxygen atoms of NO_3^-. Furthermore, there are C–H···O and/or C–H···N hydrogen bond interactions among nitrate, benzotriazole-5-carboxylate, macrocyclic oxamide and water to form three-dimensional superamolecular architecture. The fluorescence properties of the compounds **I** and **II** are also discussed.

Keywords: heterometallic complexes, solvothermal synthesis, crystal structure, fluorescence property

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INTRODUCTION

Construction of 3*d*–4*f* polynuclear complexes have been a very active area in the nowadays, because of their heterometallic nature, which can result in exploitable properties such as magnetism, catalysis, luminescence properties, and so on [1–5]. Recently, much effort has been devoted to design 3*d*–4*f* polynuclear complexes with special function [1–5], however, the assembly of 3*d*–4*f* polynuclear complexes is still full of challenges for chemist due to the competitive reactions between lanthanide and transition metal ions with the organic ligands. At present, most of the ligands usually containing both N- and O-donors were selected to construct 3*d*–4*f* polynuclear complexes by using one-pot synthetic approach [2, 5]. However, adopting this synthetic approach, the reactions are not easy to control because coordination polymers and/or homometallic polynuclear complexes may generate due to the ligand bridging interaction and coordination competition of metal ions. In this paper, in order to design and construct 3*d*–4*f* complex, mononuclear macrocyclic oxamide complex with the exo-cis conformation of the oxygen donors was used as a ligand to interact with a rare earth metal ion, which allow us to synthesize Ni–Ln systems in a more controlled fashion [6–10]. Moreover, considering the synergistic effect between the different ligands, we chose benzotriazole-5-carboxylate as co-ligands based on the following reasons: firstly, it has carboxyl oxygen donors which prefer to bond to Ln^{3+} ions; secondly, three nitrogen and two oxygen atoms can potentially be used as hydrogen bond acceptors and donors to assemble supramolecular structures; lastly, the strong π-conjugated system of large benzotriazole ring may enhance the fluorescence properties of rare earth ions [11]. On the other hand, many complexes containing rare earth ions have good fluorescence properties [11–15], but those containing 3*d*–4*f* metals have been investigated rarely [15, 16], thus the investigations on the fluorescence of 3*d*–4*f* metal complexes will give basic and useful information for the development of new fluorescent materials.

With these facts in mind and in continuation of our work on 3*d*–4*f* polynuclear complexes, the macrocyclic oxamido-nickel(II) complex and benzotriazole-5-carboxylate were used as co-ligands to synthesize 3*d*–4*f* complexes. The results show that three novel tetranuclear $Ni(II)_3Ln(III)$ complexes (Ln = Sm, Pr, Eu) have been isolated and structurally characterized, the fluorescent properties of **I** and **II** are also preliminarily investigated.

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EXPERIMENTAL

Materials and methods. All the starting reagents were of A.R. grade and were used as purchased. The complex ligand NiL was prepared as described elsewhere [17]. Analyses of C, H and N were determined on a Perkin-Elmer 240 Elemental analyzer. IR spectrum was recorded as KBr discs on a Shimadzu IR-408 infrared spectrophotometer in the 4000–600 cm^{-1} range. Luminescence spectra for the samples were recorded with a Hitachi 850 fluorescence spectrophotometer.

Synthesis of $[Ln(NiL)_3(Btca)(NO_3)] \cdot xH_2O$ (I–III). A mixture of $Ln(NO_3)_3 \cdot 6H_2O$ (0.05 mmol, Ln = Sm 22.3 mg; Pr 21.4 mg; Eu 22.2 mg), NiL (0.1 mmol, 19.6 mg), H_2Btca (0.1 mmol, 16.3 mg), H_2O (10 mL) and CH_3OH (4 mL) was stirred slightly at room temperature, and the pH value of the solution was adjusted to about 7–8 with NaOH aqueous solution. After stirring, the mixture was transferred to a 18 mL Teflon-lined reactor, and heated at 150°C for 72 h. Then the reaction system was cooled to room temperature during 36 h, and red brown crystals for **I–III** were isolated by filtering and washing with water.

For $C_{64}H_{54}N_{16}O_{12.50}Ni_3Sm$ (**I**)

Anal. calcd., %	C 48.80	H 3.43	N 14.23
Found, %	C 48.81	H 3.44	N 14.21

IR bands (ν, cm^{-1}): 1631 $\nu_s(COO^-)$, 1614 ν(C=O), 1554 ν(C=N).

For $C_{64}H_{53}N_{16}O_{12}Ni_3Pr$ (**II**)

Anal. calcd., %	C 49.38	H 3.41	N 14.40
Found, %	C 49.31	H 3.42	N 14.43

IR bands (ν, cm^{-1}): 1637 $\nu_s(COO^-)$, 1617 ν(C=O), 1556 ν(C=N).

For $C_{64}H_{53}N_{16}O_{12}Ni_3Eu$ (**III**)

Anal. calcd., %	C 49.03	H 3.38	N 14.30
Found, %	C 49.04	H 3.39	N 14.28

IR bands (ν, cm^{-1}): 1626 $\nu_s(COO^-)$, 1607 ν(C=O), 1566 ν(C=N).

X-ray crystallography. Single crystal X-ray diffraction analyses of **I–III** were carried out on a Bruker Smart Apex II CCD diffractometer equipped with a graphite monochromated MoK_α radiation (λ = 0.71073 Å) by using ϕ/ω scan technique at room temperature. Semi-empirical absorption corrections were applied using SADABS. All structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL. Hydrogen atoms were added geometrically and refined with riding model position parameters and fixed isotropic thermal parameters. The crystallographic data and selected bond lengths and angles for **I–III** are listed in Tables 1, 2, respectively.

Supplementary material for structures has been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1555557 (**I**), 1555555 (**II**), 1555556 (**III**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

By using benzotriazole-5-carboxylate and mononuclear macrocyclic oxamide complex NiL as coligands to react with $Ln(NO_3)_3 \cdot 6H_2O$ (Ln = Sm (**I**); Pr (**II**); Eu (**III**), the tetranuclear complexes $[Ln(NiL)_3(Btca)(NO_3)] \cdot xH_2O$ (**I–III**) were obtained in the same mixed-solvent systems, pH, times and temperature under solvothermal conditions. All complexes are stable under the ambient conditions and insoluble in common solvents such as water, alcohol, and acetonitrile. The elemental analyses of **I–III** are consistent with the results of single-crystal X-ray diffraction analyses.

Complexes **I–III** are all constructed from tetranuclear $[Ln(NiL)_3(Btca)(NO_3)]$ unit (Ln = Sm(III) (**I**), Pr(III) (**II**), Eu(III) (**III**), which is connected with macrocyclic oxamide NiL, $Btca^{2-}$ and nitrate ion, but for **II** and **III**, the locations of $Btca^{2-}$ and nitrate ion are disorder. As shown in Fig. 1, all of the nickel ions are four-coordinated by four nitrogen atoms from the macrocyclic oxamide group and the coordination geometry of Ni^{2+} ion is a distorted square plane. The center Ln^{3+} ion is coordinated by ten oxygen atoms from three macrocyclic oxamide NiL, one $Btca^{2-}$ and one NO_3^-, and the coordination geometry of Ln^{3+} ion is a distorted bicapped square antiprism. The Ln–O distances are in the range of 2.420(6)–2.766(7) for **I**, 2.447(9)–2.720(13) for **II** and 2.38(2)–2.81(2) Å for **III**, while the OLnO bond angles are in the range of 48.06(16)°– 159.3(2)° for **I**, 49.4(3)°–164.9(9)° for **II** and 48.7(3)°–165.0(11)° for **III**. Three Ni^{2+} and one Ln^{3+} ions are interlinked through the macrocyclic oxamide ligand to form tetranuclear Ni_3Ln unit with Ni···Ln average separations 5.7614 for **I**, 5.8124 for **II** and 5.7488 Å for **III**. As depicted in Fig. 2, the $[Ni_3Ln]$ units are linked together with C–H···O and/or C–H···N intermolecular hydrogen bonding to form three-dimensional superamolecular framework. The data of hydrogen bonds of complexes **I–III** are listed in Table 3.

For complexes **I–III**, the IR spectra show strong peaks in the region 1626–1637 cm^{-1} and 1607–1617 cm^{-1}, which are assigned to the ν(C=O) vibrations of carboxyl and oxamide groups, respectively [18]. The absorptions around 1690 cm^{-1} were not found, indicating complete deprotonation of the carboxyl groups of benzotriazole-5-carboxylate. The IR

Table 1. Crystallographic data and refinement parameters for structures **I**–**III**

Parameter	Value		
	I	**II**	**III**
Fw	1573.71	1555.26	1566.31
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2/c$	$C2/c$
a, Å	11.3361(6)	21.2229(17)	21.176(8)
b, Å	26.8632(14)	26.834(2)	27.086(10)
c, Å	21.1844(11)	11.3472(9)	11.408(6)
β, deg	102.5580(10)	101.626(2)	103.255(15)
V, Å^3	6296.8(6)	6329.6(9)	6369(5)
Z	4	4	4
ρ_{calc}, mg/m^3	1.660	1.632	1.633
Crystal size, mm	0.220 × 0.210 × 0.180	0.220 × 0.210 × 0.180	0.220 × 0.210 × 0.180
T, K	296(2)	296(2)	296(2)
Goodness-F^2	1.089	1.038	1.046
Reflections collected/ unique	40826/13045	23641/7893	20511/6626
R_{int}	0.0523	0.0402	0.0621
R_1, wR_2 ($I > 2\sigma(I)$)*	0.0747, 0.2228	0.0570, 0.1652	0.0622, 0.1706
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	2.407/–1.719	1.297/–1.202	1.276/–0.693

* $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR^2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o)^2]\}^{1/2}$.

spectra exhibit strong absorption bands in the region 1554–1566 cm^{-1} due to the ν(C=N) vibrations [18]. The bands around 3400 cm^{-1} are characteristic of the hydroxyl from H_2O.

In order to study the effects of benzotriazole-5-carboxylate and mononuclear macrocyclic oxamide complex NiL on the fluorescence of rare earth ions, the solid-state fluorescence spectra of the complexes **I** and **II** and $Ln(NO_3)_3 \cdot 6H_2O$ (Ln = Sm; Pr) were measured using the excitation wavelength of 280 nm for **I** and 298 nm for **II** under room temperature. The fluorescence spectra of the complex **I** and $Sm(NO_3)_3 \cdot 6H_2O$ were given in Fig. 3. The main emission bands for the $Sm(NO_3)_3 \cdot 6H_2O$ are at 550, 595, 616 and 662 nm, and these bands may be attributed to the $^2G_{5/2} \rightarrow {}^6H_{5/2}$, $^2G_{5/2} \rightarrow {}^6H_{7/2}$, $^2G_{5/2} \rightarrow {}^6H_{9/2}$ and $^2G_{5/2} \rightarrow {}^6H_{11/2}$ transitions of the Sm^{3+} ion, respectively. Compared with the emission spectra of the $Sm(NO_3)_3 \cdot 6H_2O$, these fluorescence intensity at 550, 595 and 616 nm decrease or disappear, while the fluorescence intensity at 662 nm increase in the complex **I**. The fluorescence spectra of the complex **II** and $Pr(NO_3)_3 \cdot 6H_2O$ were given in Fig. 4. $Pr(NO_3)_3 \cdot 6H_2O$ exhibits fluorescence bands at 504, 616 and 667 nm, which are attributable to $^3P_0 \rightarrow {}^3H_4$, $^3P_0 \rightarrow {}^3H_6$ and $^3P_0 \rightarrow {}^3F_2$ transitions of the Pr^{3+} ion, respectively. Compared with the emission spectra of the $Pr(NO_3)_3 \cdot 6H_2O$, these fluorescence intensity decrease. For complexes **I** and **II**, the fluorescence measurement proved that the phenomenon of fluorescence quenching happened, which maybe attribute to the energy transfer from the excited Sm(III) or Pr(III) to the Ni(II) center through

Table 2. Selected bond lengths (Å) and bond angles (deg) for I–**III***

Bond	*d*, Å	Bond	*d*, Å
I			
Sm(1)–O(5)	2.420(6)	Sm(1)–O(6)	2.484(5)
Sm(1)–O(1)	2.766(7)	Sm(1)–O(9)	2.534(6)
Sm(1)–O(4)	2.639(6)	Sm(1)–O(10)	2.551(6)
Ni(1)–N(1)	1.883(7)	Ni(2)–N(7)	1.873(8)
Ni(1)–N(2)	1.898(7)	Ni(2)–N(8)	1.902(8)
Ni(3)–N(10)	1.859(8)	Ni(3)–N(9)	1.903(7)
II			
Pr(1)–O(4)	2.447(9)	Pr(1)–O(3)	2.528(3)
Pr(1)–O(5)	2.720(13)	Pr(1)–O(2)	2.592(4)
Pr(1)–O(5')	2.63(2)	Pr(1)–O(4')	2.566(19)
Ni(1)–N(2)	1.875(6)	Ni(1)–N(4)	1.895(6)
Ni(2)–N(5)	1.884(5)	Ni(2)–N(6)	1.895(6)
III			
Eu(1)–O(5')	2.38(2)	Eu(1)–O(1)	2.426(4)
Eu(1)–O(2)	2.533(5)	Eu(1)–O(4')	2.66(3)
Eu(1)–O(4)	2.81(2)	Ni(1)–N(3)	1.858(9)
Ni(1)–N(1)	1.895(6)	Ni(2)–N(5)	1.887(6)
Ni(2)–N(6)	1.891(7)	Ni(2)–N(6)$^{\#1}$	1.892(7)
Angle	ω, deg	Angle	ω, deg
I			
O(2)Sm(1)O(1)	48.06(16)	O(7)Sm(1)O(8)	130.68(18)
O(8)Sm(1)O(2)	83.5(2)	O(5)Sm(1)O(6)	142.9(2)
O(4)Sm(1)O(1)	159.3(2)	O(11)Sm(1)O(9)	129.34(18)
N(3)Ni(1)N(2)	86.6(3)	N(4)Ni(2)N(2)	162.8(3)
N(5)Ni(2)N(8)	87.6(3)	N(6)Ni(2)N(8)	165.9(3)
N(12)Ni(3)N(9)	86.7(3)	N(10)Ni(3)N(12)	165.9(3)
II			
O(4')Pr(1)O(5')	49.4(3)	O(5')$^{\#1}$Pr(1)O(5')	164.9(9)
O(1)Pr(1)O(4')$^{\#1}$	85.7(6)	O(4')Pr(1)O(2)$^{\#1}$	141.8(6)
O(4')$^{\#1}$Pr(1)O(5')	116.6(8)	O(4)Pr(1)O(1)	74.8(2)
N(1)Ni(1)N(4)	87.1(2)	N(2)Ni(1)N(4)	165.9(2)
N(5)Ni(2)N(5)$^{\#1}$	87.0(3)	N(5)$^{\#1}$Ni(2)N(6)	162.7(2)
III			
O(4')Eu(1)O(4')$^{\#1}$	165.0(11)	O(1)Eu(1)O(4')$^{\#1}$	111.2(6)
O(5')$^{\#1}$Eu(1)O(2)$^{\#1}$	140.9(8)	O(5')Eu(1)O(1)	83.7(8)
O(5')$^{\#1}$Eu(1)O(2)	75.3(7)	O(5)Eu(1)O(4)	48.7(3)
N(4)Ni(1)N(1)	87.0(3)	N(3)Ni(1)N(4)	92.5(4)
N(5)Ni(2)N(5)$^{\#1}$	86.5(3)	N(5)$^{\#1}$Ni(2)N(6)	162.3(3)
N(6)Ni(2)N(6)$^{\#1}$	91.2(4)		

* Symmetry codes: $^{\#1}$ $-x + 1, y, -z + 3/2$ (**II**); $^{\#1}$ $-x + 1, y, -z + 1/2$ (**III**).

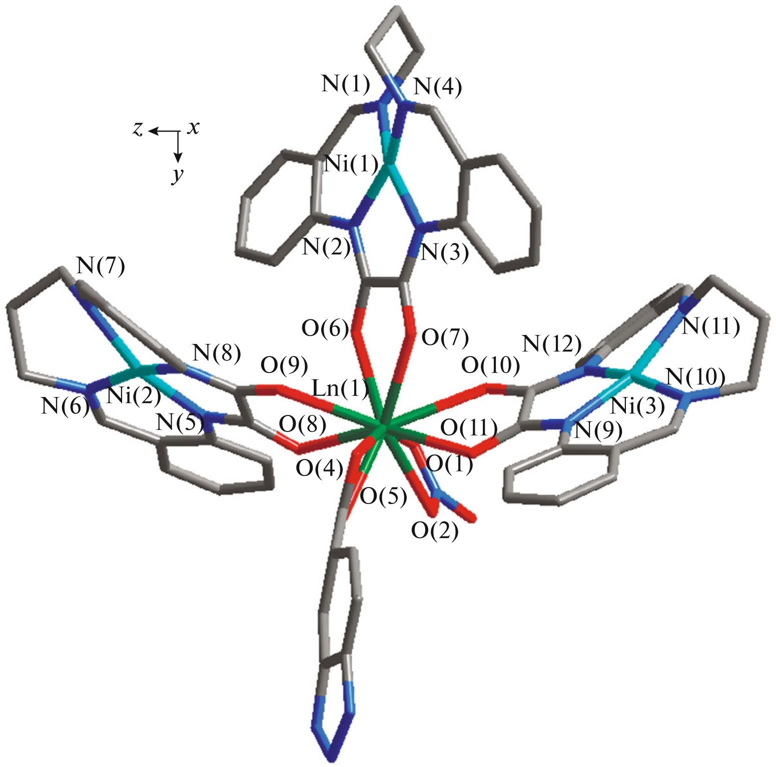

Fig. 1. Perspective view of Ni_3Ln (Ln = Sm, Pr, Eu) unit (hydrogen atoms, coordinated water were removed for clarity).

Table 3. Geometric parameters of hydrogen bonds for **I–III***

D–H···A	Distance, Å			Angle DHA, deg
	D–H	H···A	D···A	
		I		
C(6)–H(6)···O(3)[a]	0.93	2.40	3.259(15)	154
C(16)–H(16)···O(7)[b]	0.93	2.60	3.167(10)	120
C(17)–H(17*A*)···O(4)[b]	0.97	2.41	3.300(11)	152
C(19)–H(19*A*)···O(1)[c]	0.97	2.35	3.202(11)	146
C(35)–H(35)···O(12)[d]	0.93	2.43	3.355(17)	173
C(37)–H(37*A*)···O(13)[e]	0.97	2.49	3.29(2)	141
C(39)–H(39)···O(2)[f]	0.93	2.39	3.288(11)	162
C(54)–H(54)···O(13)[b]	0.93	2.50	3.391(19)	159
C(58)–H(58)···O(5)[g]	0.93	2.32	3.232(11)	168
		II		
C(16)–H(16)···O(4)[h]	0.93	2.35	3.266(9)	168
C(18)–H(18*B*)···O(6)[h]	0.97	2.70	3.57(2)	150
C(20)–H(20)···O(6)[i]	0.93	2.49	3.393(17)	163
C(35)–H(35*B*)···O(5)[j]	0.97	2.42	3.280(10)	148
O(6)–H(6*A*)···N(8)[k]	0.85	2.15	2.96(2)	157
		III		
C(9)–H(9)···O(5)[g]	0.93	2.34	3.252(15)	169
C(11)–H(11*B*)···N(7)[l]	0.97	2.68	3.65(6)	173
C(13)–H(13)···O(6)[d]	0.93	2.52	3.427(17)	165
C(29)–H(29*B*)···O(4)[m]	0.97	2.42	3.276(15)	147

* Symmetry codes: [a] $x - 1, y, z$; [b] $-x + 1, -y, -z + 1$; [c] $-x + 2, -y, -z + 1$; [d] $x, y - 1, z$; [e] $x + 1, y, z$; [f] $x + 1/2, -y + 1/2, z + 1/2$; [g] $x - 1/2, -y + 1/2, z - 1/2$; [h] $-x + 1/2, -y + 1/2, -z + 1$; [i] $-x + 1/2, y - 1/2, -z + 3/2$; [j] $x, -y, z - 1/2$; [k] $x, -y + 1, z - 1/2$; [l] $-x + 1/2, -y + 1/2, -z$; [m] $-x + 1, -y, -z$.

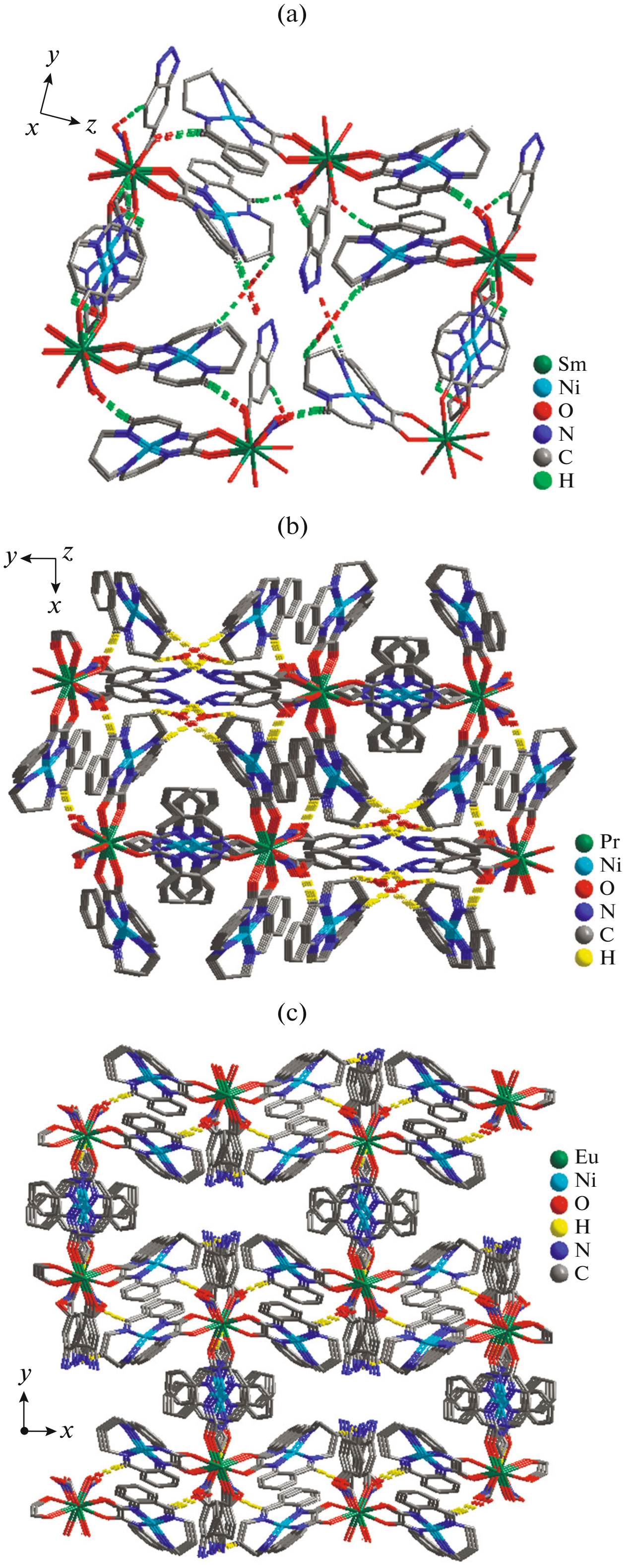

Fig. 2. View of the supermolecule framework through hydrogen bond interactions in **I** (a), **II** (b), **III** (c).

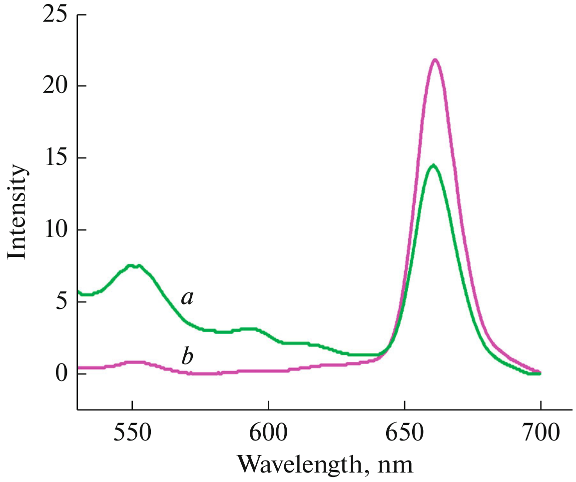

Fig. 3. The fluorescence spectra of $Sm(NO_3)_3 \cdot 6H_2O$ (*a*) and complex **I** (*b*) at $\lambda_{ex} = 280$ nm.

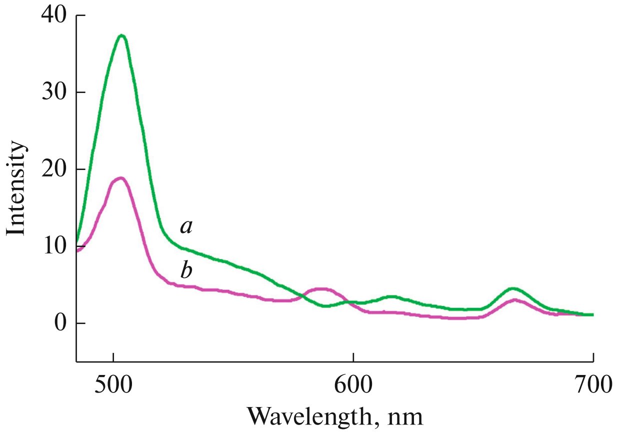

Fig. 4. The fluorescence spectra of $Pr(NO_3)_3 \cdot 6H_2O$ (*a*) and complex **II** (*b*) at $\lambda_{ex} = 298$ nm.

the oxamidic oxygen bridges [13, 15], while the fluorescence enhancement maybe attribute to the energy transfer from the π* to the Ln(III) center through the coordination interactions.

Thus, using benzotriazole-5-carboxylate and mononuclear macrocyclic oxamide complex NiL as co-ligand, we obtained tetranuclear complexes $[Ln(NiL)_3(Btca)(NO_3)] \cdot xH_2O$ (**I**–**III**), which were characterized by single crystal X-ray diffraction, elemental analysis and IR spectroscopic analysis. The hydrogen bonds play an important role in the formation of three-dimensional architectures. The fluorescence properties of the complexes **I** and **II** were also studied.

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