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Crystal Structures of Some Lanthanide(III) Complexes with Acylhydrazone and Their Coordination Chemistry[1]

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Abstract—Three new lanthanide(III) complexes with N-(2-propionic acid)–salicyloylhydrazone (H_2L, $C_{10}H_{10}N_2O_4$) ligand $[La(HL)_2(NO_3)(H_2O)_2]_3 \cdot 4H_2O$ (**I**), $[Gd(HL)_3] \cdot 2(C_2H_5)_3N$ (**II**) and $[Er(L)(HL)(H_2O)_2] \cdot 2H_2O$ (**III**) has been synthesized and characterized by elemental analyses, IR, UV, and molar conductivity. The crystal structures of three complexes have been determined by X-ray single-crystal diffractometer. In complex **I**, the La^{3+} ion is ten-coordinated by two tridentate ligands, one bidentate nitrate, and two water molecules. In complex **II**, the Gd^{3+} ion has a coordination number of nine by three tridentate ligands. In complex **III**, the Er^{3+} ion is eight-coordinated by two tridentate ligands and two water molecules. In all structures, tridentate ligands are coordinated by carboxyl O and acyl O atoms and azomethine N atom to form two stable five-membered rings sharing one side in the keto mode as indicated by the results of crystal structures and infrared spectral analysis.

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INTRODUCTION

Development of polydentate ligands capable of forming stable lanthanide(III) complexes would not only allow further study of the coordination properties of the rare-earth metal ions, but also enable chemists to exploit certain important emerging properties of these complexes [1].

The acylhydrazone Schiff base bearing nitrogen and oxygen donors, which exhibit both hard and soft base character, would form more stable complexes than the polyoxa or polyaza ligands with La^{3+} cations [2]. The ion size and the encalsulated *f*-orbital of La^{3+} ions result in their coordination properties, being quite different from those the transition mental ions. The size of the La^{3+} cations decreases dramatically along the lanthanide series and the acid character and coordination numbers also change accordingly. The acylhydrazone ligand N-(2-propionic acid)-salicyloyl hydrazone (**H_2L**) that contains nitrogen and oxygen donor atoms has three kinds of coordination modes (keto form, dehydrogenation conjugation, and enol form) and valence existence is multiple [3–5]; therefore, the ligand can form stable lanthanide(III) complexes with unusual structure features.

To our knowledge, few papers concerning binary lanthanide(III) crystal structures of such kind of ligands have been reported [6]. To better understand the coordination chemistry and properties of such complexes, we synthesized a series of stable complexes with mixed N_mO_n donor atoms of the acylhydrazone ligand H_2L and investigated the change of the complex structures with a decrease in the cation size. We report herein the synthesis, crystal structure, and coordination chemistry of three lanthanide(III) complexes $[La(HL)_2(H_2O)_2(NO_3)]_3 \cdot 4H_2O$ (**I**), $[Gd(HL)_3] \cdot 2(C_2H_5)_3N$ (**II**), $[Er(HL)(L)(H_2O)_2] \cdot 2H_2O$ (**III**). The results of the crystal structures and infrared spectral data make it clear that the ligand acts as a tridenate mixed-valence ligand with keto form coordination and the structures of complexes change with the cation size.

EXPERIMENTAL

All chemicals and solvents were of reagent grade and used without further purification. The synthesis of the ligand has been reported [3]. Hydrated Ln(III) nitrate salts were prepared by neutralization with the corresponding sesquioxide Ln_2O_3 (99.9%). IR spectra were recorded on EQUINOX55 spectrophotometer with KBr pellets in the 400–4000 cm^{-1} region. Elemental analyses of C, H, and N were performed by the a Perkin Elmer model 2400 elemental analyzer. Molar conductance measurement was made using a DDS-11A conductivity meter. The X-ray data for the crystal were collected on a Bruker Smart-1000 CCD X-ray single crystal diffractometer. Ultraviolet spectra were recorded on a Lambda 40 P UV-Vis spectrophotometer.

[1] The article is published in the original.

Syntheses of complexes I–III. Ligand H_2L (0.888 g, 4 mmol) was added to water (40 ml), the pH of which was adjusted to 5–6 by the addition of an base solution (NaOH or triethylamine); the solution turned light yellow. Then a solution of $Ln(NO_3)_3 \cdot nH_2O$ (Ln=La, Gd, Er) (2 mmol) in ethanol (20 ml) was added dropwise to the system. After stirring at 70°C for 2 h, a yellow precipitate was isolated by filtration and washed with ethanol and water. The resulting solution was allowed to evaporate slowly at room temperature, and yellow single crystals suitable for X-ray analysis were obtained.

For $C_{42}H_{57}GdN_8O_{12}$ (**II**)

anal. calcd, %:	Gd, 15.37;	C, 49.30;	H, 5.61;	N, 10.95.
Found, %:	Gd, 15.62;	C, 49.03;	H, 5.42;	N, 11.05.

For $C_{20}H_{25}ErN_4O_{12}$ (**III**)

anal. calcd, %:	Er 24.43;	C 35.34;	H 3.71;	N 8.25.
Found, %:	Er 24.36;	C 35.43;	H 3.58;	N 8.54.

Single crystal X-ray diffraction measurements of all the complexes were carried out with a Bruker Smart 1000 CCD X-ray diffractometer. Intensities of reflections were measured at 298 K using graphite monochromatized MoK_α radiation (λ = 0.71073 Å) in the ω scan mode. Empirical absorption correction was applied using the SABADS program. The crystal structures were solved by direct methods and Fourier difference syntheses. All the non-hydrogen atoms were refined anisotropically. Full-matrix least-squares refinement on F^2 was performed by the SHELXL-97 program package. The final R_1, wR_2, and other refinement parameters are presented in Table 1.

The atomic coordinates and other parameters of structure **I** have been deposited with the Cambridge Crystallographic Data Center (nos. 737908 (**I**), 737869 (**II**), 737870 (**III**); deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

All complexes are soluble in DMF and DMSO, a little soluble in water, ethanol, and methanol, insoluble in benzene, acetone, and diethyl ether. The molar conductivity of the complexes is around 21–26 $Ohm^{-1}\,cm^2\,mol^{-1}$ in DMF. This shows that all the complexes are non-electrolytes in DMF [7]. The elemental analyses of the complexes are consistent with the composition of them. The complexes are characterized by elemental analyses, molar conductance, X-ray crystallography, thermal analyses, and spectroscopy analyses.

The absorption band around 1756 cm^{-1} of free H_2L (ν(C = O) (COOH)) has been replaced by two new bands at 1616 and 1359 cm^{-1}, which were assigned to ν_s(COO) and ν_{as}(COO), respectively. The shifts suggest that the carboxylate groups of the ligand act as a monodentate ligand coordinating to the Ln^{3+} ion [8]. The ν(C=O) band of the free ligand at 1616 cm^{-1} is red-shift in the complexes, showing that the oxygen (C=O) bond to metal ion. The δ(NHN) band at 1532 cm^{-1} vibration of the free ligand still lie in the complexes (for **I** and **II**) and become weak in complex **III** indicating the active hydrogen of the –NHN= is lost partly in complex **III**. The ν(C=N) band appears at 1588 cm^{-1} in ligand, and has been red-shifted in complexes, confirming that the azomethine nitrogen has been coordinated to the Ln(III) [9]. A wide band between 3600 and 3500 cm^{-1} appears in complexes **I** and **III**, and this band could reasonably be attributable to the –OH group involved in intermolecular hydrogen bonding [10]. The in-plane and out-of-plane vibrations of water were observed in the spectrum of the complex at 774 and 581 cm^{-1}, which was associated with the coordinated water molecules in two complexes [11]. The bands in the range 1420–1460 cm^{-1} (at 1305 and 1032 cm^{-1}), clearly indentify the nitrates as co-coordinated species in the complex I [12]. This IR spectroscopic analysis is in agreement with the X-ray crystal structure of the complexes.

The UV spectra of the complexes were detected. The free ligand exhibits two absorption bands at 273 and 313 nm, which were shifted to 317–330 and 277–279 nm in the complexes, respectively. This shows that there is a large conjugate system formed by coordination with rare-earth ions. The complexes should be a chelate containing two five-membered rings shared with one side.

Selected bond lengths and bond angles of the crystals **I**–**III** are listed in Table 2. The molecule structure is shown in Fig. 1a, and the crystal packing diagram is depicted in Fig. 1b.

The crystal structure of complex **I** consists of three $[La(HL)_2(NO_3)(H_2O)_2]$ and four water molecules. The La^{3+} ion is ten-coordinated by two tridentate ligands, one bidentate nitrate, and two water molecules. The linkage of the HL ligand to the central ion is accomplished through the acyl oxygen, carboxyl oxygen, and imido nitrogen. Thus, two five-membered chelate rings shared the same edge are formed. The coordination polyhedron of La can be described as a distorted bicapped square antiprism. From the perspective view of the complex shown in Fig. 1, the atoms of each HL^- are almost located on the same plane. The two planar angles are 50°. By comparison between the ligand in the complex and the free ligand it can be noticed that the planarity of the whole molecule reduced (the dihedral angle between phenyl and the rest of ligand increases from 3.3° to 12.0°) caused by chelation and hydrogen bond strains after coordination. The mean bond length of La–O is 2.587 Å, and that of La–N is 2.722 Å. Due to the oxophilic character of lanthanide, the bond length of La–O is shorter than that of La–N. Comparing the distances C–O (1.43 Å) and C=O (1.22 Å),

Table 1. Crystallographic data and structure refinement summary for complexes **I–III**

Parameter	Value		
	I	**II**	**III**
Formula weight	2110.02	1023.21	680.70
Crystal system,	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
Unit cell dimensions:			
a, Å	14.5617(10)	11.9134(9)	12.346(3)
b, Å	14.6814(10)	17.2309(13)	14.311(4)
c, Å	21.3943(17)	23.2355(18)	17.449(4)
α, deg	94.840(5)°	90.0°	69.670(4)°
β, deg	102.690(5)°	103.2740(10)°	72.303(4)°
γ, deg	99.100(5)°	90.0°	85.290(4)°
V, Å^3	4372.1(5)	4642.3(6)	2753.2(12)
Z	6	4	6
ρ_{calcd}, g/cm^3	1.588	1.464	1.938
Absorption coefficient mm^{-1}	1.538	1.496	1.948
θ range for data collected, deg	1.46–25.10	1.49–25.04	1.53–25.10
Crystal size, mm	0.34 × 0.23 × 0.11	0.22 × 0.18 × 0.14	0.23 × 0.14 × 0.12
F(000)	2068	2100	1548
Limiting indices	$-17 \le h \le 1$ $-17 \le k \le 17$ $-25 \le l \le 25$	$-12 \le h \le 14$ $-20 \le k \le 20$ $-25 \le l \le 27$	$-14 \le h \le 10$ $-16 \le k \le 17$ $-20 \le l \le 20$
Reflections collected/unique	27006/13798	23082/8207	9633/6806
Completeness to θ = 25.10, %	88.4	100.0	98.3
Max and min transmission	0.8466 and 0.6237	0.8145 and 0.7392	0.7998 and 0.6628
Goodness-of-fit on F^2	1.010	0.998	1.083
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0735$, $wR_2 = 0.1894$,	$R_1 = 0.0557$, $wR_2 = 0.1313$,	$R_1 = 0.0230$, $wR_2 = 0.0652$
R indices (all data)	$R_1 = 0.1218$, $wR_2 = 0.2324$	$R_1 = 0.0996$, $wR_2 = 0.1583$	$R_1 = 0.0249$, $wR_2 = 0.0660$
Largest diff. peak/hole, e Å^{-3}	4424/–1504	1068/–959	731/–481

the bond lengths of O(22)–C(57), and O(18)–C(47) are 1.245 and 1.251 Å, respectively, it is seen that these bonds are double linkage and the ligand functions as a keto form.

There are abundant hydrogen bonds in the molecule. The strong hydrogen bonds have been formed between nitrogen atoms and oxygen atoms. The weak hydrogen bonds have been formed by O(8)···H–C(52) (angle 167°, O···C 3.314 Å); O(26)···H–C(55) (angle 134°, O···C 3.182 Å). The circularity was formed among complex molecules by those hydrogen bonds which not only promote the stability, but also form the 3D

Table 2. Selected bond lengths and bond angles for complex **I–III**

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
			I				
La(3)–O(19)	2.514(6)	La(3)–O(38)	2.627(9)	La(3)–O(39)	2.514(6)	La(3)–O(35)	2.656(8)
La(3)–O(22)	2.528(6)	La(3)–O(36)	2.672(7)	La(3)–O(23)	2.543(7)	La(3)–N(10)	2.712(7)
La(3)–O(18)	2.619(6)	La(3)–N(12)	2.728(7)				
			II				
Gd(1)–O(2)	2.366(5)	Gd(1)–N(6)	2.519(7)	Gd(1)–O(11)	2.382(5)	Gd(1)–N(2)	2.542(6)
Gd(1)–O(10)	2.397(5)	Gd(1)–N(4)	2.594(6)	Gd(1)–O(7)	2.397(5)	O(2)–C(7)	1.243(8)
Gd(1)–O(3)	2.453(5)	O(6)–C(17)	1.225(8)	Gd(1)–O(6)	2.460(4)	O(10)–C(27)	1.253(10)
			III				
Er(1)–O(8)	2.271(8)	Er(2)–O(17)	2.372(6)	Er(1)–O(6)	2.310(6)	Er(2)–N(7)	2.402(8)
Er(1)–O(3)	2.314(6)	Er(2)–N(6)	2.482(8)	Er(1)–O(7)	2.329(7)	N(6)–N(5)	1.383(10)
Er(1)–O(10)	2.355(7)	O(18)–C(33)	1.309(12)	Er(1)–O(2)	2.398(6)	O(14)–C(28)	1.248(11)
Er(1)–N(3)	2.429(7)	O(12)–C(27)	1.271(11)	Er(1)–N(2)	2.472(7)	O(17)–C(31)	1.214(12)
Er(2)–O(13)	2.287(7)	O(15)–C(38)	1.265(13)	Er(2)–O(20)	2.299(7)	N(7)–C(39)	1.279(13)
Er(2)–O(12)	2.302(6)	N(7)–N(8)	1.380(11)	Er(2)–O(15)	2.315(7)	N(5)–C(31)	1.368(12)
Er(2)–O(19)	2.321(7)	O(13)–C(28)	1.234(13)	N(6)–C(29)	1.249(12)		
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
			I				
O(22)La(3)O(35)	77.7(2)	O(39)La(3)O(38)	66.8(3)	O(23)La(3)O(35)	78.7(2)	O(22)La(3)O(38)	75.4(3)
O(18)La(3)O(35)	65.4(2)	O(38)La(3)O(35)	139.4(3)	O(23)La(3)O(28)	141.2(3)	O(19)La(3)O(36)	83.3(2)
O(19)La(3)O(39)	77.5(2)	O(39)La(3)O(36)	149.1(2)	O(19)La(3)O(22)	152.3(3)	O(22)La(3)O(36)	123.3(2)
O(39)La(3)O(22)	80.9(2)	O(23)La(3)O(36)	72.7(2)	O(19)La(3)O(23)	74.8(2)	O(18)La(3)O(36)	72.4(2)
O(39)La(3)O(23)	79.0(2)	O(38)La(3)O(36)	133.4(2)	O(22)La(3)O(23)	117.7(2)	O(35)La(3)O(36)	48.2(2)
O(19)La(3)O(18)	117.12(19)	O(19)La(3)N(10)	59.0(2)	O(39)La(3)O(19)	138.2(2)	O(39)La(3)N(10)	121.0(2)
O(22)La(3)O(18)	70.1(2)	O(18)La(3)O(38)	77.0(3)	O(23)La(3)O(18)	141.1(2)	O(19)La(3)O(35)	129.9(2)
O(19)La(3)O(38)	80.3(3)	O(39)La(3)O(35)	137.1(2)				
			II				
O(7)Gd(1)O(6)	123.10(16)	O(3)Gd(1)N(6)	139.11(18)	O(3)Gd(1)O(6)	77.63(16)	O(6)Gd(1)N(6)	75.12(17)
O(2)Gd(1)N(6)	74.56(17)	O(2)Gd(1)N(2)	63.23(18)	O(11)Gd(1)N(6)	63.91(19)	O(11)Gd(1)N(2)	76.29(18)
O(10)Gd(1)N(6)	62.4(2)	O(10)Gd(1)N(2)	139.86(18)	O(7)Gd(1)N(6)	135.17(19)	O(7)Gd(1)N(2)	75.04(18)
O(2)Gd(1)O(11)	86.40(18)	O(3)Gd(1)N(2)	63.04(18)	O(2)Gd(1)O(10)	83.65(16)	O(6)Gd(1)N(2)	135.77(18)
O(11)Gd(1)O(10)	126.11(19)	N(6)Gd(1)N(2)	122.9(2)	O(2)Gd(1)O(7)	81.12(17)	O(2)Gd(1)N(4)	136.06(18)
O(11)Gd(1)O(7)	151.33(17)	O(11)Gd(1)N(4)	137.26(18)	O(10)Gd(1)O(7)	78.14(18)	O(10)Gd(1)N(4)	67.22(17)
O(2)Gd(1)O(3)	126.27(16)	O(7)Gd(1)N(4)	61.77(16)	O(11)Gd(1)O(3)	81.30(18)	O(3)Gd(1)N(4)	75.99(16)
O(10)Gd(1)O(3)	143.20(18)	O(6)Gd(1)N(4)	61.48(17)	O(7)Gd(1)O(3)	85.46(17)	N(6)Gd(1)N(4)	115.15(18)
O(2)Gd(1)O(6)	149.63(17)	N(2)Gd(1)N(4)	121.88(18)	O(11)Gd(1)O(6)	78.64(17)	O(10)Gd(1)O(6)	84.12(16)
			III				
O(8)Er(1)O(6)	82.5(3)	O(8)Er(1)N(3)	81.0(3)	O(8)Er(1)O(3)	90.3(3)	O(6)Er(1)N(3)	64.5(2)
O(6)Er(1)O(3)	130.2(2)	O(3)Er(1)N(3)	65.6(2)	O(8)Er(1)O(7)	93.5(3)	O(7)Er(1)N(3)	139.4(2)
O(6)Er(1)O(7)	74.9(2)	O(10)Er(1)N(3)	83.6(3)	O(3)Er(1)O(7)	154.9(2)	O(2)Er(1)N(3)	136.2(2)
O(8)Er(1)O(10)	159.4(2)	O(8)Er(1)N(2)	64.7(2)	O(6)Er(1)O(10)	78.6(3)	O(6)Er(1)N(2)	133.9(3)
O(3)Er(1)O(10)	95.6(3)	O(3)Er(1)N(2)	83.6(2)	O(7)Er(1)O(10)	89.4(3)	O(7)Er(1)N(2)	75.7(3)
O(8)Er(1)O(2)	128.6(2)	O(10)Er(1)N(2)	135.5(3)	O(6)Er(1)O(2)	139.2(2)	O(2)Er(1)N(2)	64.1(2)
O(3)Er(1)O(2)	80.9(2)	N(3)Er(1)N(2)	133.6(3)	O(7)Er(1)O(2)	77.3(2)	O(10)Er(1)O(2)	71.9(2)

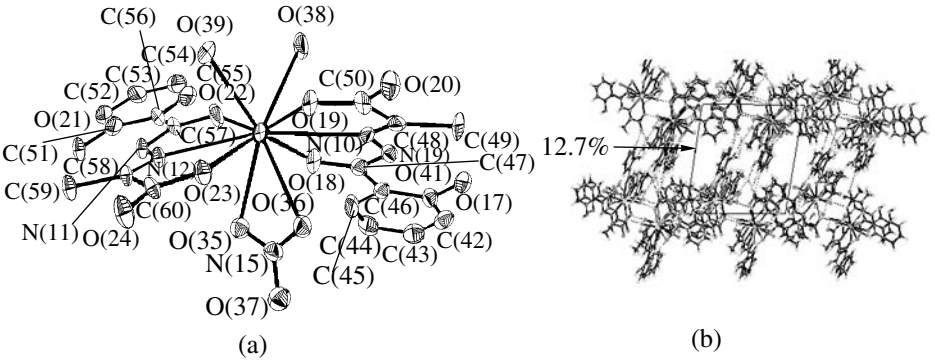

Fig. 1. Perspective view of coordination for complex **I** (a) and packing diagram (b).

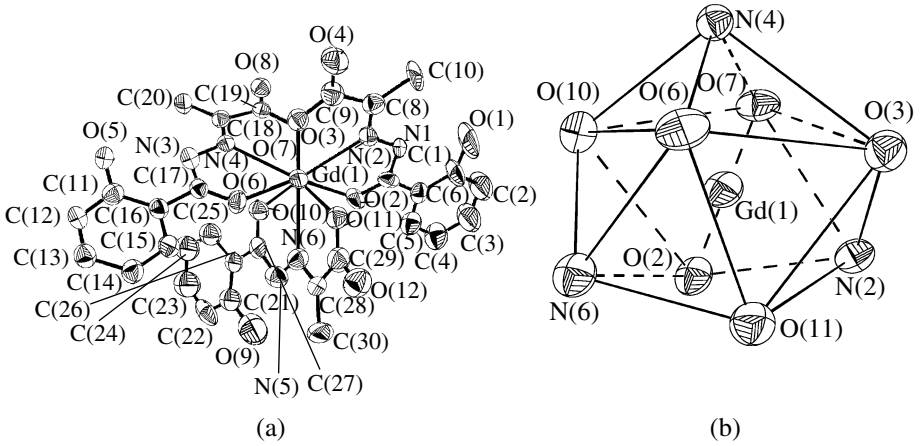

Fig. 2. Perspective view of coordination for complex **II** (a), and the coordination polyhedron (b).

supramolecule network in space. A diagram showing this network is displayed in Fig. 1b. As the result, cavities about the 12.7% occupancy were calculated by PLATON [13].

The molecule structure **II** is shown in Fig. 2a, and the coordination polyhedron around the cental ion is presentel in Fig. 2b.

In this complex, the Gd^{3+} ion has a coordination number of nine binding the acyl oxygen, carboxyl oxygen and imido nitrogen of three tridentate ligands. Thus, three sets of three coplanar five-membered chelate rings are formed. The coordination polyhedron of the Gd^{3+} ion can be described as a distorted monocapped square antiprism. The atoms O(6), O(3), O(7), O(10) and N(2), O(2), O(11), N(6) form lower and upper square planes, respectively, the angle between two planes is 0.6°, and the capping atom is N(4) for Gd^{3+} ion. Non-coordinated two triethylamine molecules are found in the crystal lattice. The mean bond length of Gd–O is 2.409 Å, and that of Gd–N is 2.552 Å. The bond lengths of acyl group O(2)–C(7), O(6)–C(17), and O(10)–C(27) are 1.243, 1.225, and 1.253 Å in the complex, respectively, indicate that these bonds are double linkage and the ligand functions as a keto form. The intramolecular hydrogen bonds have been formed between the nitrogen atom of amido and the oxygen atom of the phenolic hydroxyl. The two intermodular hydrogen bonds have been formed by O(3)···H–O(5) (O···O distance 2.627 Å, angle 173°) from two adjacent complexes, which make the dimer in space. The hydrogen bonds have been formed between nitrogens from triethylamine and carboxylic oxygen.

The molecular structure is shown in Fig. 3a, and the coordination polyhedron around central ion is shown in Fig. 3b.

The X-ray study revealed that crystal **III** was in the triclinic system with the space group $P\bar{1}$. Each unit cell contains two complexes and two crystal lattice water molecules. The Er^{3+} ion is eight-coordinated by two tridentate ligands and two water molecules. The linkage of the H_2L and HL ligand to the metal ion is accomplished through the acyl oxygen, carboxyl oxygen, and

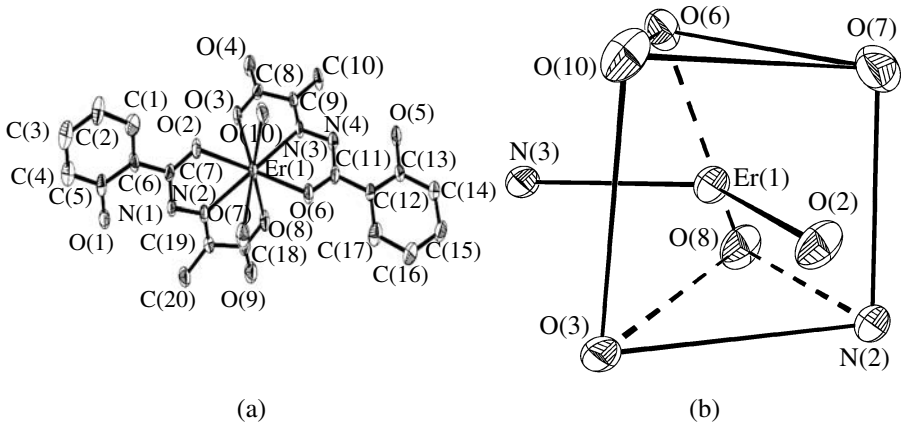

Fig. 3. Perspective view of coordination for complex **III** (a) and the coordination polyhedron (b).

imido nitrogen. Thus, two five-membered chelate rings shared the same edge are formed. The coordination polyhedron of Er^{3+} ion can be described as a distorted bicapped trigonal prism configuration. The atoms O(10), O(6), O(7) and N(2), O(8), O(3) form lower and upper trigonal planes, respectively, the angle between two planes is 1.3°, the capping atoms are N(3) and O(2) in two sides, one is O(10)–O(6)–O(8)–O(3), and an other is O(10)–O(3)–N(2)–O(7). The atoms of each N-(2-propionic acid)-salicyloyl hydrazone are almost located on the same plane. The two planes angle is 91.6°. The mean bond length of Er–O is 2.329 Å, and that of Er–N is 2.448 Å. The bond lengths of the acyl group O(6)–C(11) and O(2)–C(7) are 1.263 and 1.247 Å in the complex, respectively, indicate that these bonds are double linkage and the ligand functions as a keto form.

In the same environment, the bond lengths N(4)–C(1) (1.344 Å), N(4)–N(3) (1.379 Å) are longer than N(1)–C(7) (1.353 Å), N(1)–N(2) (1.398 Å), showing a pair electrons on N(4) are distributing on the N(3)–N(4)–C(1). The bond intensity of N(3)–N(4)–C(1) is increased because of loss of hydrogen connected with N(4), which agreed with what was described in IR. So, N-(2-propionic acid)-salicyloyl hydrazone was coordinated with Er^{3+} ion by negative univalent (H_2L) and bivalent (HL) in this complex.

Generally, for a series of analogous complexes of lanthanide ions, as the size of the lanthanide ion decreases, the repulsion between ligands in the coordination sphere increases until the crystal structure becomes unstable [14]. At this point, comparing complexes **I**, $[Pr_2(H_2L)_2(HL)_2(H_2O)_4] \cdot 3H_2O \cdot C_6H_6$ [6], **II** and **III**, we can see that as the ionic radius of the Ln^{3+} decreases, the coordination number of the Ln^{3+} ions decreases and the structure changes. The mean lengths of Ln(III)–O and Ln(III)–N are shortened. The relationships between the structure and coordination number and bond distances of four complexes are shown in Table 3.

In all complexes, the ligand H_2L is anionic, tridentate, and in keto form. The C=O bond distances of amide moieties for the complexes are 1.225–1.263 Å, which is longer than that of typical C=O, but it is normal for coordinated C=O, suggesting that the amide oxygen atom coordinates to the metal in the keto form of the ligand. This is consistent with the results of IR spectra.

Table 3. Comparison of selective structural data for some Ln^{3+} complexes based on N-(2-propionic acid)-salicyloyl hydrazone

Complex	Coordination number	Ln–O, Å	Ln–N, Å	Reference
$[La(HL)_2(NO_3)(H_2O)_2]_3 \cdot 4H_2O$	10	2.587	2.722	This work
$[Pr_2(H_2L)_2(HL)_2(H_2O)_4] \cdot 3H_2O \cdot C_6H_6$	9	2.536	2.597	[6]
$[Gd(HL)_3] \cdot 2(NC_6H_{15})$	9	2.409	2.552	This work
$[Er(L)(HL)(H_2O)_2] \cdot 2H_2O$	8	2.329	2.448	This work

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