

Synthesis and Structures of Two Lanthanide Complexes Containing a Mixed Ligand System: $[\text{Ln}(\text{Phen})_2(\text{L})_3(\text{HL})]\cdot\text{H}_2\text{O}$ [$\text{Ln} = \text{La}, \text{Ce}$; $\text{Phen} = \text{Phenanthroline}$; $\text{HL} = \text{Salicylic Acid}$]

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The reaction of $\text{LnCl}_3\cdot 7\text{H}_2\text{O}$ [$\text{Ln} = \text{La}$ (**1**), Ce (**2**)] with salicylic acid (HL) and 1,10-phenanthroline (Phen) at 20 °C in H_2O /ethanol gave after work-up and recrystallization two novel lanthanide complexes with general formula $[\text{Ln}(\text{Phen})_2(\text{L})_3(\text{HL})]\cdot\text{H}_2\text{O}$. Compounds **1** and **2** were characterized by IR and UV-Vis spectroscopy, TGA, CHN as well as by X-ray analysis. According to these results, compounds **1** and **2** are isostructural and contain Ln^{3+} ions with coordination number nine. Complexes **1** and **2** consist of two Phen, one neutral HL and three L anions (two L anions act as monodentate ligands and the third one is chelating to Ln^{3+}). Thermal decomposition led to primary loss of the Phen molecules. Then HL molecules and finally L moieties left the material to give Ln_2O_3 .

Key Words : Lanthanide, Salicylate complexes, Thermal decomposition, Crystal structure

Introduction

A massive interest in Ln^{3+} complexes is registered in more recent times, which stems from their possible use in biomedical and telecommunication fields and for various photonic applications.¹⁻⁷ Many of the stable lanthanide complexes are synthesized from aromatic acid and nitrogen-containing ligands having certain conjugate system. They show interesting and various structures due to the different coordination modes of the carboxyl groups and have been widely applied as functional materials.⁸⁻¹⁵ 1,10-Phenanthroline (Phen) is a good nitrogen-containing ligand for lanthanide ions and can construct supramolecular structure *via* π - π aromatic interactions and the bulk of Phen can effectively prevent the formation of interpenetration. Because of the strong absorptions within a large wavelength range for its π - π^* transition, Phen was considered as an important “antenna”, from which the energy can be transferred to Ln^{3+} ions for intense emissions.¹⁶ Five rare earth complexes were identified as the general formula $\text{Ln}(\text{L})_3\cdot 2\text{H}_2\text{O}$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}$, L = salicylic acid).¹⁷ There were also a series of dinuclear complexes of L and Phen with different mol ratios of Eu^{3+} to Y^{3+} , which have been synthesized and characterized by UV, IR and fluorescence spectra.¹⁸ $\text{Ln}(\text{L})_3\cdot n\text{H}_2\text{O}$ is the general formula of some other complexes of rare earth metals with L synthesized and characterized with elemental analysis and thermal decomposition mechanism.¹⁹ $[\text{Dy}_3(\text{HL})_5(\text{L})_2(\text{Phen})_3]$ is the formula of an interesting trinuclear complex, which was synthesized under hydrothermal conditions and characterized by single-crystal crystallography.²⁰ Its crystal structure showed three different coordination types.²⁰ We were interested in studying some lanthanide complexes

with a mixed ligand system (Phen and HL) and see if just one type or both types of ligands coordinate to metal center. The coordination mode of HL to Ln^{3+} center (monodentate or chelating bidentate fashion) was also important to be determined. All these information including the mole ratio of ligands to complete the coordination sphere of Ln^{3+} would be found by X-Ray crystallographic methods. In our investigation, we have synthesized and characterized two new complexes with a general formula of $[\text{Ln}(\text{Phen})_2(\text{L})_3(\text{HL})]\cdot\text{H}_2\text{O}$ ($\text{Ln} = \text{La}^{3+}$ (**1**), $\text{Ln} = \text{Ce}^{3+}$ (**2**)). We have shown that HL reacts with LnCl_3 and CeCl_3 as monodentate and bidentate ligand at the same time in a mol ratio 4:1. In addition to HL, two Phen molecules are coordinated to Ln^{3+} . Both of the complexes have been characterized by IR spectroscopy, UV spectroscopy and single crystal structure determinations. The thermal-decomposition processes of the complexes were investigated by TGA technique.

Experimental

Materials and Methods. $\text{LaCl}_3\cdot 7\text{H}_2\text{O}$, $\text{CeCl}_3\cdot 7\text{H}_2\text{O}$, salicylic acid and 1,10-phenanthroline were acquired from commercial sources as analytical grade and used directly.

The IR spectra were recorded on a Bruker Vector22 (KBr pellets, 4000-400 cm^{-1}). UV spectra were depicted in a VARIAN-CARY 3 spectrometer. TGA experiments were conducted with a RHEOMETRIC SCIENTIFIC-STA 1500 thermogravimetric analyzer under the linear heating rate of 10 °C $\cdot\text{min}^{-1}$. The atmosphere was argon gas with a flow rate of 35 $\text{mL}\cdot\text{min}^{-1}$. CHN Analyses were carried out on an Elementar Analyzer VARIO EL III.

Crystal Structure Analysis of Compounds 1 and 2. The

selected crystals of **1** and **2**, covered with perfluorinated oil, were mounted on the tip of a glass capillary under a flow of cold gaseous nitrogen. The orientation matrix and preliminary unit cell dimensions were determined on a STOE IPDS II single crystal diffractometer with Mo K α radiation ($\lambda = 71.073$ pm). The intensities were corrected for Lorentz and polarization effects. In addition, the numerical absorption corrections were applied for Compounds **1** and **2**. The structures were solved by the direct methods (SHELXS-97²¹), and refined against F² by full-matrix least-squares using the program SHELXL-97.²² The hydrogen atoms were calculated in ideal positions (refinement with a common displacement parameter). The programs SHELXS-97,²¹ SHELXL-97²² and PLATON²³ were used.

Crystallographic Data Deposition. Crystallographic data for the structures reported here have been deposited with CCDC (Deposition No. CCDC-902475 (**1**) and -902476 (**2**)). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, E-mail: deposit@ccdc.cam.ac.uk

Preparation of Complexes 1 and 2, General Procedure. $\text{LnCl}_3 \cdot 7\text{H}_2\text{O}$ (0.05 mmol) was dissolved in distilled water. Both of the HL (0.028 g, 0.2 mmol) and Phen (0.018 g, 0.1 mmol) were dissolved in 96% ethanol, and NaOH solution ($c = 1$ mol/L) was used to adjust the pH of the solution within 6–7. The resulting solution of the ligands was then added dropwise into the aqueous solution of $\text{LnCl}_3 \cdot 7\text{H}_2\text{O}$. The reaction mixture was stirred about 8 h at room temperature. After filtration, the remaining solution was kept at room temperature. Colorless blocks (**1**) and Colorless plates (**2**) were crystallized after few days from the solution.

Complex 1 $[\text{La}(\text{Phen})_2(\text{L})_3(\text{HL})] \cdot \text{H}_2\text{O}$. Used La^{3+} salt amount: $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ (0.019 g, 0.05 mmol). Yield: 0.036 g (66.67%).

Elemental Analysis: $\text{C}_{52}\text{H}_{39}\text{LaN}_4\text{O}_{13}$ (1066.78) Calcd.: C, 58.49; H, 3.65; N, 5.25. Found: C, 58.45; H, 3.61; N, 5.27.

IR (KBr pellet, cm^{-1}): 3450 (b, $\nu(\text{OH})$), 1634 (s, $\nu(\text{C}=\text{O})$ (HL)), 1585 (s, $\nu_{\text{as}}(\text{COO}^-)(\text{L}^-)$), 1453 (m, $\nu(\text{C}=\text{N})$), 1376 (s, $\nu_{\text{s}}(\text{COO}^-)(\text{L}^-)$), 1255 (m, $\nu(\text{C}-\text{O})$, Phenolic), 1300 (w), 1085 (m), 844 (m), 772 (m, $\delta(\text{C}-\text{H})$), 723 (m), 668 (m), 569 (vw), 454 (vw), 432 (vw).

Complex 2 $[\text{Ce}(\text{Phen})_2(\text{L})_3(\text{HL})] \cdot \text{H}_2\text{O}$. Used Ce^{3+} salt amount: $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (0.019 g, 0.05 mmol). Yield: 0.041 g (75.93%).

Elemental Analysis: $\text{C}_{52}\text{H}_{39}\text{CeN}_4\text{O}_{13}$ (1067.99) Calcd.: C, 58.43; H, 3.65; N, 5.24. Found: C, 58.39; H, 3.62; N, 5.26.

IR (KBr pellet, cm^{-1}): 3450 (b, $\nu(\text{OH})$), 1634 (s, $\nu(\text{C}=\text{O})$ (HL)), 1590 (s, $\nu_{\text{as}}(\text{COO}^-)(\text{L}^-)$), 1464 (m, $\nu(\text{C}=\text{N})$), 1393 (s, $\nu_{\text{s}}(\text{COO}^-)(\text{L}^-)$), 1305 (m, $\nu(\text{C}-\text{O})$ Phenolic), 987 (w), 844 (m, $\delta(\text{C}-\text{H})$), 723 (m), 696 (m), 668 (m), 652 (m), 613 (m), 531 (m), 471 (w).

Results and Discussion

Syntheses and Characterization of 1 and 2. Treatment

of $\text{LnCl}_3 \cdot 7\text{H}_2\text{O}$ [$\text{Ln} = \text{La}$ (**1**), Ce (**2**)] with HL and Phen in $\text{H}_2\text{O}/\text{EtOH}$ at room temperature after adjusting the pH of the solution within 6–7 give the corresponding complexes **1** and **2**, which can be obtained by the reaction of the corresponding lanthanum salt, Phen and HL in the molar ratio 1:2:4. The synthesized compounds **1** and **2** are crystalline solids in form of colorless blocks and colorless plates respectively and are air-stable.

Infrared Spectra. In the IR spectra of complexes **1** and **2**, the strong absorptions around 3450 cm^{-1} are assigned to stretching vibration of OH, implying the presence of water molecules. The $\nu(\text{C}=\text{O})$ (1680 cm^{-1}) of the acidic group in the HL takes place red shift in the infrared spectra of the complexes **1** and **2** to 1634 cm^{-1} . The reason is the weakening of C=O bond as the result of coordination between the HL and Ln^{3+} . There are two characteristic bands around $1585\text{--}1590\text{ cm}^{-1}$ and $1376\text{--}1393\text{ cm}^{-1}$ attributed to asymmetric and symmetric vibrations of the carboxylate groups (COO^-) in carboxylate anions (L). These vibration bands indicate that oxygen atoms of the carboxylate groups have formed coordinative bonds with Ln^{3+} ions. The absorption band of $\nu(\text{C}=\text{N})$ (1561 cm^{-1}) in the spectrum of Phen exhibits a red shift in the IR spectra of the complexes **1** and **2** (1453 and 1464 cm^{-1} respectively) suggesting the coordination of the two nitrogen atoms of the Phen to Ln^{3+} ions.²⁴ Similarly such an absorption band ($\nu(\text{C}=\text{N})$) could be seen at 1623 cm^{-1} for azomethine, undergoes a red shift ($13\text{--}17\text{ cm}^{-1}$) on account of zwitterion formation.²⁵ IR spectra support the results of the single crystal X-ray analysis.

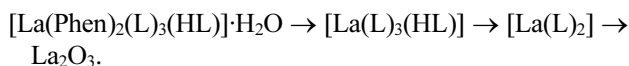
Ultraviolet Spectra. The ultraviolet spectra of the Phen, HL and complexes **1** and **2** were recorded in DMSO as solvent. The data are listed in Table 1. The maximum absorbance wave number (λ_{max}) of the HL is 237 nm. The absorption peaks of the complexes **1** and **2** are 265 nm and 266 nm respectively, this fact shows that the HL ligands are coordinated to the lanthanide ions (La^{3+} , Ce^{3+}) forming a π -conjugated system.²⁶ Moreover, the maximum absorption peak of Phen at 265 nm is similar to that of in the complexes **1** and **2**. It means that the formation of the coordination bonds between nitrogen atoms and lanthanide centers should have no much influence on the UV absorption of the Phen, which is reflected by the literature.²⁷ However, the enhanced absorbance of the complexes may be due to the increase of the chromophore, which suggested forming the new complexes.

Thermal Decomposition Processes. TGA curves of complexes **1** and **2** were recorded at a heating rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ under a dynamic argon atmosphere. The profiles of thermal decomposition processes of the two complexes are

Table 1. UV absorption of the ligands and complexes **1** and **2** ($\lambda_{\text{max}}/\text{nm}$)

Compound	λ_{max}
Phen	265
HL	237
1 (La^{3+})	265
2 (Ce^{3+})	266

similar. According to these TGA curves, Phen and HL in the two complexes should probably undergo three thermal decomposition stages. For the complex **1** $[\text{La}(\text{Phen})_2(\text{L})_3(\text{HL})] \cdot \text{H}_2\text{O}$, the first stage can be seen from 124 °C to 298 °C with a mass loss of around 35.5%, which indicates that, one molecule H_2O (theoretical mass loss of 1.68%) and two Phen molecules (theoretical mass loss of 16.88% for each Phen) decomposed together. The second and third stages took place in the temperature ranges of about 298–412 °C, 412–445 °C and the mass losses were 27% (probably HL+L) and 23.3% (probably 2L), corresponding to the loss of the remaining HL molecule and L ligands. The complex is finally degraded into Ln_2O_3 with a total mass loss of 84.1% (theoretical value 84.6%), verified for complex **1** by the similar powder patterns of the residue compound and the reported pattern for La_2O_3 . There is no change more till 900 °C. Based on the TGA analysis, the thermal decomposition of the complex **1** can be expressed as the following process:



Decomposition of the complex **2** can also be described similar to complex **1**.

$\text{Ln}-\text{N}$ bonds of the complexes were broken firstly in the TGA experiments, which may be explained by the weaker bond energy of $\text{Ln}-\text{N}$ comparing with $\text{Ln}-\text{O}$ because of the anionic nature of salicylate ligands. In this way, weaker coordination ability of the nitrogen atom with lanthanide center than that of the oxygen atom may be because of charge difference between ligands.

Crystal Structures. The complexes **1** and **2** were crystallized in form of colorless blocks and colorless plates respectively. Table 3 shows the crystallographic data. Selected bond lengths and angles are given in Table 4. Compounds **1** and **2** crystallize both in the monoclinic space group $\text{P}2_1/\text{c}$ and are isostructural. In both compounds, two crystallographic independent complex molecules are present. One of the two central Ln^{3+} ions is disordered in two positions (occupation parameters 0.5/0.5) together with a part of the L positions. Figure 1 and Figure 2 show the none-disordered molecules of **1** and **2**.

Four acid ligands are coordinated to Ln^{3+} through their oxygen atoms. Three acid molecules are deprotonated (L) but the last one is not deprotonated (HL). The coordination of two Phen ligands *via* their nitrogen atoms completes the coordination sphere of lanthanides of **9**, which is totally normal for lanthanide ions. One L ligand is chelating the metal ion (La1-O1: 262.8(5), La1-O2: 255.1(5); Ce1-O1: 260.6(4), Ce1-O2: 253.2(6) pm), while the other two L are monodentate ligands (La1-O4: 244.7(5), La1-O7: 247.4(5); Ce1-O4: 241.0(5), Ce1-O7: 247.6(5) pm). The HL molecules are also involved in the coordination spheres as monodentate ligands (La1-O10: 241.3(5); Ce1-O10: 238.5(5) pm). Together with the nitrogen atoms with long $\text{Ln}-\text{N}$ distances (272.3(8)–280.4(6) pm), the metal ions possess coordination number 9.

Comparable distances were observed in La and Ce complexes with two Phen ligands and coordination number 9.^{28–37}

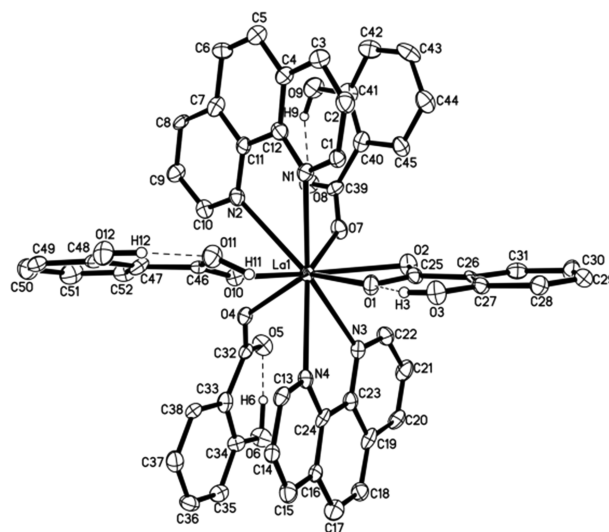


Figure 1. Molecular structure of **1** (thermal ellipsoids 30% due to clearance). Only one of the independent molecules is shown.

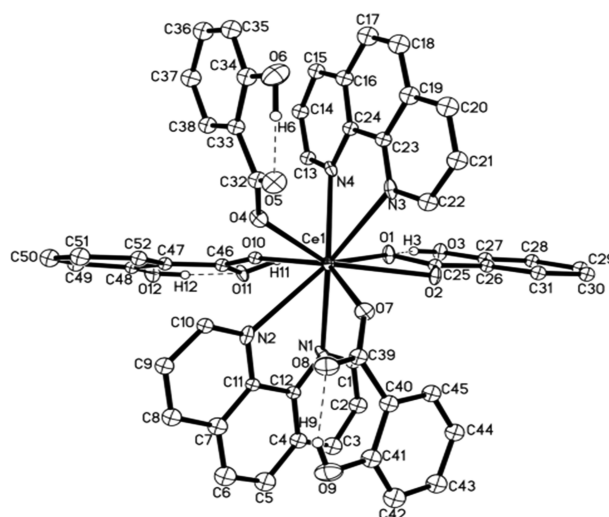


Figure 2. Molecular structure of **2** (thermal ellipsoids 30% due to clearance). Only one of the independent molecules is shown.

In a trinuclear example of Dy(III), three different types of coordination types were found.²⁰ The monodentate (A) and the chelating type (B) were realized in **1** and **2** (Fig. 3). Both of Complexes exhibit two crystallographic independent complex molecules. One of the metal atoms is disordered in two positions (occupancies 0.5:0.5). In addition two ligands L are disordered, too. Those two ligands follow the positions of the two metal atom positions. One of the L ligands binds according type A and the other one according type B or *vice*

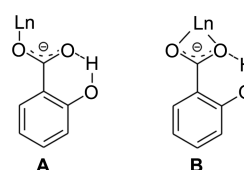


Figure 3. Coordination modes of salicylic acid.

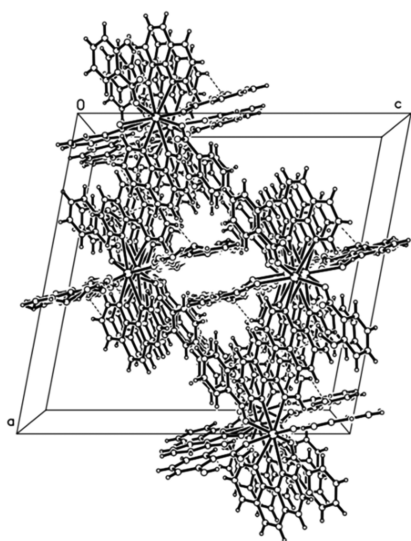


Figure 4. Packing of the molecules of 2.

versa causing the disorder problem. The refined models of Complexes 1 and 2 were better reflected in Complex 2. Therefore, the R values differ in the two structures (Table 2).

Strong intramolecular hydrogen bonds are present in the L ligands and the HL molecules (see Tab. 3). The intermolecular hydrogen bonds force the complex molecules in columns along [010] (Fig. 4).

π - π Interactions can be found in both of the complexes. In addition 348, 340 and 365 pm are the mean contact values for the sequences of $L \cdots \text{Phen} \cdots \text{Phen} \cdots L$ in Compounds 1 and 2.

In summary, Two novel lanthanide complexes with general

formula $[\text{Ln}(\text{Phen})_2(\text{L})_3(\text{HL})] \cdot \text{H}_2\text{O}$ ($\text{Ln} = \text{La}$ (1), Ce (2)), have been synthesized successfully. Complexes 1 and 2 show a similar thermal decomposition behavior demonstrating that they are isotypical, which fact was proved at the next step through the determined crystal structures. The thermal decomposition processes of the two complexes present multi-step processes related to the release of the ligand molecules, followed by oxidation. This processes led to primary loss of the Phen molecules. Then HL molecules and finally L moieties left the material to give Ln_2O_3 . The final residue for crystal 1 was found to be La_2O_3 .

As is well known, lanthanide ions possess high coordination numbers (more than 6). Especially, the ionic radii of light lanthanide ions (La-Gd) are larger than ionic radii of the heavy lanthanide ions (Tb-Lu) because of the lanthanide contraction phenomenon, so the coordination numbers of light lanthanide ions are usually bigger than those of heavy lanthanide ions. Lanthanide aromatic carboxylate complexes

Table 3. Bond lengths (pm) and Bond angles ($^\circ$) for Complexes 1 and 2

Chemical Bond	1 (La^{3+})	2 (Ce^{3+})
$\text{Ln1} - \text{O1}$	262.8(5)	260.6(6)
$\text{Ln1} - \text{O2}$	255.1(5)	253.2(4)
$\text{Ln1} - \text{O4}$	244.7(5)	241.0(5)
$\text{Ln1} - \text{O7}$	247.4(5)	247.6(6)
$\text{Ln1} - \text{O10}$	241.3(5)	238.5(5)
$\text{Ln1} - \text{N1}$	272.9(6)	272.3(8)
$\text{Ln1} - \text{N2}$	280.4(6)	274.5(8)
$\text{Ln1} - \text{N3}$	274.9(6)	274.1(8)
$\text{Ln1} - \text{N4}$	272.3(6)	269.8(8)
$\text{C25} - \text{O1}$	130.5(8)	132.8(8)
$\text{C25} - \text{O2}$	125.2(8)	124.1(8)
$\text{C27} - \text{O3}$	136.4(8)	136.3(8)
$\text{C32} - \text{O4}$	126.8(9)	125(1)
$\text{C32} - \text{O5}$	126.8(9)	128(1)
$\text{C34} - \text{O6}$	134.7(9)	137(1)
$\text{C39} - \text{O7}$	126.2(9)	125(1)
$\text{C39} - \text{O8}$	127.1(9)	128(1)
$\text{C41} - \text{O9}$	137(1)	136(1)
$\text{C46} - \text{O10}$	129.0(8)	133.9(9)
$\text{C46} - \text{O11}$	125.7(8)	126.5(9)
$\text{O11} - \text{H11}$	104	104.4(8)
$\text{C48} - \text{O12}$	134.3(8)	139.1(8)
$\text{X} - \text{H} \cdots \text{Y}$	$\text{X} \cdots \text{Y}$	$\text{X} \cdots \text{Y}$
$\text{O3} - \text{H3} \cdots \text{O1}$	259.2(7)	258.5(8)
$\text{O6} - \text{H6} \cdots \text{O5}$	255.6(9)	257(1)
$\text{O9} - \text{H9} \cdots \text{O8}$	269.9(9)	260(1)
$\text{O12} - \text{H12} \cdots \text{O11}$	253.6(7)	254.7(7)
$\text{O1} - \text{La1} - \text{O2}$	50.7(1)	51.5(2)
$\text{O1} - \text{La1} - \text{O4}$	145.4(2)	143.9(2)
$\text{O1} - \text{La1} - \text{O7}$	120.5(2)	121.8(2)
$\text{O1} - \text{La1} - \text{O10}$	82.1(2)	82.3(2)
$\text{O4} - \text{La1} - \text{O7}$	87.2(2)	87.3(2)
$\text{O4} - \text{La1} - \text{O10}$	84.9(2)	83.9(2)
$\text{O7} - \text{La1} - \text{O10}$	145.3(2)	144.8(2)

Table 2. Crystallographic data for 1 and 2

Compound	1	2
Empirical formula	$\text{C}_{52}\text{H}_{39}\text{LaN}_4\text{O}_{13}$	$\text{C}_{52}\text{H}_{39}\text{CeN}_4\text{O}_{13}$
Formula mass	1066.78	1067.99
Crystal system	monoclinic	monoclinic
Space group	$\text{P2}_1/\text{c}$	$\text{P2}_1/\text{c}$
a/pm	2159.2(1)	2158.1(1)
b/pm	1922.6(1)	1923.6(2)
c/pm	2204.4(1)	2207.4(1)
$\alpha/^\circ$	90	90
$\beta/^\circ$	100.80(1)	100.80(1)
$\gamma/^\circ$	90	90
V/pm^3	$8989.0(7) \cdot 10^6$	$9001(1) \cdot 10^6$
Z	8	8
$D_{\text{calc}}/\text{g} \cdot \text{cm}^{-3}$	1.577	1.576
T/K	100	100
$2\theta_{\text{max}}/^\circ$	52.02	51.86
Reflns collected	47140	48522
Unique reflns (R_{int})	17412 (0.0966)	17431 (0.1078)
R_1	0.0762	0.0484
wR_2 (all data)	0.2294 ^a	0.1161 ^b

^a $w = 1/[\sigma^2(F_o^2) + (0.1 \cdot P)^2]$; $P = [\max(F_o^2, 0) + 2 \cdot F_c^2]/3$. ^b $w = 1/[\sigma^2(F_o^2) + (0.04 \cdot P)^2]$.

have typically coordination number 8 and 9. According to crystal structure studies of complexes **1** and **2**, four acid ligands are coordinated to Ln^{3+} . Three acid molecules are deprotonated (L) but the last one is not deprotonated (HL). One L ligand is chelating the metal, while the other two L anions are monodentate. The HL molecules are involved in the coordination spheres as monodentate ligands. All these facts in addition to the coordination of two Phen ligands lead to coordination number 9.

Conclusion

Complexes $[\text{Ln}(\text{Phen})_2(\text{L})_3(\text{HL})]\cdot\text{H}_2\text{O}$ ($\text{Ln} = \text{La}$ (**1**), Ce (**2**)) can be obtained by the reaction of HL and Phen (after pH adjustment using 0.1 mol/L NaOH solution) with $\text{LnCl}_3\cdot 7\text{H}_2\text{O}$ and crystallized as colorless blocks and plates. According to the Crystal structures of complexes **1-2**, the composition of products is Ln (**1**) : HL (**4**) : Phen (**2**). HL and L are neutral and anionic ligands respectively. A neutral HL and two L anions act as monodentate ligands. However the third anionic L ligand in each structure is chelating to Ln^{3+} . The intermolecular hydrogen bonds force the complex molecules in columns along [010]. π - π -Interactions can be found in both complexes. In addition 348, 340 and 365 pm are the mean contact values for sequences of $\text{L}\cdots\text{Phen}\cdots\text{Phen}\cdots\text{L}$ in **1-2**.

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