

Synthesis and Solution Properties of La(III)-*N*-ethylmorpholine Complex

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The complex of the composition $\text{LaL}(\text{NO}_3)_3(\text{H}_2\text{O})_2$ is prepared by the reaction of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with *N*-ethylmorpholine in aqueous medium. The ligand is involved in the complex as a neutral species where the chelation occurs via the oxygen of the ligand moiety and the nitrate groups as bidentate ligand. The chemical structure of the studied complex is confirmed through IR, XRD, and thermal analysis data. The complexation equilibria of La(III) with *N*-ethylmorpholine is studied in aqueous medium at ionic strength $I = 0.1 \text{ mol} \cdot \text{dm}^{-3}$ KNO_3 and at 25, 35 and 45 °C, respectively. The thermodynamic parameters ΔG , ΔH and ΔS values were calculated to prove the association with the complex formation. It is clearly observed that the process is accompanied by absorption of heat, *i.e.* endothermic process, while the entropy does not change greatly attributed to the release of constant number of water molecules during chelate formation.

Key Words : La(III) complex, Ethylmorpholine complex, *N*-Ethylmorpholine, Ligand, Chelate formation

Introduction

The complexes of trivalent lanthanide ions are widely investigated due to their relevance to some important domains including lanthanide/actinide separation during nuclear fuel reprocessing, catalysis, and design of luminescent probes, NMR imaging and other industrial applications. The similarity in size of La(III) and Ca(II) has led to various lanthanides being substituted for Ca in biological systems with the physical properties of the lanthanide being used as a probe.¹⁻³ This flurry of activity has been a boon to those interested in studying lanthanide coordination chemistry. The aqueous solution of La(III) ions is dominated by their oxophilicity.^{4,5} Lanthanide ions and their complexes are known to be excellent catalysts for the hydrolysis of biozide-type phenylphosphate esters of DNA and of related oligonucleotides^{6,7} where the cleavage of nucleotides and of DNA or RNA by metal catalysts is an area of much current activity.⁸ Good and coworkers⁹ recommended a series of zwitterionic buffer compounds which are compatible with most media of physiological and biological importance. Some new zwitterionic buffer substances have been discovered.¹⁰

Potentiometric equilibrium measurements have been performed at 25 °C and ionic strength $I = 0.1 \text{ mol} \cdot \text{dm}^{-3}$ KNO_3 for the interaction of adenosine 5'-monophosphate, guanosine 5'-monophosphate, cytidine 5'-monophosphate, and La(III), Ce(III), Pr(III) and Eu(III) with the biologically important secondary ligand zwitterionic buffers MOPSO, MES, ACES and HEPES. Formation constants of the normal, protonated, monohydroxy, dihydroxy and dimeric ligand complexes have been calculated.¹¹ Potentiometric equilibrium measurements have been performed at 25 °C and ionic strength $I = 0.1 \text{ mol} \cdot \text{dm}^{-3}$ KNO_3 for the interaction of the dipeptides glycylglycine, glycylleucine, glycylphenylalanine, glycylhistidine and lanthanide metal ions Er(III),

Y(III) and Pr(III) with biologically important zwitterionic buffers HEPES, PIPES, EPPS, HEPPSO and POPSO. The formation of various 1 : 1 : 1 normal and protonated mixed ligand complex species was inferred from the potentiometric pH titration curves. The formation constants of the monohydroxy and Ln(III) + zwitterionic buffers were also calculated.¹²

Using different small additives of the synthesized complex under investigation may enhance the electrical, thermal and mechanical properties of poly(vinyl alcohol) samples.¹³ The interaction of the new promising buffer *N*-ethylmorpholine may be existed in most media of physiological and biological importance. The important role of the new buffer and lanthanide ions gives us the justification to study their interaction in solution as well as in solid state.

In the present paper, the complex $\text{LaL}(\text{NO}_3)_3(\text{H}_2\text{O})_2$ has been synthesized by the reaction of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with *N*-ethylmorpholine in aqueous medium. The chemical structure of the synthesized complex is confirmed through IR, XRD and thermal analysis data in this investigation. The complexation equilibria of La(III) with *N*-ethylmorpholine is also studied in aqueous medium at ionic strength $I = 0.1 \text{ mol} \cdot \text{dm}^{-3}$ KNO_3 at 25, 35 and 45 °C, respectively. The thermodynamic parameters such as ΔG , ΔH , and ΔS values were also calculated to prove the association with the complex formation.

Experimental Section

Materials and Solutions. $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was purchased from Sigma Com.. The lanthanide metal ion solution was prepared by dissolving an accurately weighed amount of the salt in the appropriate volume of doubly distilled water, and standardized with the disodium salt of EDTA.¹⁴ Nitric acid and KOH were from Merck p.a. Stock solutions were prepared using bidistilled water free from CO_2 . The KOH

used for the titration was standardized against potassium hydrogen phthalate (Merck AG). HNO₃ solutions were prepared and standardized potentiometrically against tris-(hydroxy)methylamino methane). The N-ethylmorpholine was obtained from Sigma and used without purification. Synthesis of the solid complex has been made as follows: 10 mmol (4.3291 g) of La(NO₃)₃·H₂O as dissolved in 20 cm³ of bidistilled water and added to an equal volume of aqueous solution containing 10 mmol (1.15 g) of N-ethylmorpholine. The mixture was refluxed for 2 hours; after cooling, the separated white solid complex was filtered; washed several times with ethanol, and then dried *in vacuo*.

Apparatus and Measurements. Potentiometric pH-measurements were made on the solutions in a bidistilled water in double glass vessel at 25.0 ± 0.1 °C, using a commercial Fischer combined electrode coupled to a Fischer Accumet pH/ion meter model 825 MP. Purified nitrogen was bubbled through the solutions during titrations. The instrument was calibrated against standard aqueous buffers of pH 4.01 (phthalate buffer) and 9.18 (borate buffer).

The electrode system was calibrated in terms of hydrogen ion concentration instead of activities. Provided the ionic strength of the test solution remains constant, the free hydrogen ion activity can be expressed in terms of concentration. Thus, all the constants determined in this work are concentration constants. The temperature was controlled by a Fisher Scientific Isotemp Refrigerated Circular model 9000 water thermostat, and it was maintained within ± 0.1 °C. Efficient stirring of the solution was achieved with a magnetic stirrer. The test solution (1 × 10⁻³ mol·dm⁻³ ligand + 4 × 10⁻³ mol·dm⁻³ HNO₃) was prepared in a constant ionic strength medium such as 0.1 mol·dm⁻³ KNO₃ by mixing the appropriate molar concentration of ligand, nitric acid and potassium nitrate. At least four titrations were performed for the solution. The protonation constant was then determined by the use of the Bjerrum function.¹⁵

$$\bar{n} = \frac{\left(H_T - h + \frac{K_W}{H}\right)}{A_T} = \frac{(\beta_1 h + 2\beta_2 h^2)}{(1 + \beta_1 h + \beta_2 h^2)} \quad (1)$$

where \bar{n} is calculated from the experimental quantities, h , the total concentration of titrable hydrogen ion H_T , and the total reagent concentration A_T . The pK_{a2} value of the studied buffer was determined from the overall protonation constant calculated by the linearization method of Irving and Rossotti.¹⁶

Initial estimates of pK_{a2} value was refined with the ESAB2M computer program¹⁷ by minimizing the error squares sum.

$$U_v = \sum_i W_i (V_i - V_{calcd,i})^2 \quad (2)$$

where V_i and $V_{calcd,i}$ are experimental and calculated values of the titrant volume for every point i of the titration curve.

The weight is calculated by

$$1/W_i = S_i^2 = S_v^2 + \left(\frac{\partial V_i}{\partial E_i}\right)^2 \cdot S_E^2 \quad (3)$$

where S_i is the estimated overall variance and S_v , S_E are estimates of standard deviation in titrant volume and potential, respectively. Titrant volume, $V_{calcd,i}$, can be calculated from an explicit equation.¹⁸ The calculation was performed with a Gaussian error in V of $S_v = 0.005$.

For the complex under investigation the reaction mixture (1 × 10⁻³ mol·dm⁻³ ligand + 1 × 10⁻³ mol·dm⁻³ La(III) + 4 × 10⁻³ mol·dm⁻³ HNO₃) at constant ionic strength 0.1 mol·dm⁻³ of KNO₃ was titrated against the standard potassium hydroxide solution at $t = 25.0 \pm 0.1$, 35.0 ± 0.1 and 45.0 ± 0.1 °C.

The value of E⁰ for the electrode was determined from a Gran plot derived from a separate titration of nitric acid with standard KOH under the same temperature and medium conditions as for the test solution titration. The results obtained were analyzed by the nonlinear least squares computer program ESAB2M¹⁷ to refine E⁰ and the autoprotolysis constant of water, K_W . During the calculations, the K_W was refined until the best value for Q was obtained. The results obtained indicated the reversible Nernstian response of the glass electrode used. The Irving and Rossotti method¹⁶ was applied for determination of the initial estimates of the formation constants for the complex at the studied conditions.

Ultraviolet absorption spectra were made on the examined solutions in a 1 cm quartz cell using Perkin-Elmer Spectrophotometer (Model No. PERKIN-ELMER Lambda 4B UV/VIS). X-ray diffraction pattern were conducted on solid compound using CuK_α target from 20 = 4° up to 70° of 2θ/min rotation rate.

IR absorption spectra of the ligand (liquid) and the complex were recorded as KBr pellets on a Perkin-Elmer IR Spectrophotometer (Model No. PERKIN-ELMER 1430 Ratio Recording IR in the range of 4000-400 cm⁻¹) by a standard procedure. The thermal analysis of the studied complex is conducted using Shimadzu-DTA and TG 50 in nitrogen atmosphere with a flow rate of 30.00 mL/min.

Chemical Analysis. The complex was analyzed for metal content by gravimetry (weight from La₂O₃) and for nitrogen and carbon content by microanalysis. The qualitative reaction for NO₃-group test with diphenylamine after preliminary destruction of the complex supported the presence of nitrate groups in the compound.

For LaL(NO₃)₃(H₂O)₂

anal. Calcd. (%) = C, 15.12; N, 11.76; La 29.18; H, 3.27

found (%) = C, 15.00; N, 11.56; La, 29.30; H, 3.66

Results and Discussion

The deprotonation constant of the ligand N-ethylmorpholine at 25.0 ± 0.1 °C and ionic strength I = 0.1 mol·dm⁻³ KNO₃ is found to be 7.75 ± 0.01. The effect of rising the temperature has been studied to evaluate the effect of temperature on the deprotonation constant of the studied ligand at the same condition as shown in Figure 1.

The obtained values are summarized in Table 1. The results indicate clearly that the deprotonation process

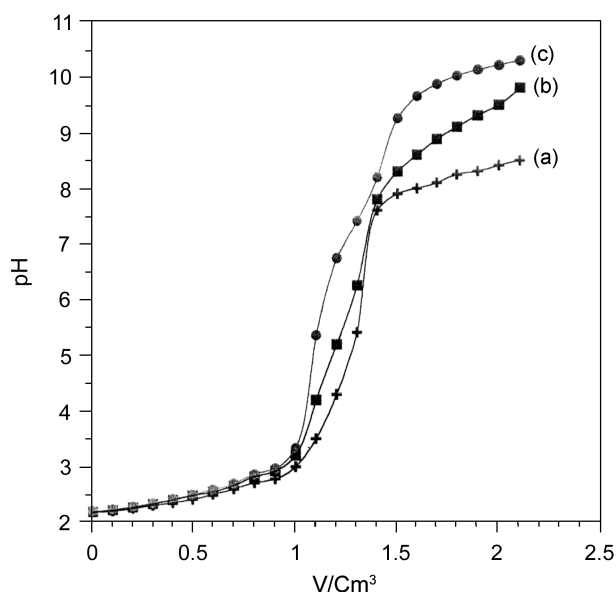


Figure 1. Potentiometric titration curves for 1×10^{-3} mol-dm $^{-3}$ *N*-ethylmorpholine ligand solution in presence of 1×10^{-3} mol-dm $^{-3}$ HNO $_3$, $I = 0.1$ mol-dm $^{-3}$ KNO $_3$ against 0.0235 mol-dm $^{-3}$ KOH at different temperatures. (a) at 25.0 ± 0.1 °C (+); (b) at 35.0 ± 0.1 °C (■); (c) at 45.0 ± 0.1 °C (●)

becomes more difficult to occur on rising the temperature, hence basicity of the ligand increases with temperature elevation.

The accompanied thermodynamic values for *N*-ethylmorpholine deprotonation are depicted in Table 2. The free energy changes of the deprotonation process increases positively with temperature elevation, *i.e.* the deprotonation process is not spontaneous. The deprotonation reaction of the ligand is an exothermic process in nature with evolution of 0.4 kcal/mol. The deprotonation process is also accompanied by decrease in entropy, which reflects the difficulty of proton ionization of the ligand molecule, with increasing temperature.

The complexation of free La(III) with *N*-ethylmorpholine at different temperatures as shown in Figure 2 is accompanied by decrease in free energy which indicates the spontaneity of the formation of La(III)-*N*-ethylmorpholine complex. The complexation of the compound is of endothermic nature. The entropy change is not greatly observed, since very slight change occurs (Table 3) which indicates that the complexation process is accompanied by release of constant number of water molecules.

The ultraviolet absorption spectra of the free ligand ($1 \times$

Table 2. Free energy, enthalpy and entropy changes for deprotonation of *N*-ethylmorpholine ligand HL $^+$ in aqueous medium, $I = 0.1$ mol-dm $^{-3}$ KNO $_3$

Thermodynamic parameters	Temperature / °C		
	25	35	45
+ ΔG° / Kcal mole $^{-1}$	10.63	11.17	11.71
- ΔH° / Kcal mole $^{-1}$	←	0.4386	→
- ΔS° / cal mole $^{-1}$ K $^{-1}$	37.14	37.69	38.20

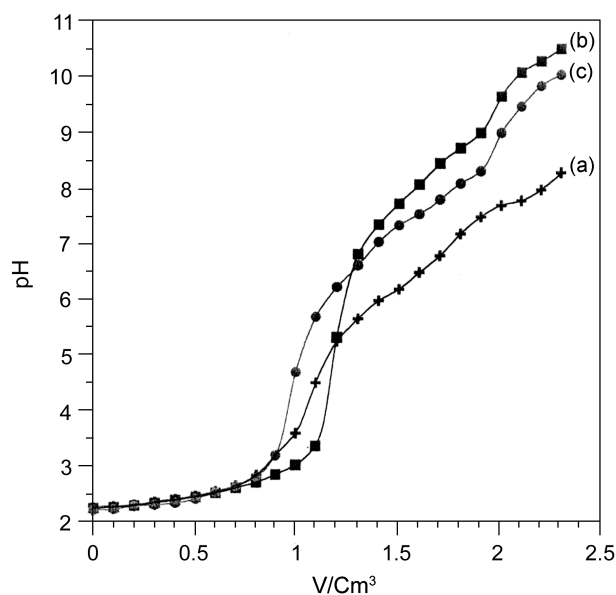


Figure 2. Potentiometric titration curves for 1×10^{-3} mol-dm $^{-3}$ *N*-ethylmorpholine + 1×10^{-3} mol-dm $^{-3}$ La(III) complex solution in presence of 4×10^{-3} mol-dm $^{-3}$ HNO $_3$, $I = 0.1$ mol-dm $^{-3}$ KNO $_3$ against 0.0235 mol-dm $^{-3}$ KOH at different temperatures. (a) at 25.0 ± 0.1 °C (+); (b) at 35.0 ± 0.1 °C (■); (c) at 45.0 ± 0.1 °C (●)

Table 3. Free energy, enthalpy and entropy changes for complex formation of *N*-ethylmorpholine with lanthanum ion (LaL) in aqueous medium, $I = 0.1$ mol-dm $^{-3}$ KNO $_3$

Thermodynamic parameters	Temperature / °C		
	25	35	45
- ΔG° / Kcal mole $^{-1}$	4.51	4.73	4.96
ΔH° / Kcal mole $^{-1}$	←	2.19	→
ΔS° / cal mole $^{-1}$ K $^{-1}$	22.48	22.46	22.48

10^{-3} mol dm $^{-3}$) in aqueous medium at constant ionic strength $I = 0.1$ mol-dm $^{-3}$ KNO $_3$ as in Figure 3 shows two characteristic peaks, the main one is observed at 210 nm due

Table 1. The deprotonation constant (pKa) of *N*-ethylmorpholine ligand (HL $^+$) in aqueous medium in addition to formation constant (Log K) of lanthanum-*N*-ethylmorpholine complex (LaL), $I = 0.1$ mol-dm $^{-3}$ KNO $_3$ at different temperatures

Compound	pKa			Log K		
	25°	35°	45°	25°	35°	45°
HL $^+$	7.75 ± 0.01	7.88 ± 0.02	8.00 ± 0.01	—	—	—
LaL	—	—	—	3.29 ± 0.02	3.34 ± 0.02	3.39 ± 0.02

± refer to 3 times standard deviation (3s)

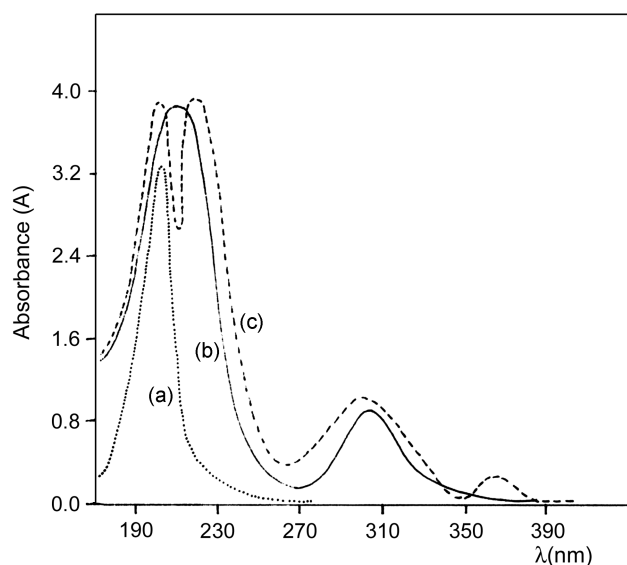


Figure 3. UV absorption spectra for La(III), *N*-ethylmorpholine and its lanthanum binary complex, $I = 0.1 \text{ mol}\cdot\text{dm}^{-3} \text{ KNO}_3$ and at 25°C . (a) $1 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3} \text{ La(III)}$, (b) $1 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3} \text{ N-ethylmorpholine}$, (c) $1 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3} \text{ La(III)} + 1 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3} \text{ N-ethylmorpholine}$

to $\pi\text{-}\pi^*$ transition with molar extinction coefficient ϵ equals to $3840 \text{ cm}^{-1} \text{ mol dm}^{-3}$ while the second peak takes place at 298 nm which may be attributed to $n\text{-}\pi^*$ with $\epsilon = 880 \text{ cm}^{-1} \text{ mol dm}^{-3}$. For the free lanthanum (III) metal ion, the solution has an absorption maximum peak at 205.7 nm with molar extinction coefficient equals to $3330 \text{ cm}^{-1} \text{ mol dm}^{-3}$. Upon complexation of *N*-ethylmorpholine with La (III), the first main peak is splitted into two peaks located at 200 and 219 nm , due to the coordination of lanthanum metal ion to the oxygen of the morpholine group, in addition the peak observed at 298 nm is enhanced due to the bonding of the central metal ion to the oxygen atom of the morpholine ring. A new third peak takes place at 365 nm which may be attributed to the coordination of the nitrate group to La(III) in the complex, as bidentate ligand as shown in Table 4.

The molecule of *N*-ethylmorpholine (L) has two potential

Table 4. The electronic absorption spectra of *N*-ethylmorpholine (L) and its La(III)-complex in aqueous medium, $I = 0.1 \text{ mol}\cdot\text{dm}^{-3} \text{ KNO}_3$ at 25°C

Compound	λ_1 (nm) $\log \epsilon_1$	λ_2 (nm) $\log \epsilon_2$	λ_3 (nm) $\log \epsilon_3$
Free ligand	210 (3.58)	298 (2.94)	–
La(III) complex	200 (3.57)	298 (3.00)	365 (2.36)
	219 (3.58)	–	–
La(NO ₃) ₃ ·6H ₂ O	205 (3.52)	–	–

centers for metal coordination, the oxygen and nitrogen atoms of the morpholino group. The infrared spectra of the *N*-ethylmorpholine and its La(III) complex are depicted in Figure 4, where the strong band observed at 1130 cm^{-1} which is attributed to the $\nu_{\text{C-O}}$ band disappears in the spectrum of the complex, where this indicate that the mode of coordination of the lanthanum metal ion occur through the morpholine oxygen atom. Three strong bands are observed at $1500, 1700, 1040 \text{ cm}^{-1}$ which could be assigned to the bidentate nitrate groups in the complex spectra.¹⁹ The wide diffuse band in the $3600\text{-}3400 \text{ cm}^{-1}$ range without a pronounced maximum is assigned to the stretching modes of coordinated water molecules in the spectrum of the studied complex as shown in Table 5.

The x-ray powder diffraction spectra for the $\text{LaL}(\text{NO}_3)_3\text{-(H}_2\text{O)}_2$ (L = *N*-ethylmorpholine) as shown in Figure 5 indicate that the complex is of crystalline nature with a characteristic d value of 1.40 \AA . However, the structure of the studied complex is proposed to be in the nine

Table 5. The frequencies (cm^{-1}) and assignments of the bands in the IR absorption spectra of *N*-ethylmorpholine (L) and its La(III) complex

Assignments	Ligand (L)	La(III) complex
ν (H ₂ O)	–	3600-3400 (b)
ν (C-O)	1160 (s)	–
ν (C-N)	1310 (w)	1320 (w)
ν (NO ₃ ⁻)	–	1500, 1300, 1040 (s)

b: broad band, s: strong band, w: weak band

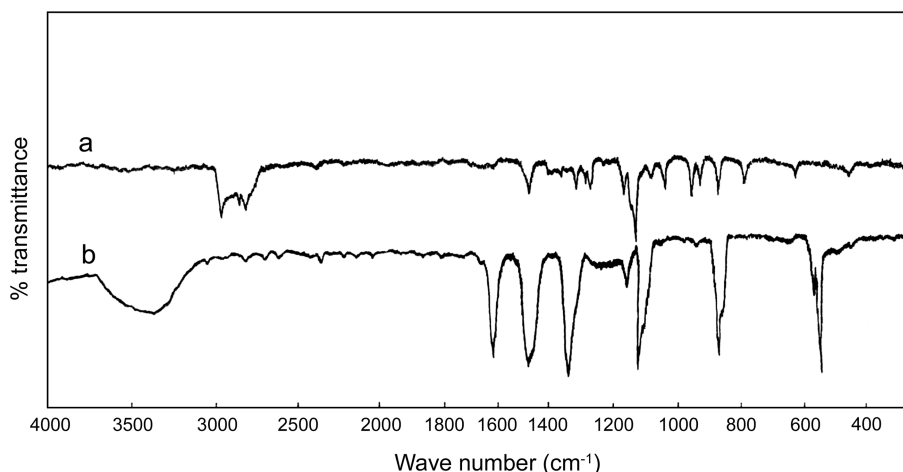


Figure 4. Infra-red absorption spectra of: (a) *N*-ethylmorpholine ligand, (b) La(III)-*N*-ethylmorpholine complex.

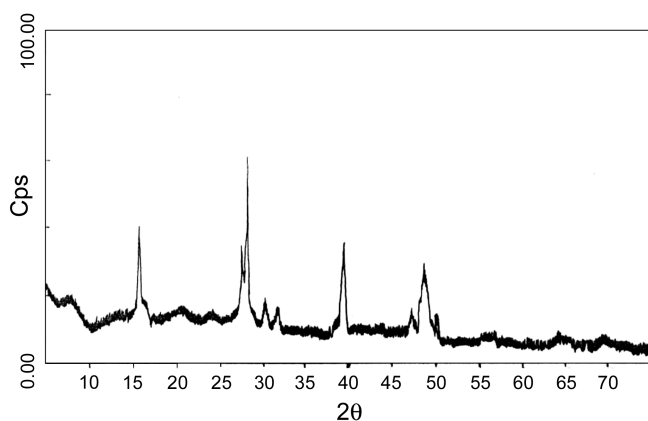


Figure 5. X-ray diffraction for La(III)-N-ethylmorpholine solid complex.

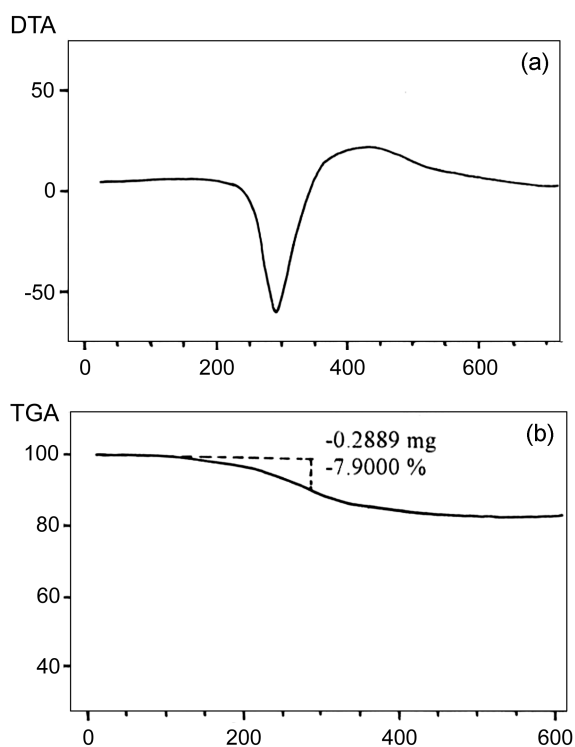


Figure 6. Thermal analysis curves for La(III)-N-ethylmorpholine solid complex. (a) DTA for the complex, (b) TGA for the complex

coordination form. Inspecting the thermal analysis data for the crystalline solid complex, the differential thermal analysis (DTA) exhibits an endothermic peak at 285 °C which may be attributed to the loss of coordinated water

molecules from the complex. This observation is confirmed through the thermogravimetric curves for the concerned complex as shown in Figure 6 where the weight loss can be assigned to the water molecules coordinated to the lanthanum metal ion (calcd. 7.54%, found 7.90%).

On the basis of the infra-red, x-ray diffraction, and thermal analysis data for the complex, it has been concluded that the lanthanum atom in the crystal is located on the three fold axis and coordinate nine oxygen atoms six atoms of nitrate groups, one oxygen atom of the *N*-ethylmorpholine ligand, and the oxygen atoms of the two coordinated water molecules.

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