



## Some Mixed Ligand Complexes of Lanthanum(III) Using 1-Nitroso-2-naphthol and Amino Acids

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This work describes the synthesis of three new mixed ligand ternary complexes of La(III) having the general formula  $[M(1N2N)_2 \cdot (L) \cdot 2H_2O]$  by employing 1-nitroso-2-naphthol (1N2N) primary ligand and L-valine, L-serine, L-isoleucine as secondary ligand. The complexes were characterized by thermal analysis, elemental analysis, electrical conductance, UV-visible spectrum and magnetic susceptibility measurement study. The non-electrolytic nature of the complexes was confirmed by molar conductance studies. Furthermore, the magnetic susceptibility study at room temperature showed that the lanthanum(III) complexes were diamagnetic in nature. Electronic absorption studies of the complexes also show intra-ligand and LMCT transitions, respectively. FT-IR studies confirmed the bonding between the metal ion and ligands *via* N- and O-donor atoms. The presence of coordinated water molecules was confirmed by thermal study. Additionally, these complexes were tested for antibacterial study by using agar cup and tube dilution method. All the complexes show moderate to good antibacterial activity.

**Keywords:** Lanthanum, 1-Nitroso-2-naphthol, Amino acids, Mixed ligand ternary complexes, Antibacterial study.

### INTRODUCTION

In recent decades, the mixed ligand complexes were widely studied due to their significant importance in the biological processes [1]. Many mixed ligand complexes possess significant biological activities such as antibacterial [2,3], antimicrobial [4,5], anticancer [6] and antitumor [7]. Further, chiral mixed ligand complexes also used as catalysts in various important chemical transformations like epoxidation [8], resolution of racemic compounds [9] and other asymmetric synthesis [10,11]. In addition to these, some mixed ligand complexes also have potential applications in advanced materials such as semiconductors [12], magnetic [13] and non-linear optical materials [14]. Amongst these, mixed ligand complexes with amino acids as a ligand are of great importance for enzyme-metal ion substrate complexes [15]. Similarly 1-nitroso-2-naphthol is also important for estimation of cobalt and tyrosine residue [16].

The literature search revealed that, some coordination compounds of 1-nitroso-2-naphthol and amino acids shows promising biological activities [17,18]. To be specific, Ghanim *et al.* [19] showed that such complexes possess notable antimicrobial activity. In this context, we envisioned the synthesis of new mixed ligand ternary complexes of La(III) having 1-nitroso-2-naphthol as a primary ligand with amino acids *viz.*,

L-valine, L-serine, L-isoleucine as a secondary ligand for their biological evaluation. We herein report the synthesis of new mixed ligand complexes of La(III) by using 1-nitroso-2-naphthol (1N2N) as a primary ligand and L-valine, L-serine, L-isoleucine as a secondary ligand and their antibacterial study.

### EXPERIMENTAL

Ligands 1-nitroso-2-naphthol, amino acids L-valine, L-serine, L-isoleucine and analytical reagent grade lanthanum(III) chloride heptahydrate were used as such as received from S.D. Fine Chemicals. Solvents used in this work like DMF, DMSO and laboratory grade chemicals were distilled and purified as per the standard methods [20-23].

The C, H, N elemental analysis was carried out by using Thermo Finnigan Elemental Analyzer. Thermal analysis (TG and DTA) studies were done on a Perkin-Elmer Diamond TG-DTA instrument. The UV-visible absorption studies were carried out using Shimadzu UV/VIS-1800 spectrophotometer. Similarly FT-IR spectra were recorded using Shimadzu FT-IR spectrophotometer. Amount of lanthanum in the complexes was determined by standard complexometric method [24,25]. Electrical conductance was measured on an Equiptronics Autoranging Conductivity Meter. Guoy method was adopted for measurements of magnetic susceptibilities by using mercury tetrathiocyanatocobaltate (II) as a calibrant.

**General procedure for synthesis of ternary complexes of lanthanum:** The complexes were prepared from  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ , 1-nitroso-2-naphthol (1N2N) and L-valine, L-serine and L-isoleucine. In the 10 mL aqueous solution of lanthanum(III) chloride heptahydrate (0.372 g, 1 mmol), 20 mL ethanolic solution of 1-nitroso-2-naphthol (0.346 g, 2 mmol) was added. This mixture was heated in boiling water bath with constant stirring for 10 min. Then 10 mL aqueous solution of corresponding amino acids (1 mmol) was added to this hot reaction mixture with stirring. Further, this reaction mixture was heated in a water bath up to 50 °C. Desired ternary complexes of lanthanum were obtained by complete precipitation by adding diluted ammonia solution until the pH of mixture raised up to 7.0. The resulting mixture was cooled to room temperature and the solid product was collected by filtration. Then water and ethanol washing were given to this solid product. Finally, these complexes were obtained by drying under vacuum and subjected to various physico-chemical, spectral as well as antibacterial studies.

### Antibacterial study

**Agar cup method:** The antibacterial screening of the test compounds was assayed against *Staphylococcus aureus*, *Corynebacterium diphtheria*, *Escherichia coli* and *Salmonella typhi* bacteria by agar cup method [26]. In this method, the test strain with sterile nutrient agar was filled in a plate up to 5 mm height and was permitted to solidify. At the center of this plate, a single cup with 8 mm diameter was cut using sterile cork borer. Subsequently the sample solution of (1000 µg/mL) in dimethyl sulphoxide was filled into this cup and the resulting plate was kept for incubation for 24 h at 37 °C. The antibacterial activity was noted by measuring zone of inhibition from the edge of cup. In the present study, tetracycline standard has been selected to compare the activity of metal complexes.

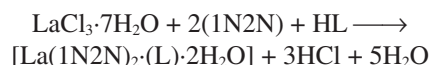
**Tube dilution method:** For this method, 10 mL stock solution of lanthanum complexes was prepared having 1 mg/mL concentration by dissolving 10 mg of complex in 10 mL dimethyl sulphoxide. From this stock solution, aliquots of 5 to 1000 µg/mL were obtained in test broth. The complexes were tested against *Staphylococcus aureus*, *Corynebacterium diphtheria*, *Escherichia coli* and *Salmonella typhi* organism. Sterilized Muller Hinton broth was used to prepare the bacterial inoculum which was incubated for 4 h at 37 °C. They were dispersed (5 cm<sup>3</sup>) in each test tube of borosilicate (150 × 20 mm). The test sample solution was added in order to attain a final concentration as 5 to 1000 µg/mL. Thereafter 0.1 mL of inoculums of desired bacteria was added in the tubes. The

tubes, then incubated for 24 h at 37 °C and the results were noted in the form of minimum inhibitory growth of the test organisms. The lowest concentration which does not show the visible growth of desired bacteria was noted as minimum inhibitory concentration (MIC). The tetracycline was used as a control in this study, which was screened simultaneously and obtained results were compared with the test sample.

## RESULTS AND DISCUSSION

### Characterization of ternary complexes of lanthanum:

The synthesis reaction of lanthanum complexes is summarized as follows:



where, (1N2N) is 1-nitroso-2-naphthol and HL denote an amino acid.

All the ternary complexes of lanthanum were found coloured and non-hygroscopic solids in nature. The high thermal stability of complexes attributes to a strong metal-ligand bond (Table-1). All the synthesized complexes are partially soluble in polar aprotic DMF, DMSO solvents, but were insoluble in some common organic solvents like ethyl alcohol or acetone.

The ternary complexes were studied for elemental analysis and obtained data is incorporated in Table-1. These data were found in accordance with the desired formulation as 1:2:1 complex of the type  $[\text{La}(1\text{N2N})_2(\text{L}) \cdot 2\text{H}_2\text{O}]$ . The electrical conductivity of these complexes was measured in dimethyl formamide at 10<sup>-3</sup> M concentration (Table-1). The obtained molar conductance values were in the range of 0.000153-0.000157 Mhos cm<sup>2</sup> mol<sup>-1</sup> which designate the non-electrolytic nature of complexes [27]. Also the diamagnetic nature [28] of La(III) complexes were confirmed from the magnetic susceptibility measurements employing diamagnetic corrections (Table-1). The electronic absorption study in UV-visible region was carried out in dimethylformamide solution with 10<sup>-3</sup> M concentration (Table-2). In the spectrum of La(III) complexes, three transitions were observed, namely  $\pi \rightarrow \pi^*$  at 263-268 nm (38023-37313 cm<sup>-1</sup>),  $n \rightarrow \pi^*$  at 363-373 nm (27548-26810 cm<sup>-1</sup>) and ligand to metal charge transfer transitions at 420-425 nm (23810-23529 cm<sup>-1</sup>), respectively [29]. The FT-IR spectrum of the La(III) ternary complexes were recorded at 4000-400 cm<sup>-1</sup> by using KBr discs and obtained spectral data is incorporated in Table-3. The significant bands can be assigned from the reported FT-IR data of metal complexes, 1-nitroso-2-naphthol and amino acids. The FT-IR spectra of La(III) complex not showed the band at about 3448 cm<sup>-1</sup> which assigned to free O-H group

TABLE-1  
PHYSICO-CHEMICAL DATA OF MIXED LIGAND COMPLEXES OF LANTHANUM(III)

Complex (m.f.)	m.w. (g) [colour]	Elemental analysis (%): Found (Calcd.)				Molar conductance (Mhos cm <sup>2</sup> mol <sup>-1</sup> )	$\mu_{\text{eff}}$ (B.M.)	Decomposition temperature (°C)
		La	C	H	N			
$[\text{La}(1\text{N2N})_2(\text{Val}) \cdot 2\text{H}_2\text{O}]$ ( $\text{LaC}_{23}\text{H}_{26}\text{N}_3\text{O}_8$ )	635.39 [Green]	21.84 (21.86)	47.24 (47.26)	4.12 (04.13)	06.61 (06.61)	0.000155	Diamagnetic	220
$[\text{La}(1\text{N2N})_2(\text{Ser}) \cdot 2\text{H}_2\text{O}]$ ( $\text{LaC}_{23}\text{H}_{22}\text{N}_3\text{O}_9$ )	623.24 [Green]	22.27 (22.28)	44.31 (44.32)	3.56 (03.56)	06.72 (06.74)	0.000153	Diamagnetic	240
$[\text{La}(1\text{N2N})_2(\text{Iso}) \cdot 2\text{H}_2\text{O}]$ ( $\text{LaC}_{26}\text{H}_{28}\text{N}_3\text{O}_8$ )	649.42 [Green]	21.40 (21.39)	48.08 (48.09)	4.34 (04.35)	06.45 (06.47)	0.000157	Diamagnetic	215

where, (1N2N) represents the deprotonated primary ligand 1-nitroso-2-naphthol whereas Val, Ser, Iso indicates deprotonated secondary ligands L-valine, L-Serine, L- Isoleucine, respectively.

TABLE-2  
ELECTRONIC SPECTRAL DATA OF  
LANTHANUM(III) COMPLEXES

Complex	$\lambda$ (nm)	$\nu$ (cm <sup>-1</sup> )	Proposed assignments
[La(1N2N) <sub>2</sub> (Val)·2H <sub>2</sub> O]	268	37313	$\pi \rightarrow \pi^*$
	373	26810	$n \rightarrow \pi^*$
	420	23810	Charge-transfer
[La(1N2N) <sub>2</sub> (Ser)·2H <sub>2</sub> O]	265	37736	$\pi \rightarrow \pi^*$
	373	26810	$n \rightarrow \pi^*$
	422	23697	Charge-transfer
[La(1N2N) <sub>2</sub> (Iso)·2H <sub>2</sub> O]	263	38023	$\pi \rightarrow \pi^*$
	363	27548	$n \rightarrow \pi^*$
	425	23529	Charge-transfer

of 1-nitroso-2-naphthol. Therefore, it can be concluded that, hydroxyl group of 1-nitroso-2-naphthol moiety undergoes deprotonation to form complexes. The metal complexes show the variation in position of  $\nu(\text{CO})$  band in 1-nitroso-2-naphthol. Prakash *et al.* [30] reported  $\nu(\text{CO})$  band in the range of 1170-1109 cm<sup>-1</sup> for silver metal complexes with 1-nitroso-2-naphthol. Synthesized complexes show strong  $\nu(\text{CO})$  band at 1155 cm<sup>-1</sup> which indicates the presence of 1-nitroso-2-naphthol moiety in the complexes. Hence it confirms the coordination of metal through hydroxyl oxygen atom. The observed  $\nu(\text{N=O})$  band at 1527 cm<sup>-1</sup> in the spectrum of 1-nitroso-2-naphthol ligand was shifted to higher wave number 1554 cm<sup>-1</sup> in the spectra of complexes, which indicates the coordination of 1-nitroso-2-naphthol to metal *via* nitrogen atom. A broad band showed in the range of 3415-3429 cm<sup>-1</sup> due to O-H asymmetric and O-H symmetric stretching vibrations indicates presence of coordinated water molecule [31,32], which was further confirmed by thermal studies. Bands observed at the range 3062-3061 cm<sup>-1</sup> and 3055-3037 cm<sup>-1</sup> can be allocated to N-H asymmetric and N-H symmetric vibrations, respectively. In free amino acid spectra, these bands are observed at 3040 and 2960 cm<sup>-1</sup>. This shift of N-H vibrations to higher wave numbers, suggest the

coordination between metal atom and amino group through nitrogen atom. This further confirms the participation of amino acids in the formation of desired metal complexes.

Additionally the coordination bonding between -NH<sub>2</sub> group in amino acid moiety was authenticated by symmetrical C-N stretching frequency. The band detected at about 900 cm<sup>-1</sup> in the free amino acid spectrum was shifted to 839 cm<sup>-1</sup> in the spectra of metal complexes. Furthermore the coordination between oxygen atom of carboxylic acid ligand and the metal ion was specified by the interpretation of the  $\nu_{\text{asymmetric}}$  and the  $\nu_{\text{symmetric}}$  mode of vibration of (COO<sup>-</sup>) band. The  $\nu_{\text{asymmetric}}$  (COO<sup>-</sup>) band obtained at 1600-1560 cm<sup>-1</sup> in free amino acid spectra was shifted [33] to 1618-1616 cm<sup>-1</sup> in metal complexes. Furthermore,  $\nu_{\text{symmetric}}$  (COO<sup>-</sup>) band at 1415 cm<sup>-1</sup> of free amino acid shifted to 1402-1390 cm<sup>-1</sup> in metal complexes. Usually intense band is observed because of O-H stretching vibrations in the region 3650-3200 cm<sup>-1</sup> shows the presence of hydroxyl groups in the molecule of carboxylic acid. In the spectra of La(III) complexes, O-H stretching vibrations bands were not observed, which indicates the bonding between OH group and metal ion through oxygen atom. It is important to mention that, some new bands were observed in the range of 523-524 and 634 cm<sup>-1</sup> with weak intensity attributes to the La-N and La-O vibrations, respectively. These vibrational bands are absent in the FT-IR spectra of free 1-nitroso-2-naphthol as well as amino acid ligands.

**Thermal studies:** The synthesized complexes were analyzed for thermal studies to know the decomposition temperature and its stages. The thermogravimetric and differential thermal analysis of La(III) ternary complexes was done under inert nitrogen atmosphere with 10 °C/min with constant heating rate. The obtained data are summarized in Table-4. The most probable decomposition mode of these complexes can be anticipated on the basis of the cautious observations obtained TG and DTA curves [34]. The thermogram of lanthanum complexes indicates high thermal stability. However, with

TABLE-3  
FT-IR SPECTRAL DATA OF LANTHANUM(III) COMPLEXES (cm<sup>-1</sup>)

Complex	$\nu(\text{O-H})$ H <sub>2</sub> O	$\nu(\text{N-H})$ Asym. (AA)	$\nu(\text{N-H})$ Sym. (AA)	$\nu(\text{C=O})$ (AA)	$\nu(\text{C-O})$ (AA)	$\nu(\text{C-N})$ (AA)	$\nu(\text{N=O})$ 1N2N	$\nu(\text{C-N})$ 1N2N	$\nu(\text{C-O})$ 1N2N	$\nu(\text{La-O})$	$\nu(\text{La-N})$
<b>1</b>	3415(b)	3062(w)	3037(w)	1618(s)	1402(w)	839(m)	1554(s)	1211(m)	1155(w)	634(w)	523 (w)
<b>2</b>	3425(b)	3061(w)	3055(w)	1616(s)	1392(w)	839(m)	1554(s)	1211(m)	1155(w)	634(w)	523(w)
<b>3</b>	3429(b)	3061(w)	3055(w)	1616(s)	1390(w)	839(m)	1554(s)	1209(m)	1155(w)	634(w)	524(w)

**1** = [La(1N2N)<sub>2</sub>(Val)·2H<sub>2</sub>O]; **2** = [La(1N2N)<sub>2</sub>(Ser)·2H<sub>2</sub>O]; **3** = [La(1N2N)<sub>2</sub>(Iso)·2H<sub>2</sub>O]; AA = Amino Acids, 1N2N = 1-nitroso-2-naphthol

TABLE-4  
THERMAL STUDY DATA OF SYNTHESIZED LANTHANUM(III) COMPLEXES

Complex	Temperature range (°C)	Weight loss due to	Weight loss (%)	
			Found	Calculated
[La(1N2N) <sub>2</sub> (Val)·2H <sub>2</sub> O]	115-150	Two water molecules	5.67	5.52
	220-290	Amino acids	17.0	18.24
	340-680	Two 1N2N molecules	54.67	53.87
[La(1N2N) <sub>2</sub> (Ser)·2H <sub>2</sub> O]	110-155	Two water molecules	6.0	5.78
	240-290	Amino acids	16.0	16.70
	330-660	Two 1N2N molecules	54.0	54.92
[La(1N2N) <sub>2</sub> (Iso)·2H <sub>2</sub> O]	120-170	Two water molecules	5.34	5.55
	215-280	Amino acids	20.0	20.04
	310-700	Two 1N2N molecules	54.0	52.71

increasing temperature, the complexes showed steady loss of weight because of decomposition by fragmentation. Further, these complexes of L-valine and L-serine, L-isoleucine, showed similar behaviour in thermal studies. The TG study of these complexes confirms the loss of two water molecules in the temperature range 110-170 °C. In the second step of decomposition, amino acid weight loss was observed in the temperature range 215-290 °C. In the last step of decomposition, weight loss of two molecules of 1-nitroso-2-naphthol was observed from complexes in the temperature range 310-700 °C. The DTA study shows the endothermic peak in the temperature range of 110-170 °C which proves the presence of coordinated water molecules. As the temperature increases, the differential thermal analysis curve showed small and broad exothermic peak in the temperature range of 215-290 °C and 310-700 °C due to decomposition of amino acids and 1-nitroso-2-naphthol moieties from the complexes. The constant weight plateau observed after 700 °C indicates decomposition of complexes to a fine powder of metal oxide, which was authenticated through XRD study of decomposed product [35].

On the basis of the characterization, physico-chemical and spectroscopic studies, the bonding and structure of synthesized lanthanum(III) complexes are shown in the following Figs. 1-3, respectively.

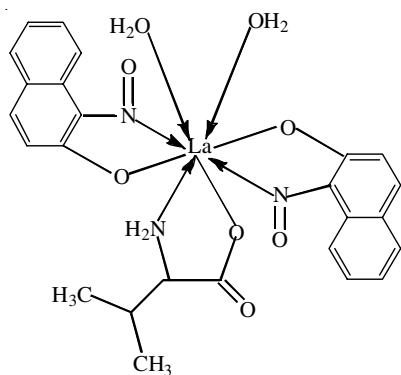


Fig. 1. Proposed structures of  $[La(1N2N)_2(Val) \cdot 2H_2O]$

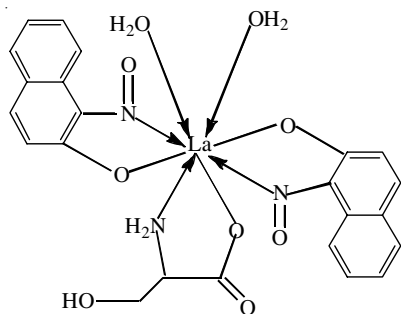


Fig. 2. Proposed structures of  $[La(1N2N)_2(Ser) \cdot 2H_2O]$

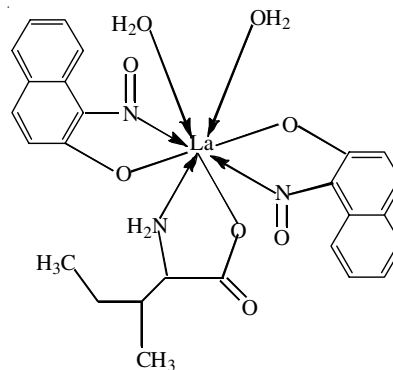


Fig. 3. Proposed structures of  $[La(1N2N)_2(Iso) \cdot 2H_2O]$

**Biological studies:** The biological studies of the synthesized complexes were performed by employing agar cup and tube dilution method. The results of the agar cup method indicate that the La(III) complexes are more sensitive against *S. aureus* and *S. typhi* as compared to *C. diphtheria* and *E. coli* (Table-5). The MIC values of ligand and metal salts was found in the range of 25-250 µg/mL while that of metal complexes ranges between 05-35 µg/mL (Table-5). Tested samples were found more potent against *S. aureus* and *S. typhi* as compared to *C. diphtheria* and *E. coli*. The simultaneous study was also carried out with tetracycline as a control, which shows that the complexes have moderate activity against selected bacterial strains.

The results of the biological studies showed that the lanthanum(III) complexes have higher antibacterial activity in comparison with metal salt and free ligands. The obtained result showed the activity enhancement of complexes due to chelation. The enriched activity of metal complexes is due to chelate effect which increases the hydrophobic nature that enables the dispersion of the complex through the lipid layer of microorganisms [36].

## Conclusion

In conclusion, we have reported the synthesis of three new ternary complexes from lanthanum(III) chloride heptahydrate salt by utilizing 1-nitroso-2-naphthol and amino acids as a ligands. The obtained data confirm the stoichiometry of these complexes as 1:2:1 with respect to lanthanum metal, 1-nitroso-2-naphthol and amino acid, respectively. The conductivity measurements show the complexes are non-electrolytic in nature. Furthermore, these complexes are diamagnetic in nature which was confirmed by magnetic susceptibility studies. Electronic absorption study of the complexes in the UV-visible region illustrates the LMCT and intra ligand  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions. FT-IR analysis of complexes confirmed the coor-

TABLE-5  
ANTIBACTERIAL AND MIC STUDY FOR LANTHANUM(III) COMPLEXES BY AGAR CUP METHOD

Complex	Antibacterial activity (mm)				MIC (µg/mL)			
	<i>S. aureus</i>	<i>C. diphtheriae</i>	<i>E. coli</i>	<i>S. typhi</i>	<i>S. aureus</i>	<i>C. diphtheriae</i>	<i>E. coli</i>	<i>S. typhi</i>
$[La(1N2N)_2(Val) \cdot 2H_2O]$	26	16	13	20	10	25	35	15
$[La(1N2N)_2(Ser) \cdot 2H_2O]$	28	15	10	23	15	30	35	15
$[La(1N2N)_2(Iso) \cdot 2H_2O]$	28	15	13	22	10	25	30	10
Tetracycline	30	20	18	25	1.5	2.0	4.0	1.5
1-Nitroso-2-naphthol	—	—	—	—	75	200	150	100
$LaCl_3 \cdot 7H_2O$	—	—	—	—	50	100	100	75



dination between lanthanum metal and ligands *via* nitrogen and oxygen atoms of the 1-nitroso-2-naphthol and amino acid. From the thermal analysis study, the presence of the strong coordination bond between metal and ligand as well as the existence of two coordinated water molecules was confirmed. The above results show that the coordination number in these lanthanum complexes is eight. The biological study of these complexes shows the good antibacterial activity for *S. aureus* and *S. typhi* in comparison with *C. diphtheria* and *E. coli*. The synthesized La(III) complexes demonstrate mild activity against the selected strains with respect to control tetracycline.

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