



Synthesis and Structural Characterization of Lanthanum(III) Complexes of 4-Nitrosoantipyridine

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Received: 29 October 2020;

Accepted: 14 January 2021;

Published online: 16 February 2021;

AJC-20258

A new series of La(III) complexes of the ligand with the general formula $[La(L)_2(aa)_3]$ and $[La_2(L)_4(aa)_3]$, ($a =$ nitrate (1), thiocyanate (2), acetate (3) and propionate (4) ions, $aa =$ sulphate (5), thiosulphate (6), oxalate (7) and malonate (8) ions with the ligand 4-nitrosoantipyridine (L) were synthesized and characterized using various physico-chemical studies. The primary ligand L acts as a bidentate ligand utilizing the carbonyl group and the nitroso group for bonding. The nitrate, thiocyanate, acetate and propionate ions are monovalent unidentate ligands, whereas sulphate, thiosulphate, oxalate and malonate ions are divalent bidentate ligands in the complexes 1-8. Based on spectral data and magnetic susceptibility measurements, geometry of the lanthanum(III) complexes were also proposed.

Keywords: 4-Nitrosoantipyridine, Lanthanum(III) complexes.

INTRODUCTION

The coordination chemistry of lanthanides has been one of the most intriguing areas of research [1-3]. The diversity in structures [4-6] coupled with their potential uses in a wide variety of areas such as diagnostic tools in biology [7], catalysis [8], luminescence [9,10] and magnetism [11] strengthen the interest in their investigation [12].

The unique magnetic, spectroscopic and luminescent properties of lanthanide(III) ions are the main reasons for the importance of these complexes in industrial, biochemical, chemical and medicinal fields [13]. Lanthanide(III) complexes are also used for photodynamic therapy as radiopharmaceuticals [14]. In their stable oxidation state, the lanthanides usually form trivalent cations, the size of which decreases from lanthanum to lutetium [15,16]. The coordination chemistry of lanthanides differs significantly from that of main group elements and transition metal elements as the $4f$ orbitals in these are buried inside the atom and are shielded from the ligand field. Hence, the chemistry of the lanthanide ions is primarily determined by their sizes [17]. Since the $4f$ electrons are well shielded, the mixing of the orbitals of the ligand and the metal becomes insignificant and bonding between the ligands and the Ln(III) ions is mostly electrostatic. Higher coordination numbers (> 6) exhibited by the Ln(III) ions is due to lack of any directional

bonding character and large ionic size, which results in weak stereochemical preferences and the ligands coordinating to the central metal ion hold positions in a way that leads to the minimum steric repulsions. Accordingly, the coordination environment around the Ln(III) centre cannot be regarded as an ideal coordination polyhedron [17]. All the above features make the coordination chemistry of lanthanides complicated as well as fascinating.

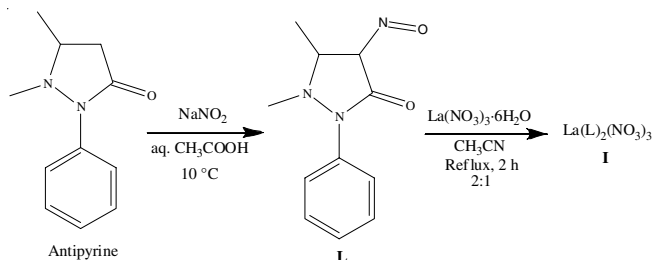
In previous reports, the versatility of the coordination pattern of lanthanide ions have been demonstrated, wherein they exhibit a coordination number higher than six [18,19]. Lanthanide(III) complexes of pyrazolone derivatives form one of the largest and significant groups of complexes, in which antipyridine acts as a neutral unidentate ligand coordinating the lanthanide ions through the carbonyl oxygen [20-26]. In order to expand the knowledge in the coordination behaviour of Ln(III) ions, we report herein the synthesis and characterization of eight La(III) complexes using 4-nitrosoantipyridine (L) as the ligand. All the lanthanum(III) complexes have been characterized based on the elemental analyses, molar conductivity, magnetic susceptibility and spectroscopic studies.

EXPERIMENTAL

La_2O_3 (99.9 %) was purchased from the Indian Rare Earths Ltd., Udyogamandal, India and used without further purifi-

cation. Antipyrine, sodium nitrite, ammonium thiocyanate, sodium acetate, sodium propionate, sodium sulphate, sodium thiosulphate, ammonium oxalate and disodium malonate (BDH) were purified by recrystallizing from hot ethanol and dried over P_4O_{10} *in vacuo* before use. Solvents like acetonitrile, benzene, diethyl ether, ethanol, methanol, nitrobenzene and petroleum ether (E. Merck, India) were purchased and used as such. The C, H and N contents in the complexes were determined using CHN-2400 (Perkin-Elmer). The lanthanum content of the complexes was determined gravimetrically by the oxalate-oxide method [27]. The anions present in the complexes, *viz.*, nitrate, thiocyanate, oxalate, sulphate and thiosulphate ions were estimated by gravimetric methods [28]. Molecular weights of the complexes were determined by the rasi method using biphenyl as the solvent [29]. Molar conductivities of the complexes in acetonitrile, methanol and nitrobenzene were determined at room temperature using an ELICO conductivity bridge type CM 82T with a dip-type conductance cell having platinized platinum electrodes (cell constant, 1.64 cm^{-1}). The IR spectra of the ligand and the complexes were recorded on a double beam Perkin-Elmer 397 infrared spectrophotometer in the range $4000\text{--}400 \text{ cm}^{-1}$ employing the KBr disc technique. The electronic spectra of the ligand and the complexes were recorded using a double beam Hitachi 220 A UV-visible spectrophotometer in the range $185\text{--}900 \text{ nm}$. The room temperature magnetic susceptibilities of the complexes were determined using a Gouy balance [30,31].

Synthesis of 4-nitrosoantipyrine (L): Ligand, 4-nitrosoantipyrine was synthesized by the standard method as shown in **Scheme-I** [32]. Antipyrine (27 g) was dissolved in a minimum quantity of 50 % (v/v) aqueous acetic acid (150 mL) and the resulting solution was cooled to 10°C in an ice bath. To this solution, sodium nitrite (10 g) was added in small quantities with constant stirring. A green precipitate was formed immediately and the reaction mixture was kept in an ice bath for 1 h with occasional stirring. The crystals of ligand separated were filtered and washed first with 2 N acetic acid and then with distilled water. Recrystallized from hot 50% (v/v) aqueous methanol and dried over P_4O_{10} *in vacuo*.

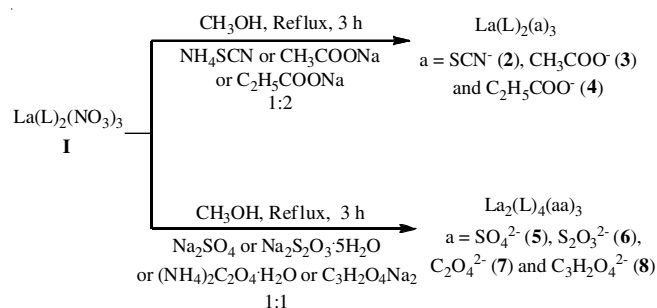


Scheme-I: Synthesis route for the synthesis of ligand L and $\text{La}(\text{L})_2(\text{NO}_3)_3$ (1)

Synthesis of $\text{La}(\text{L})_2(\text{NO}_3)_3$ (1): The $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was synthesized by dissolving a slight excess of La_2O_3 in hot 50 % (v/v) nitric acid. Undissolved La_2O_3 was removed by filtration. The filtrate was concentrated on a water bath to 20% of its original volume and cooled to get the crystals of $\text{La}(\text{NO}_3)_3$. Filtered and dried over P_4O_{10} *in vacuo*.

$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.4330 g; 1 mmol) and ligand (0.4340 g; 2 mmol) were separately dissolved in a minimum amount of acetonitrile. The solutions were mixed and refluxed on a water bath for 2 h. The reaction mixture was transferred into a beaker and cooled to room temperature. Diethyl ether (50 mL) was added to it with vigorous stirring and a reddish-brown mass settled down. The viscous mass was recovered by decanting the supernatant liquid and washed several times with small quantities of hot benzene to remove excess ligand. Complex **1** was washed finally with diethyl ether and dried over P_4O_{10} *in vacuo* (**Scheme-I**).

Synthesis of $\text{La}(\text{L})_2(\text{a})_3$ (2, 3 and 4) [where a = SCN^- (2), CH_3COO^- (3) and $\text{C}_2\text{H}_5\text{COO}^-$ (4)]: The synthetic route of lanthanum(III) complexes of type $\text{La}(\text{L})_2(\text{a})_3$ is shown in **Scheme-II**. $\text{La}(\text{L})_2(\text{NO}_3)_3$ (1) (0.5 g; 0.7 mmol) was dissolved in methanol and was mixed with an aqueous methanolic solution (50 % v/v) of NH_4SCN (0.15 g; 2 mmol), CH_3COONa (0.27 g; 2 mmol), $\text{C}_2\text{H}_5\text{COONa}$ (0.1920 g; 2 mmol) in the synthesis of complexes **2**, **3** and **4**, respectively. The reaction mixture was refluxed on a water bath for 3 h. The resulting solution was concentrated to 10 mL by evaporation on the water bath and the concentrate was cooled. The solid complex precipitated out was collected, washed repeatedly with hot 50 % (v/v) aqueous-methanol and dried over P_4O_{10} *in vacuo*.



Scheme-II: Synthesis route for the synthesis of $\text{La}(\text{L})_2(\text{a})_3$ and $\text{La}_2(\text{L})_4(\text{aa})_3$

Synthesis of $\text{La}_2(\text{L})_4(\text{aa})_3$ (5, 6, 7 and 8) [where aa = SO_4^{2-} (5), $\text{S}_2\text{O}_3^{2-}$ (6), $\text{C}_2\text{O}_4^{2-}$ (7) and $\text{C}_3\text{H}_2\text{O}_4^{2-}$ (8)]: The synthetic route of the lanthanum(III) complexes of the type $\text{La}(\text{L})_2(\text{a})_3$ is shown in **Scheme-II**. $\text{La}(\text{L})_2(\text{NO}_3)_3$ (1) (0.5 g; 0.7 mmol) was dissolved in methanol. This was mixed with an aqueous methanolic solution (50 % v/v) of Na_2SO_4 (0.1420 g; 1 mmol), $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (0.2482 g, 1 mmol), $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (0.1420 g; 1 mmol) and disodium malonate $\text{C}_3\text{H}_2\text{O}_4\text{Na}_2$ (0.1480 g; 1 mmol) in the synthesis of complexes **5**, **6**, **7** and **8**, respectively. The reaction mixture was refluxed on a water bath for 3 h. The resulting solution was concentrated to 10 mL by evaporation on the water bath and the concentrate was cooled. The solid complex precipitated out was collected, washed repeatedly with hot 50 % (v/v) aqueous-methanol and dried over P_4O_{10} *in vacuo*.

RESULTS AND DISCUSSION

All the complexes **1-8** are coloured, non-hygroscopic solids, soluble in acetonitrile, methanol and nitrobenzene and insoluble in benzene, carbon tetrachloride, chloroform, diethyl ether and petroleum ether. The results of elemental analyses

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF THE LANTHANUM(III) COMPLEXES OF L (1-8)

Complex	Colour	m.f.	m.w. Found (calcd.)	Elemental analyses (%): Found (calcd.)			
				C	H	N	La
La(L) ₂ (NO ₃) ₃ (1)	Brown	C ₂₂ H ₂₂ N ₉ O ₁₃ La	701.69 (759.37)	32.28 (34.80)	2.43 (2.92)	15.72 (16.60)	18.27 (18.29)
La(L) ₂ (NCS) ₃ (2)	Yellow	C ₂₅ H ₂₂ N ₉ O ₄ S ₃ La	710.53 (747.60)	42.12 (40.17)	3.98 (2.97)	10.78 (16.86)	18.50 (18.58)
La(L) ₂ (CH ₃ COO) ₃ (3)	Brown	C ₂₈ H ₃₁ N ₆ O ₁₀ La	731.73 (750.49)	44.48 (44.81)	4.60 (4.16)	10.01 (11.20)	17.50 (18.51)
La(L) ₂ (C ₂ H ₅ COO) ₃ (4)	Brown	C ₃₁ H ₃₁ N ₆ O ₁₀ La	718.83 (792.57)	42.37 (46.98)	2.02 (4.71)	16.63 (10.60)	18.54 (17.53)
La ₂ (L) ₄ (SO ₄) ₃ (5)	Brown	C ₄₅ H ₄₅ N ₁₁ O ₁₀ S ₃ La ₂	1401.72 (1433.90)	36.04 (37.69)	3.32 (3.16)	12.01 (10.75)	19.36 (19.37)
La ₂ (L) ₄ (S ₂ O ₃) ₃ (6)	Yellow	C ₄₅ H ₄₅ N ₁₁ O ₁₇ S ₆ La ₂	1410.76 (1482.49)	35.02 (36.47)	3.08 (3.06)	11.01 (10.40)	18.72 (18.74)
La ₂ (L) ₄ (C ₂ O ₄) ₃ (7)	Brown	C ₅₁ H ₄₅ N ₁₁ O ₂₀ La ₂	1367.56 (1409.79)	40.10 (43.45)	3.02 (3.22)	11.12 (10.93)	19.66 (19.71)
La ₂ (L) ₄ (C ₃ H ₂ O ₄) ₃ (8)	Brown	C ₅₄ H ₃₁ N ₁₁ O ₂₀ La ₂	1401.37 (1451.87)	42.12 (44.67)	3.12 (3.54)	11.53 (10.61)	19.10 (19.13)

(C, H, N and La) and other physical properties are presented in Table-1. The analytical data of the complexes indicates 1:2 (metal:ligand) stoichiometry. The data obtained suggest that the complexes may be formulated as La(L)₂(a)₃ where a = NO₃⁻ (**1**), SCN⁻ (**2**), CH₃COO⁻ (**3**) and C₂H₅COO⁻ (**4**) and La₂(L)₄(aa)₃ where aa = SO₄²⁻ (**5**), S₂O₃²⁻ (**6**), C₂O₄²⁻ (**7**) and C₃H₂O₄²⁻ (**8**), respectively.

Molar conductance: The molar conductance (Λ_m) of the La(III) complexes (**1-8**) in three non-aqueous solvents, viz. acetonitrile, methanol and nitrobenzene (10⁻³ M) were measured at room temperature and are listed in Table-2. The molar conductance values obtained are in the range reported for non-electrolytes in the same solvents [33,34]. Thus, the anions present in the complexes are coordinated to the La(III) centre.

TABLE-2
MOLAR CONDUCTANCE Λ_m ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$)
DATA OF La(III) COMPLEXES (10⁻³ M SOLUTION)

Complex	Conductance ($\text{ohm}^{-1} \text{ mol}^{-1} \text{ cm}^2$)			μ_{eff} (B.M.)
	Aceto-nitrile	MeOH	Nitro-benzene	
La(L) ₂ (NO ₃) ₃ (1)	90.93	60.52	8.92	0.00
La(L) ₂ (NCS) ₃ (2)	80.72	72.70	12.24	0.00
La(L) ₂ (CH ₃ COO) ₃ (3)	93.64	58.62	13.49	0.00
La(L) ₂ (C ₂ H ₅ COO) ₃ (4)	98.33	66.72	10.61	0.00
La ₂ (L) ₄ (SO ₄) ₃ (5)	96.43	71.08	14.84	0.00
La ₂ (L) ₄ (S ₂ O ₃) ₃ (6)	89.37	68.42	12.46	0.00
La ₂ (L) ₄ (C ₂ O ₄) ₃ (7)	94.38	66.68	10.33	0.00
La ₂ (L) ₄ (C ₃ H ₂ O ₄) ₃ (8)	85.64	58.63	11.02	0.00

Magnetic susceptibility: The room temperature (28 ± 2 °C) magnetic moments of the complexes are presented in Table-2. All the La(III) complexes were found to be diamagnetic and

their magnetic moment values are in agreement with the Van Vleck values indicating weak interaction of 4f electrons in the metal-ligand bond formation [30]. Hence, the bonding in these complexes is electrostatic.

FT-IR spectra: The most critical IR bands of the ligand L and its La(III) complexes **1-8** are summarized in Table-3. The IR spectrum of the ligand has been previously reported [22]. Two very strong bands observed at 1680 and 1410 cm⁻¹ is attributed to the C=O and N=O stretching vibrations, respectively in the ligand. In all the complexes the $\nu(\text{C}=\text{O})$ bands are red-shifted to about 1620 cm⁻¹ and the $\nu(\text{N}=\text{O})$ bands are shifted to around 1380 cm⁻¹, indicating the coordination of the carbonyl group and the nitroso group in the pyrazolone ring of the ligand to the La(III) ion. The ligand acts as a neutral bidentate ligand coordinating La(III) ion through the carbonyl oxygen and the nitroso oxygen in the complexes. The bands corresponding to $\nu(\text{C}-\text{H})$ of phenyl ring (3020 cm⁻¹), $\nu(\text{C}-\text{H})$ of methyl groups (2980 cm⁻¹), stretching vibrations of pyrazolone and phenyl rings (1560, 1490 and 1430 cm⁻¹), $\nu(\text{C}=\text{C})$ of phenyl ring (1590 cm⁻¹), the bending modes of methyl group (1360 cm⁻¹), C-H twist and wagging (1240 cm⁻¹), $\nu_a(\text{C}-\text{C})$ and $\nu_s(\text{C}-\text{C})$ (1160 and 830 cm⁻¹) and δCH (out-of-plane) of phenyl ring (760 cm⁻¹) in the ligand remain unchanged in the La(III) complexes.

The presence of coordinated nitrate ions in complex **1** are indicated by bands *ca.* 1450 cm⁻¹ (s), 1310 cm⁻¹ (m) and 1030 cm⁻¹ (m) assigned as the ν_4 , ν_1 and ν_2 vibrations of the nitrate of C_{2v} symmetry. The difference between ν_4 and ν_1 may be used to distinguish the binding modes of the nitrate ion. The separation ($\nu_4-\nu_1$) is found to be 140 cm⁻¹, indicating the coordination of the nitrate ion to the metal in a monodentate fashion [35,36]. The IR spectrum of complex **2** exhibits three

TABLE-3
KEY IR SPECTRAL FREQUENCIES (cm⁻¹) OF THE LIGAND L AND ITS La(III) COMPLEXES 1-8

Compound	$\nu(\text{C}=\text{O})$	$\nu(\text{N}=\text{O})$	Additional frequencies due to the anions	
L	1680s	1410s		
1	1620s	1380s	1450s, 1310m, 1030m	ν_4 , ν_1 and ν_2 of the nitrate
2	1620s	1380s	2050s, 840w, 520w	$\nu(\text{CN})$, $\nu(\text{CN})$ and $\delta(\text{NCS})$ of the thiocyanate
3	1620s	1380s	1650s, 1300m	$\nu_a(\text{CO})$, $\nu_s(\text{CO})$ of the acetate
4	1620s	1380s	1650s, 1300m	$\nu_a(\text{CO})$, $\nu_s(\text{CO})$ of the acetate
5	1620s	1380s	1220s, 1130m, 1070w	ν_3 of the sulphate
6	1620s	1380s	1110s	$\nu_a(\text{SO})$ of the thiosulphate
7	1620s	1380s	1710s, 1320m	$\nu_a(\text{CO})$, $\nu_s(\text{CO})$ of the oxalate
8	1620s	1380s	1720s, 1320m	$\nu_a(\text{CO})$, $\nu_s(\text{CO})$ of the malonate

bands at 2050, 840 and 520 cm^{-1} , which are assigned, respectively to the $\nu(\text{CN})$, $\nu(\text{CS})$ and $\delta(\text{NCS})$ modes of the coordinated thiocyanate anion. It has been ascertained that $\nu(\text{CN})$ occurs at a lower wavenumber around 2050 cm^{-1} in N-bonded complexes as compared to the position in the case of S-bonded complexes appearing around 2100 cm^{-1} . Moreover, $\nu(\text{CS})$ mode appears in the range 860–780 cm^{-1} for N-bonded complexes, while it appears in the range 720–690 cm^{-1} for S-bonded complexes. N-bonded complexes also exhibit a single sharp band corresponding to $\delta(\text{NCS})$ mode around 480 cm^{-1} , whereas the S-bonded complexes show several bands of low intensity near 420 cm^{-1} . Hence, the thiocyanate ions of the present complex are coordinated unidentately to the lanthanide ions through the nitrogen atom [37–39].

The IR spectra of the lanthanum acetate (**3**) and propionate (**4**) complexes show two bands at 1650(s) and 1300(m) cm^{-1} , which are assigned, respectively to asymmetric and symmetric stretching vibrations of carboxylate ion. The ν_a and ν_s bands of the uncoordinated carboxylate acid occur at 1560 and 1420 cm^{-1} , respectively. The ν_a mode is shifted to higher frequency, whereas ν_s mode is shifted to a lower frequency. This shift indicates the coordination of both acetate and propionate ions to La(III) ion in the complexes. The value of $\Delta\nu = \nu_a - \nu_s$ in both the complexes is 223 cm^{-1} which is characteristic of monodentate coordination of the acetate and propionate anions [40].

The IR spectrum of the lanthanum sulphate complex **5** exhibits three additional bands appearing at 1220, 1130 and 1070 cm^{-1} . These three bands are assigned to the split bands of the ν_3 mode of the sulphate ion. Splitting of the ν_3 mode indicates lowering of the symmetry to C_{2v} and the bidentate coordination of the sulphate ion in the complex [35,41]. In the thiosulphate complex **6**, a strong band is observed at 1110 cm^{-1} , which is attributed to $\nu_a(\text{SO})$ mode of the coordinated thiosulphate ion. The uncoordinated thiosulphate ion has $\nu_a(\text{SO})$ mode at 1130 cm^{-1} in the spectrum of sodium thiosulphate. It has been reported that the thiosulphate ion is coordinated bidentately through its oxygen atom if $\nu_a(\text{SO})$ mode appears at a region lower than 1130 cm^{-1} . It is thus inferred that in the present complex, thiosulphate ions are coordinated bidentately through two of its oxygen atoms [42].

In the IR spectra of oxalate and malonate complexes of La(III), complexes **7** and **8**, two bands are observed at 1720–1710 and 1320 cm^{-1} , which are attributed, respectively to $\nu_a(\text{CO})$ and $\nu_s(\text{CO})$ modes of the coordinated carboxylate ions. When compared with the vibrational modes of the free carboxylic acids, these two bands are shifted in the spectra of the complexes, indicating their coordination with the metal centre. The band corresponding to the asymmetric stretching is shifted to a higher frequency, while the band due to symmetric stretching is shifted to a lower frequency. The positions of the bands due to ν_a and ν_s suggest that both the carboxylate ions (oxalate and malonate) are coordinated bidentately in the respective complexes [35,40,43].

Electronic spectra: The electronic spectrum of the ligand exhibits three bands ca. 335, 275 and 235 nm. The weak band ca. 335 nm is assigned to the $n \rightarrow \pi^*$ transition. The other two

bands, which are intense bands appearing at 275 and 235 nm, are assigned to $\pi \rightarrow \pi^*$ transitions of the ligand, the latter band being more intense than the former. The spectra of the complexes **1–8** also exhibit these three bands, but they are shifted to slightly longer wavelengths supporting the coordination of the ligand to the central metal ion. Also, the electronic spectra of the complexes show an additional broad band in the visible region with a λ_{max} at 390 nm. This band is attributed to strong $L \rightarrow M$ charge-transfer transitions in the complexes. The absence of $f-f$ transitions is due to the absence of electrons in the 4f orbitals of La(III) ion.

Based on the results of the above physico-chemical and spectral studies, the following tentative structures (Figs. 1 and 2) has been proposed for the lanthanum(III) complexes (**1–8**). In these complexes, 4-nitrosoantipyrine acts as a neutral bidentate ligand coordinating the lanthanum ions through the ring carbonyl oxygen and the nitroso oxygen. Among the anions, monovalent anions such as nitrate, thiocyanate, acetate and propionate ions are coordinated unidentately, while divalent anions sulphate, thiosulphate, oxalate and malonate ions are coordinated bidentately to the La(III) ion.

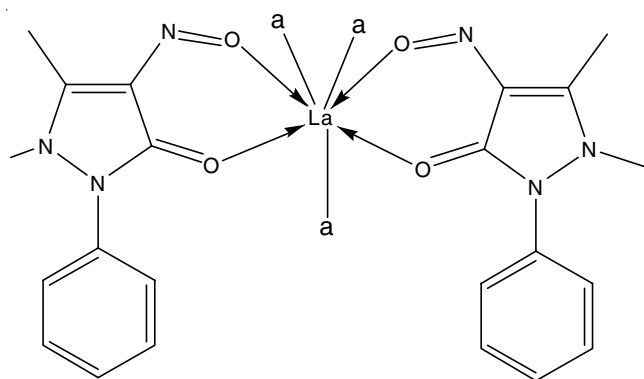


Fig. 1. Tentative structures of complexes of the type $\text{La}(\text{L})_2(\text{a})_3$ [$\text{a} = \text{NO}_3^-$ (**1**), SCN^- (**2**), CH_3COO^- (**3**) and $\text{C}_2\text{H}_5\text{COO}^-$ (**4**)]

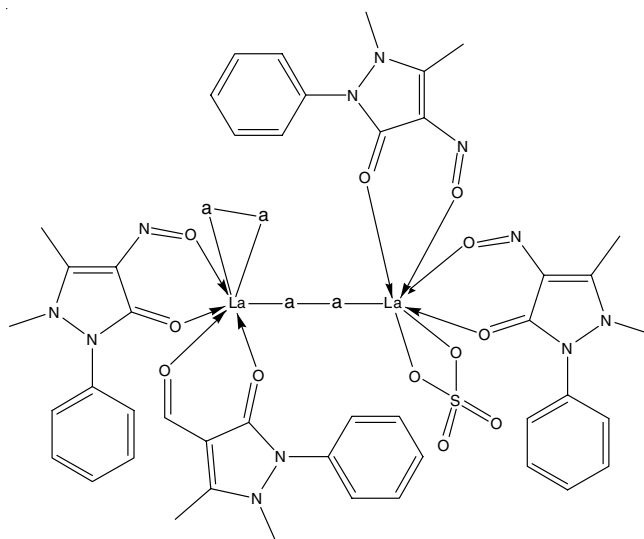


Fig. 2. Tentative structures of complexes of the type $\text{La}_2(\text{L})_4(\text{aa})_3$ [$\text{aa} = \text{SO}_4^{2-}$ (**5**), $\text{S}_2\text{O}_3^{2-}$ (**6**), $\text{C}_2\text{O}_4^{2-}$ (**7**) and $\text{C}_3\text{H}_2\text{O}_4^{2-}$ (**8**)]

Conclusion

Eight lanthanum(III) complexes of 4-nitrosoantipyridine with the general formula $[La(L)_2(aa)_3]$ and $[La_2(L)_4(aa)_3]$, ($a =$ nitrate, thiocyanate, acetate and propionate ions, $aa =$ sulphate, thiosulphate, oxalate and malonate ions) were synthesized and characterized based on elemental analysis, molar conductivity, magnetic susceptibility and spectroscopic studies. The conductance studies in acetonitrile, methanol and nitrobenzene indicate non-electrolytic behaviour of these complexes. Magnetic moments of the complexes at room temperature show that the $4f$ electrons present in lanthanide ions have not been disturbed much by the ligand field and hence, the involvement of $4f$ orbitals in bonding is less probable. The IR spectral studies show that 4-nitrosoantipyridine acts as a neutral bidentate ligand coordinating the lanthanide ions through the carbonyl oxygen and the nitroso oxygen. The monovalent anions such as nitrate, thiocyanate, acetate and propionate ions are coordinated to the lanthanide ions in a unidentate fashion, while the divalent anions sulphate, thiosulphate, oxalate and malonate ions are coordinated in a bidentate fashion.

ACKNOWLEDGEMENTS

The authors are thankful to IIT Chennai, University of Kerala, Thiruvananthapuram and Maharaja's College, Ernakulam, India for the spectral analyses.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

- S. Procházková, J. Hraníček, V. Kubíček and P. Hermann, *Polyhedron*, **111**, 143 (2016); <https://doi.org/10.1016/j.poly.2016.03.039>
- Z.-Q. Xu, X.-J. Mao, L. Jia, J. Xu, T.-F. Zhu, H.-X. Cai, H.-Y. Bie, R.-H. Chen and T.-L. Ma, *J. Mol. Struct.*, **1102**, 86 (2015); <https://doi.org/10.1016/j.molstruc.2015.07.047>
- X. Yang, R.A. Jones and S. Huang, *Coord. Chem. Rev.*, **273-274**, 63 (2014); <https://doi.org/10.1016/j.ccr.2013.11.012>
- S.-D. Han, X.-H. Miao, S.-J. Liu and X.-H. Bu, *Inorg. Chem. Front.*, **1**, 549 (2014); <https://doi.org/10.1039/C4QI00073K>
- R.W. Wen, S.D. Han, G.J. Ren, Z. Chang, Y.W. Li and X.H. Bu, *Dalton Trans.*, **44**, 10914 (2015); <https://doi.org/10.1039/C4DT02445A>
- D. Tian, Y. Li, R.-Y. Chen, Z. Chang, G.-Y. Wang and X.-H. Bu, *J. Mater. Chem. A Mater. Energy Sustain.*, **2**, 1465 (2014); <https://doi.org/10.1039/C3TA13983B>
- N. Cakic, S. Gündüz, R. Rengarasu and G. Angelovski, *Tetrahedron Lett.*, **56**, 759 (2015); <https://doi.org/10.1016/j.tetlet.2014.12.087>
- H. Zhou, Y. Jiang, M. Chen, Y. Wang, Y. Yao, B. Wu and D. Cui, *J. Organomet. Chem.*, **763-764**, 52 (2014); <https://doi.org/10.1016/j.jorganchem.2014.04.017>
- M.G. Lahoud, R.C.G. Frem, D.A. Gállico, G. Bannach, M.M. Nolasco, R.A.S. Ferreira and L.D. Carlos, *J. Lumin.*, **170**, 357 (2016); <https://doi.org/10.1016/j.jlumin.2015.08.050>
- Y. Hasegawa, Y. Kitagawa and T. Nakanishi, *NPG Asia Mater.*, **10**, 52 (2018); <https://doi.org/10.1038/s41427-018-0012-y>
- B. Cristóvão and Z. Hnatejko, *J. Mol. Struct.*, **1088**, 50 (2015); <https://doi.org/10.1016/j.molstruc.2015.01.032>
- R. Singh, K. Sharma and R.V. Singh, *J. Sulfur Chem.*, **31**, 61 (2010); <https://doi.org/10.1080/17415990903173529>
- S. Radhika, M. Kanthimathi, R. Parthasarathi and B.U. Nair, *Transition Met. Chem.*, **32**, 362 (2007); <https://doi.org/10.1007/s11243-006-0180-4>
- E. Niyama, H.F. Brito, M. Cremona, E.E.S. Teotonio, R. Reyes, G.E.S. Brito and M.C.F.C. Felinto, *Spectrochim. Acta A Mol. Spectrochim. Acta*, **61**, 2643 (2005); <https://doi.org/10.1016/j.saa.2004.10.006>
- S. Cotton, Lanthanides and Actinides, John Wiley & Sons Ltd. (2006).
- E.G. Moore, A.P.S. Samuel and K.N. Raymond, *Acc. Chem. Res.*, **42**, 542 (2009); <https://doi.org/10.1021/ar800211j>
- A. Hussain and A.R. Chakravarty, *J. Chem. Sci.*, **124**, 1327 (2012); <https://doi.org/10.1007/s12039-012-0332-3>
- H. Jayasankar and P. Indrasenan, *Indian J. Chem.*, **27A**, 545 (1988).
- B. Kuncheria and P. Indrasenan, *Indian J. Chem.*, **27A**, 1005 (1988).
- H. Jayasankar and P. Indrasenan, *J. Less Common Met.*, **132**, 43 (1987); [https://doi.org/10.1016/0022-5088\(87\)90172-X](https://doi.org/10.1016/0022-5088(87)90172-X)
- S. Umetani and H. Freiser, *Inorg. Chem.*, **26**, 3179 (1987); <https://doi.org/10.1021/ic00266a023>
- H. Jayasankar and P. Indrasenan, *Indian J. Chem.*, **27A**, 362 (1988).
- D. Zhou, Q. Li, C. Huang, G. Yao, S. Umetani, M. Matsui, L. Ying, A. Yu and X. Zhao, *Polyhedron*, **16**, 1381 (1997); [https://doi.org/10.1016/S0277-5387\(96\)00382-8](https://doi.org/10.1016/S0277-5387(96)00382-8)
- J. Li, L. Zhang, L. Liu, G. Liu, D. Jia and G. Xu, *Inorg. Chim. Acta*, **360**, 1995 (2007); <https://doi.org/10.1016/j.ica.2006.10.010>
- A.S. Orabi, *Maced. J. Chem. Chem. Eng.*, **32**, 25 (2013).
- E.M. Jincy and M.K. Muraleedharan Nair, *Asian J. Chem.*, **30**, 1037 (2018); <https://doi.org/10.14233/ajchem.2018.21151>
- I.M. Kolthoff and P.J. Elving, Treatise on Analytical Chemistry, vol. 8, Part II, Interscience: New York (1963).
- A.I. Vogel, A Text-book of Quantitative Inorganic Analysis, edn 3, Longman: London (1961).
- W.G. Palmer, Experimental Physical Chemistry, Cambridge University Press: Cambridge (1954).
- J.H. Van Vleck and N. Frank, *Phys. Rev.*, **34**, 1494 (1929); <https://doi.org/10.1103/PhysRev.34.1494>
- A. Earnshaw, Introduction to Magnetochemistry, Academic Press: New York (1968).
- B. Nanda, S. Padmanavan, B. Tripathy and A.S. Mitra, *J. Indian Chem. Soc.*, **52**, 533 (1975).
- W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971); [https://doi.org/10.1016/S0010-8545\(00\)80009-0](https://doi.org/10.1016/S0010-8545(00)80009-0)
- I. Ali, W.A. Wani and K. Saleem, *Synth. React. Inorg.*, **43**, 1162 (2013); <https://doi.org/10.1080/15533174.2012.756898>
- K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B, Wiley, edn 5th (1997).
- N.F. Curtis and Y.M. Curtis, *Inorg. Chem.*, **4**, 804 (1965); <https://doi.org/10.1021/ic50028a007>
- A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 1665 (1965); <https://doi.org/10.1021/ic50033a032>
- M.M. Chamberlain and J.C. Bailar Jr., *J. Am. Chem. Soc.*, **81**, 6412 (1959); <https://doi.org/10.1021/ja01533a021>
- A. Turco and C. Pecile, *Nature*, **191**, 66 (1961); <https://doi.org/10.1038/191066a0>
- G.B. Deacon and R.J. Phillips, *Coord. Chem. Rev.*, **33**, 227 (1980); [https://doi.org/10.1016/S0010-8545\(00\)80455-5](https://doi.org/10.1016/S0010-8545(00)80455-5)
- K. Nakamoto, J. Fujita, S. Tanaka and M. Kobayashi, *J. Am. Chem. Soc.*, **79**, 4904 (1957); <https://doi.org/10.1021/ja01575a020>
- A.N. Freedman and B.P. Straughan, *Spectrochim. Acta A Mol. Spectrosc.*, **27A**, 1455 (1971); [https://doi.org/10.1016/0584-8539\(71\)80095-8](https://doi.org/10.1016/0584-8539(71)80095-8)
- S. Hussain, X. Chen, W.T.A. Harrison, S. Ahmad, M.R.J. Elsegood, I.U. Khan and S. Muhammad, *Front Chem.*, **7**, 260 (2019); <https://doi.org/10.3389/fchem.2019.00260>