

Lanthanide(III) Complexes of 2-(N-Salicylideneamino)-4-Phenylthiazole

G.N. SASIDHARAN*, K. MOHANAN† and A.N. LAKSHMI PRABHA‡
Department of Chemistry, Government College, Chavara, Kollam-691 583, India

Lanthanide(III) complexes of 2-(N-salicylideneamino)-4-phenylthiazole (HSAT) have been synthesised and characterised by elemental analytical, thermogravimetric, molar conductance, UV-visible, IR and NMR spectral data. The ligand coordinates to the lanthanide(III) ion in a tridentate fashion without deprotonation, giving complexes of the type $[\text{Ln}(\text{HSAT})_2(\text{NO}_3)_3]$ and $[\text{Ln}(\text{HSAT})_2(\text{H}_2\text{O})_3\text{Cl}_3]$. The spectral data reveal that the ligand is bonded to the lanthanide ion through azomethine nitrogen, ring nitrogen and phenolic oxygen without deprotonation. The nitrate group acts in a bidentate fashion. The ligand and the metal complexes exhibit antibacterial and antifungal activities.

Key Words: Lanthanide, Complexes, 2-(N-Salicylideneamino)-4-phenylthiazole.

INTRODUCTION

Lanthanide(III) ions are known to pose interesting bonding interactions with various types of ligands. Although extensive literature is available on metal complexes formed by heterocyclic Schiff bases with d-block elements, those of lanthanides have received comparatively less attention.¹ Lanthanide ions are often used as spectroscopic probe as surrogates for calcium ion in the studies of biological system as well as diagnostic agent in clinical medicine.² In this communication we describe the synthesis, characterisation, thermal behaviour, and antimicrobial activities of some lanthanide(III) chloride and lanthanide(III) nitrate complexes with a host of heterocyclic Schiff base derived from salicylaldehyde and 2-amino-4-phenylthiazole.

EXPERIMENTAL

All the chemicals used were AR grade. Commercial solvents were distilled and used for synthesis. For physico-chemical measurements, they were purified by standard methods. Infrared spectra were recorded on a Shimadzu 8201 PC FT infrared spectrophotometer and electronic spectra were recorded on a Hitachi 320

*Department of Chemistry, University College, Trivandrum-695 034, Kerala, India.

‡Chemical Examiners Laboratory, Trivandrum-695 037, Kerala, India.

UV-visible spectrophotometer. Molar conductance values of the complexes were determined in DMSO, DMF and nitrobenzene (10^{-3} M solution) using a Toshniwal conductivity bridge. Percentages of carbon, hydrogen and nitrogen were determined microanalytically and sulphur was estimated by standard method. The metal content was estimated by oxalate-oxide method.³ Thermal analysis was carried out in nitrogen atmosphere, using a Shimadzu TGA-50H differential thermomicrobalance. The ligand and some selected metal complexes were screened for antibacterial and antifungal activities by agar diffusion method.⁴

Preparation of ligand: 2-Amino-4-phenylthiazole (0.01 mol), prepared by a reported method,⁵ was dissolved in methanol (30 mL). To this solution, salicylaldehyde (0.01 mol) dissolved in 20 mL methanol was added slowly with constant stirring. Added a drop of piperidine and the mixture was refluxed on a water-bath for about 2 h. It was then concentrated to half its original volume and allowed to crystallise. The Schiff base formed was filtered and dried. It was further purified by recrystallisation from methanol.

Preparation of complexes: Lanthanide(III) nitrates/chlorides were prepared by dissolving the respective oxide in 50% nitric acid/hydrochloric acid and crystallizing the salt on evaporating the solution on a steam-bath. The complexes were prepared by the following procedure.

To a magnetically stirred and warmed methanolic solution (50 mL) of the ligand (0.01 mol, pH adjusted to 5), a methanolic solution of the hydrated lanthanide(III) nitrate/chloride (0.005 mol) was added. After continued refluxing for 5–6 h, the resulting solution was allowed to stand overnight and the powdery material formed was filtered, washed successively with water, ethanol and ether. Finally, the complex was dried in vacuum over P_4O_{10} .

RESULTS AND DISCUSSION

Analytical data are in good agreement with the formulation of the complexes as in Tables 1 and 2. All the complexes are non-hygroscopic and possess good keeping qualities. Molar conductance values of the complexes adequately confirm the non-electrolytic nature of the complexes.⁶ No loss in weight has been observed on heating the aquachloro complexes at 373 K *in vacuo* over P_4O_{10} . This is a clear evidence that the water molecules are coordinated to the lanthanide ion and not held loosely in the crystal lattice. This has been further confirmed by thermal analysis. In the case of nitrate complexes, coordination by water molecule has not been observed.

Ultraviolet spectrum of the ligand showed a peak at 325 nm, characteristic of enol-imine form of the ligand. In the metal chelates, this band did not undergo any appreciable change, indicating that the ligand moiety exists in the complexes in enol-imine form itself. The visible spectral bands of lanthanides are hypersensitive to stereochemistry.⁸ The visible spectra of the complexes have shown a shift of spectral bands towards lower energy as compared to those of aqueous ions due to nephelauxetic effect. The observed red shift indicates the involvement of metal 4f and ligand orbitals in bond formation.

TABLE-1
ANALYTICAL DATA AND OTHER DETAILS OF LANTHANIDE(III) CHLORIDE COMPLEXES
OF 2-(N-SALICYLIDENEAMINO)-4-PHENYLTHIAZOLE

Complex	Yield (%)	Analytical data (%)*							Molar conductance ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)				
		Ln	C	H	N	S	DMSO	DMF	Nitrobenzene				
[La(HSAT) ₂ (H ₂ O) ₃ Cl ₃]	78	15.95 (16.16)	44.18 (44.67)	3.44 (3.49)	6.42 (6.51)	7.34 (7.44)	7.2	10.7	4.6				
[Pr(HSAT) ₂ (H ₂ O) ₃ Cl ₃]	80	16.14 (16.35)	44.18 (44.57)	3.43 (3.48)	6.41 (6.50)	7.32 (7.43)	7.3	9.5	4.5				
[Nd(HSAT) ₂ (H ₂ O) ₃ Cl ₃]	81	16.43 (16.67)	44.00 (44.40)	3.42 (3.49)	6.38 (6.47)	7.30 (7.40)	7.6	9.4	5.7				
[Sm(HSAT) ₂ (H ₂ O) ₃ Cl ₃]	77	17.00 (17.27)	43.72 (44.11)	3.35 (3.47)	6.34 (6.43)	7.25 (7.35)	7.4	10.6	5.6				
[Eu(HSAT) ₂ (H ₂ O) ₃ Cl ₃]	79	17.14 (17.41)	43.66 (44.02)	3.06 (3.46)	6.01 (6.41)	7.00 (7.33)	7.8	10.8	5.8				
[Gd(HSAT) ₂ (H ₂ O) ₃ Cl ₃]	79	17.65 (17.91)	43.28 (43.74)	3.36 (3.44)	6.29 (6.38)	7.19 (7.29)	7.8	10.3	5.9				
[Dy(HSAT) ₂ (H ₂ O) ₃ Cl ₃]	78	18.15 (18.40)	42.98 (43.48)	3.34 (3.42)	6.25 (6.34)	7.14 (7.24)	7.5	10.1	4.4				
[Tm(HSAT) ₂ (H ₂ O) ₃ Cl ₃]	80	18.73 (18.99)	42.71 (43.17)	3.32 (3.39)	6.20 (6.29)	7.09 (7.19)	7.9	11.8	5.1				
[Yb(HSAT) ₂ (H ₂ O) ₃ Cl ₃]	78	19.10 (19.36)	42.60 (42.97)	3.30 (3.38)	6.17 (6.26)	7.06 (7.16)	7.3	10.3	3.6				
[Lu(HSAT) ₂ (H ₂ O) ₃ Cl ₃]	76	19.28 (19.54)	42.40 (42.88)	3.30 (3.38)	6.16 (6.25)	7.04 (7.14)	7.5	10.4	3.8				

* Calculated values are given in brackets

TABLE-2
ANALYTICAL DATA AND OTHER DETAILS OF LANTHANIDE(III) NITRATE COMPLEXES
OF 2-(N-SALICYLIDENEAMINO)-4-PHENYLTHIAZOLE

Complex	Yield (%)	Analytical data (%) [*]							Molar conductance (ohm ⁻¹ cm ² mol ⁻¹)			
		Ln	C	H	N	S	DMSO	DMF	Nitrobenzene			
[La(HSAT) ₂ (NO ₃) ₃]	78	15.49 (15.69)	42.88 (43.88) [*]	2.67 (2.73)	10.92 (11.07)	7.13 (7.23)	7.3	10.3	3.6			
[Pr(HSAT) ₂ (NO ₃) ₃]	74	15.68 (15.88)	42.81 (43.29)	2.66 (2.73)	10.89 (11.04)	7.11 (7.21)	7.9	10.8	3.8			
[Nd(HSAT) ₂ (NO ₃) ₃]	72	15.95 (16.19)	42.77 (43.12)	2.65 (2.72)	10.86 (11.00)	7.09 (7.19)	7.7	11.7	4.4			
[Sm(HSAT) ₂ (NO ₃) ₃]	78	16.51 (16.77)	42.48 (42.83)	2.63 (2.69)	10.78 (10.93)	7.04 (7.14)	7.3	10.6	3.7			
[Eu(HSAT) ₂ (NO ₃) ₃]	82	16.72 (16.92)	42.15 (42.75)	2.49 (2.69)	10.71 (10.91)	7.00 (7.12)	8.1	11.1	3.2			
[Gd(HSAT) ₂ (NO ₃) ₃]	80	17.15 (17.40)	41.95 (42.50)	2.61 (2.68)	10.70 (10.85)	6.98 (7.08)	7.2	12.1	3.3			
[Dy(HSAT) ₂ (NO ₃) ₃]	81	17.64 (17.88)	41.82 (42.26)	2.60 (2.65)	10.63 (10.78)	6.94 (7.04)	8.5	12.4	2.1			
[Tm(HSAT) ₂ (NO ₃) ₃]	80	18.21 (18.46)	41.51 (41.96)	2.58 (2.64)	10.56 (10.71)	6.89 (6.99)	7.3	11.3	3.9			
[Yb(HSAT) ₂ (NO ₃) ₃]	81	18.57 (18.82)	41.22 (41.77)	2.57 (2.63)	10.51 (10.66)	6.86 (6.96)	8.4	12.7	3.5			
[Lu(HSAT) ₂ (NO ₃) ₃]	78	18.75 (18.99)	41.13 (41.69)	2.56 (2.63)	10.49 (10.64)	6.84 (6.95)	7.1	10.3	2.8			

^{*} Calculated values are given in brackets

Infrared spectrum of the ligand showed a medium intensity band at 1645 cm^{-1} assignable to azomethine group and a broad band in the range $3400\text{--}3100\text{ cm}^{-1}$ characteristic of internally hydrogen bonded OH group. The phenolic $\nu(\text{C—O})$ is observed at 1300 cm^{-1} . The band due to $\nu(\text{C}=\text{N})$ of the ring is observed at 1612 cm^{-1} . In the metal complexes, the azomethine $\nu(\text{C}=\text{N})$ is depressed by $ca. 25\text{ cm}^{-1}$ indicating the involvement of azomethine nitrogen in bond formation.⁹ The band due to phenolic OH becomes less broad, showing a peak centred at $ca. 3300\text{ cm}^{-1}$ and the $\nu(\text{C—O})$ is slightly shifted towards higher frequency by $ca. 15\text{ cm}^{-1}$, indicating that the oxygen of the phenolic group is coordinated to the metal ion without deprotonation. This type of coordination by phenolic oxygen without deprotonation has already been reported.⁹ However, in the spectra of aquachloro complexes, the above band is overlapped by the band due to coordinated water, so that a broad band with an additional peak $ca. 3450\text{ cm}^{-1}$ is also observed in the range $3600\text{--}3000\text{ cm}^{-1}$ region. The band at 1612 cm^{-1} in the free ligand assignable to the ring $\nu(\text{C}=\text{N})$ is slightly shifted to lower frequency in the metal complex. The negative shift of this band is a clear indication of coordination by ring nitrogen.¹⁰ Apart from this, the band appearing at 2600 cm^{-1} in the ligand, attributable to thiazole ring is shifted to $ca. 2550\text{ cm}^{-1}$ in all the complexes, gives added evidence of the coordination of the ring nitrogen.¹¹ Bonding mode of nitrate ion is also revealed by infrared spectral data. The nitrate complexes exhibited three additional strong bands centred around 1480 cm^{-1} , 1280 cm^{-1} and 1025 cm^{-1} which are not present in the free ligand. These are due to ν_4 , ν_1 and ν_2 vibrations of coordinated nitrate ion. The magnitude of separation between ν_1 and ν_4 in the complexes is found to be $> 200\text{ cm}^{-1}$, which clearly indicates that the nitrate group is coordinated to the metal ion in a bidentate fashion.¹² There are recent reports that high coordination number is possible for lanthanide(III) complexes with similar type of ligands and nitrate ion.¹³ The non-ligand bands of medium intensity observed in the regions $440\text{--}430\text{ cm}^{-1}$, $360\text{--}350\text{ cm}^{-1}$ and $325\text{--}310\text{ cm}^{-1}$ can be assigned to $\nu(\text{Ln—N})$, $\nu(\text{Ln—O})$ and $\nu(\text{Ln—Cl})$ modes respectively.¹⁴

Proton magnetic resonance spectrum of the ligand recorded in DMSO-d_6 reveals peaks in three regions. One of them between 6.2 and $8.2\ \delta$ is characteristic of aromatic protons. The second signal appearing at $8.27\ \delta$ is due to aldehydic proton. The signals observed at $10.59\ \delta$ in the free ligand and at $10.41\ \delta$ in $[\text{La}(\text{HSAT})_2(\text{NO}_3)_3]$ are due to phenolic proton. This observation further confirms the conclusion drawn on the basis of IR spectra regarding the coordination of phenolic oxygen without deprotonation. The peak positions of the phenolic proton in the free ligands as well as in the complex indicate that the interaction between the phenolic oxygen atom and the lanthanide(III) ion does not increase the acidity sufficiently for ionisation of the proton.⁹ Hence the phenolic oxygen coordinates to the lanthanide(III) ion without deprotonation. Thiazole proton signal appearing at $7.95\ \delta$ is measured with the signal of the aromatic protons.

Thermogravimetric studies

The complexes $[\text{La}(\text{HSAT})_2(\text{NO}_3)_3]$ and $[\text{La}(\text{HSAT})_2(\text{H}_2\text{O})_3\text{Cl}_3]$ have been subjected to thermogravimetric analysis. The aquachloro complex has decom-

posed in three stages, while the nitrate complex has decomposed in two stages. The formed complex has been stable up to 393 K. The first stage of decomposition of this complex has started at 393 K and completed at 413 K. The mass loss has been equivalent to three moles of coordinated water per mole of the complex. The second stage of decomposition has taken place in the temperature range 453–626 K and the third stage occurred in the range 643–828 K. The decomposition was complete at 883 K and the final product obtained has been La_2O_3 without forming any stable intermediate. However, in the nitrate complex the decomposition started at 440 K and two stage decomposition pattern has been observed in the temperature range 443–573 K and 653–823 K. The final residue obtained has been La_2O_3 . The weight loss obtained was in good agreement with calculated values and values obtained by independent pyrolysis. Apart from the thermal stability of the two complexes, this study also provided adequate support for the formulation of the above complexes.

Biological activity

Antibacterial and antifungal activities of HSAT, $[\text{La}(\text{HSAT})_2(\text{NO}_3)_3]$ and $[\text{La}(\text{HSAT})_2(\text{H}_2\text{O})_3\text{Cl}_3]$ have been studied against some bacteria and fungi, viz., *Escherichia coli*, *Staphylococcus aureus*, *Shigella caure*, *Aspergillus niger* and *Candida albicans*.

It has been observed that the complexes are more active than the free ligand, that is, chelation enhanced the activity. The increased activity of the complexes is due to a comparatively faster diffusion of the metal complexes as a whole through the cell membrane of the bacteria and fungi. It has been also observed that the presence of chloride ion in the coordination sphere further increased the activity when compared to the nitrate complex.

REFERENCES

1. A.A.T. Ramadan, *Thermochim. Acta*, **206**, 327 (1992).
2. H.G. Brittain, F.S. Richardson and R.B. Martin, *J. Am. Chem. Soc.*, **98**, 8255 (1978).
3. I.M. Kalthaff and P.S. Elving, *Treatise on Analytical Chemistry*, Vol. VIII, Part II, Interscience, New York (1963).
4. O.E. Offiong and S. Martelli, *IL Farmaco*, **49**, 513 (1994).
5. R.M. Dodson and L.C. King, *J. Am. Chem. Soc.*, **67**, 2242 (1945).
6. W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
7. R.C. Burrows and J.C. Bailar (Jr.), *J. Am. Chem. Soc.*, **88**, 4150 (1966).
8. D.G. Karrakar, *Inorg. Chem.*, **6**, 1863 (1967).
9. G.F. De sa, E. Giesbrecht and L.C. Thompson, *J. Inorg. Nucl. Chem.*, **37**, 109 (1975).
10. K. Krishnankutty and D.K. Babu, *J. Indian Chem. Soc.*, **73**, 379 (1996).
11. H.S. Verma, A. Pal, R.C. Saxena and A.K. Katiyar, *J. Indian Chem. Soc.*, **60**, 83 (1983).
12. N.R. Curtis and Y.M. Curtis, *Inorg. Chem.*, **4**, 804 (1965).
13. K. Singh and B.N. Agarwala, *Synth. React. Inorg. Met.-Org. Chem.*, **26**, 473 (1996).
14. R.K. Agarwal and R.K. Sarin, *Polyhedron*, **12**, 2411 (1994).