

Synthesis and Characterization of Ternary Hetero Chelates of La(III), Pr(III), Nd(III) and Sm(III)

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Ternary hetero chelates of La(III), Pr(III), Nd(III) and Sm(III) with 7-hydroxy-4-phenyl-6-(α -naphthyl)-aminomethyl coumarin (HPAC) as primary and 2-thiopyrogallol as co-ligand have been synthesised and characterised on the basis of analytical, magnetic, spectral and thermal studies. The chelates have the general formula $[Ln(HPAC)(TG)X_2]$, where $Ln = La(III), Pr(III), Nd(III), \text{ and } Sm(III)$, HPAC = 7-hydroxy-4-phenyl-6-(α -naphthyl)-aminomethyl coumarin, TG = 2-thiopyrogallol (mono deprotonated), $X = Cl, NO_3$. The lower Λ_m values (4.0-4.8 moles) in DMSO indicate their non-electrolytic nature. The compounds are non-hygroscopic and air stable. They are insoluble in common organic solvents but dissolve in DMSO and DMF considerably. The magnetic moment and reflectance spectral data of the complexes suggested octahedral configuration. IR spectra of the ternary chelates showed bidentate behaviour of both the ligands. In HPAC, nitrogen atom of —NH group and oxygen of —OH group form bond with the metal ion while TG participates through the oxygen atom of —OH group and sulphur of deprotonated —SH group.

All the complexes decompose endothermally at $\sim 430^\circ C$ with the elimination of HPAC. In the temperature range $670-730^\circ C$, thiopyrogallol molecule is also lost and finally, a metallic oxide residue is obtained.

INTRODUCTION

The Mannich bases of 7-hydroxy coumarin derivatives synthesised with aliphatic, aromatic and heterocyclic amines have been found to have antibacterial activity¹⁻³. The complexes of sulphur containing ligands are of much interest due to their increased commercial value. Here we report the spectral and thermal characterisation of the ternary chelates of La(III), Pr(III), Nd(III) and Sm(III) with 7-hydroxy-4-phenyl-6-(α -naphthyl)-aminomethyl coumarin as primary and 2-thiopyrogallol as co-ligand.

Materials and methods

7-Hydroxy-4-phenyl-6-(α -naphthyl)-amino methyl coumarin was synthesised by refluxing a mixture of 7-hydroxy-4-phenyl coumarin (0.01 mol), α -naphthyl amine (0.01 mol) and formalin (40%) in aqueous ethanol for 2 h and crystallising the solid product from DMF. Yield, 60%, m.p. $198^\circ C$. 2-Thio pyrogallol was obtained by following the procedure of Pantlitschke and Banger⁴. All chemicals used were of A.R. grade.

Conductivity measurements were carried out on Toshniwal conductivity bridge. IR spectra were recorded on Perkin Elmer 621 spectrophotometer. The

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magnetic susceptibility at room temperature was determined on Gouy's electromagnetic balance and corrected for diamagnetism⁵. The metal contents were determined as metal oxides⁶.

Preparation and isolation of the chelates

The ternary chelates were synthesised by refluxing a mixture of 10 mmol ethanolic solution of each of Ln(III) chloride/nitrate, HPAC and TG in 1:1:1 mole ratio for 2–3 h on a water bath at about 70°C and cooling at room temperature. The precipitated compounds were filtered off and washed with ethanol, acetonitrile and a little of dry ether to remove the excess of ligand and dried *in vacuo* over P₄O₁₀.

RESULTS AND DISCUSSION

Analytical data reported in Table-1 suggested the formula [Ln(C₂₆H₁₉NO₃)(C₆H₅O₂S)_X]₂, where Ln = La(III), Pr(III), Nd(III) and Sm(III) and X = Cl or NO₃ for the chelates. The compounds are insoluble in ethanol, acetone, chloroform and benzene but show considerable solubility in DMSO and DMF. They are non-electrolytes as evidenced by their low conductance data (4.0–4.8 mhos) in DMSO. The magnetic moments of the complexes are within the predicted range^{7, 8}.

TABLE-1
ANALYTICAL AND MAGNETIC MOMENT DATA OF
La(III), Pr(III), Nd(III) and Sm(III) Chelates

S. No.	Compound (μ_{eff} in B.M.)	% Analysis, calcd. (found)					
		C	H	N	S	Cl	Ln
1.	[La(HPAC)(TG)Cl ₂] (Diamag.)	51.62 (51.38)	3.22 (3.20)	1.88 (1.87)	4.30 (4.27)	9.53 (9.57)	18.67 (18.60)
2.	[La(HPAC)(TG)(NO ₃) ₂] (Diamag.)	48.18 (48.32)	3.01 (3.02)	5.27 (5.29)	4.01 (3.98)	—	17.43 (17.34)
3.	[Pr(HPAC)(TG)Cl ₂] (3.67)	51.48 (51.27)	3.21 (3.23)	1.87 (1.86)	4.29 (4.32)	9.50 (9.46)	18.89 (18.79)
4.	[Pr(HPAC)(TG)(NO ₃) ₂] (3.71)	48.06 (47.82)	3.0 (2.99)	5.25 (5.28)	4.0 (4.02)	—	17.63 (17.57)
5.	[Nd(HPAC)(TG)Cl ₂] (3.54)	51.25 (51.02)	3.20 (3.17)	1.86 (1.88)	4.27 (4.29)	9.46 (9.42)	19.25 (19.18)
6.	[Nd(HPAC)(TG)(NO ₃) ₂] (3.78)	47.86 (47.61)	2.99 (2.97)	5.23 (5.25)	3.98 (3.95)	—	17.98 (17.92)
7.	[Sm(HPAC)(TG)Cl ₂] (2.49)	50.84 (50.67)	3.17 (3.19)	1.85 (1.87)	4.23 (4.20)	9.38 (9.42)	19.91 (19.97)
8.	[Sm(HPAC)(TG)(NO ₃) ₂] (2.56)	47.50 (47.26)	2.96 (2.94)	5.19 (5.23)	3.95 (3.93)	—	18.60 (18.52)

HPAC = C₂₆H₁₉NO₃ and TG (deprotonated) = C₆H₅O₂S

Reflectance spectra

In the visible region, the absorption bands of Pr(III), Nd(III) and Sm(III) appeared due to the transitions from the ground level 3H_4 , $^4I_{9/2}$ and $^6H_{5/2}$ to the excited J levels of 4f-configuration respectively. The spectra of the complexes show a shift of the spectral bands towards lower energy in comparison to those of the aquo ion^{9,10} due to the nephelauxetic effect. Bonding parameter ($b^{1/2}$), nephelauxetic ratio (β), % covalency parameter (δ) and covalency angular overlap parameter (η) are calculated and reported in Table-2. The values of $b^{1/2}$ and $\delta\%$ are indicative of a considerable amount of covalency between the metal and ligand^{11,12}.

TABLE-2
REFLECTANCE SPECTRAL DATA OF LANTHANIDE CHELATES

Compound	λ_{\max} (cm^{-1})	Transitions	Calculated Parameters			
			β	$\delta\%$	$b^{1/2}$	η
[Pr(HPAC)(TG)Cl ₂]	16,630	$^3H_4 \rightarrow ^1D_2$	0.981	1.83	0.0974	0.00969
	20,400	$\rightarrow ^3P_0$				
	22,300	$\rightarrow ^3P_2$				
[Pr(HPAC)(TG)(NO ₃) ₂]	16,720	$^3H_4 \rightarrow ^1D_2$	0.986	1.41	0.0836	0.00715
	20,300	$\rightarrow ^3P_0$				
	22,260	$\rightarrow ^3P_2$				
[Nd(HPAC)(TG)Cl ₂]	12,190	$^4I_{9/2} \rightarrow ^4F_{5/2}, ^2H_{9/2}$	0.980	2.04	0.1000	0.01020
	13,270	$\rightarrow ^4F_{7/2}$				
	14,300	$\rightarrow ^4F_{9/2}$				
	16,870	$\rightarrow ^4G_{5/2}, ^2G_{7/2}$				
	18,670	$\rightarrow ^4G_{7/2}$				
	19,170	$\rightarrow ^4G_{9/2}$				
[Nd(HPAC)(TG)(NO ₃) ₂]	12,140	$^4I_{9/2} \rightarrow ^4F_{5/2}, ^2H_{9/2}$	0.9808	1.95	0.0979	0.00979
	13,300	$\rightarrow ^4F_{7/2}$				
	14,270	$\rightarrow ^4F_{9/2}$				
	16,800	$\rightarrow ^4G_{5/2}, ^2G_{7/2}$				
	18,690	$\rightarrow ^4G_{7/2}$				
	19,200	$\rightarrow ^4G_{9/2}$				
[Sm(HPAC)(TG)Cl ₂]	21,250	$^6H_{5/2} \rightarrow ^4I_{13/2}$	0.985	1.52	0.0866	0.00765
	23,730	$\rightarrow ^4P_{5/2}$				
	24,640	$\rightarrow ^4F_{9/2}$				
[Sm(HPAC)(G)(NO ₃) ₂]	21,300	$^6H_{5/2} \rightarrow ^4I_{13/2}$	0.987	1.31	0.0806	0.00664
	23,840	$\rightarrow ^4P_{5/2}$				
	24,580	$\rightarrow ^4F_{9/2}$				

IR spectra

A strong band around $3,500 \text{ cm}^{-1}$ occurring in the spectrum of primary as well as of co-ligand is assigned to $\nu(\text{OH})$ (phenolic)¹³. In the spectra of ternary complexes, a band, in addition to it, is seen at $3,470\text{--}3465 \text{ cm}^{-1}$ which shows that all the —OH groups present in the ligands do not participate in complexation. It

is further verified by the appearance of band at $3,500\text{ cm}^{-1}$ as well as at $3470\text{--}3465\text{ cm}^{-1}$ in the binary complexes with 2-thiopyrogallol. The involvement of nitrogen atom of NH group is evidenced by the shifting of $\nu(\text{NH})$ band to a higher frequency band (*i.e.*, from $3,330\text{ cm}^{-1}$ to *ca.* $3,365\text{ cm}^{-1}$). A moderately weak band existing at $2,560\text{ cm}^{-1}$ in the spectrum of co-ligand due to S—H stretch gets disappeared in the spectra of complexes which shows the deprotonation of —SH group. The formation of M-S bond in the chelates is confirmed by the appearance of a new weak band at *ca.* 310 cm^{-1} in their spectra.

Some non-ligand bands at *ca.* 500 , $420\text{--}410$ and $250\text{--}240\text{ cm}^{-1}$ may be assigned to M—O, M—N and M—Cl (in chloro complexes) stretching vibrations, respectively. In the nitrate complexes, two NO stretching bands around at $1,425$ and $1,310\text{ cm}^{-1}$ exist indicating the monodentate behaviour of nitrate group. The chelates are tentatively assigned six coordinated configuration.

Thermal behaviour

All these chelates decompose endothermally at *ca.* 430°C . At this stage, 7-hydroxy-4-phenyl-6-(α -naphthyl)-aminomethyl coumarin moiety is eliminated. Ultimately, lanthanide oxides are obtained at $670\text{--}730^\circ\text{C}$.

REFERENCES

1. S.S. Kumari, K.S.M.H. Rao and N.V.S. Rao, *Proc. Indian Acad. Sci.*, **77**, 149 (1973).
2. A.K. Rao, M.S. Raju and K.M. Raju, *J. Indian Chem. Soc.*, **58**, 1021 (1981).
3. M. Nagesam, M.S. Raju and K.M. Raju, *J. Indian Chem. Soc.*, **64**, 418 (1987); **65**, 380 (1988).
4. M. Pantlitschke and H. Banger, *Mh. Chem.*, 81 (1950).
5. B.N. Figgis and J. Lewis, in: J. Lewis & R.C. Wilkins (Eds.), *Modern Co-ordination Chemistry* Interscience, N.Y., p. 403 (1960).
6. I.M. Kolthoff and P.J. Elving, *Treatise on Analytical Chemistry*, Wiley-Interscience, N.Y., Vol. VIII, Part II (1963).
7. M.C. Jain, P.K. Sharma, A.K. Srivastava and P.C. Jain, *J. Inorg. Nucl. Chem.*, **41**, 1305 (1979).
8. M. Srivastava and G.S. Pandey, *Indian J. Chem.*, **27A**, 447 (1988).
9. G.R. Choppin, D.E. Henrie and K. Bujs, *Inorg. Chem.*, **5**, 1743 (1966).
10. S. Misumi, S. Kida and M. Aihara, *Coord. Chem. Rev.*, **3**, 193 (1968).
11. D.E. Henrie and G.R. Choppin, *J. Chem. Phys.*, **49**, 477 (1968).
12. S.P. Sinha, *Spectrochim. Acta*, **22**, 57 (1966).
13. D.K. Rastogi, A.K. Srivastava and B.R. Agarwal, *Indian J. Chem.*, **7**, 732 (1969).