

SYNTHETIC AND SPECTRAL STUDIES OF COMPLEXING BEHAVIOR OF ISOTHIO CYANATO COMPLEXES OF 4 [N-4-ETHOXY BENZALIDINE AMINO] ANTIPYRINE (C₂₀H₂₁N₃O₂)

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Abstract

Trivalent Lanthanides behave as hard acid and thus are expected to form stronger stable complexes with ligands having N-donor atoms. Coordination number less than six are uncommon for the lanthanides. Substituted Pyrazolones have been reported to possess strong pharmaceutical properties. Complexes were prepared by adding 40 ml hot ethanolic solution of ligand (3M mol) to ethanolic solution of lanthanide (III) isothiocyanate (1M mol). Molar conduction, molecular weight, magnetic susceptibility, infrared and electronic spectroscopy were used to characterization of newly synthesized complexes.

Key Words: Lanthanide isothio-cyanato complexes, Pyrazolones, Magnetic susceptibility, Infra red and electronic spectroscopy, Molar conductance and Thermal studies of the complexes.

INTRODUCTION

Substituted pyrazolones have been reported to possess strong pharmaceutical properties. However the complexation and antifungal activities of a few substituted pyrazolones have been reported¹⁻³. The coordination chemistry of pyrazole and 5-pyrazolone derived ligands has received much attention in recent years, primarily because of their biological importance⁴⁻⁵. Koppikar et al⁶ have discussed in detail the geometry of various Lanthanide (III) complexes involving different hetero donor atom.

Trivalent lanthanides behave as hard acids and thus are expected to form stronger stable complexes with ligands having oxygen or N-donor atoms.

Bombieri et al⁷ have reported the synthesis and characterization of tris-isothiocyanato complexes of Y (III) and Eu (III) with the formula [M (NCS)₃ L]. The prime object of the present work has therefore been to Synthesis of some new schiff bases derived from 4-aminoantipyrine i.e. 4[(N-4-diethylaminobenzalidene) amino] antipyrine and Isolation of solid complexes of Ln (NCS)₃ (Ln = La, Pr, Nd, Sm, Gd, Tb and Dy) with these schiff base and Characterization of the newly synthesized complexes by molar conductance, molecular weight magnetic susceptibility, infrared and electronic spectroscopy.

MATERIALS

Lanthanide thiocyanates were prepared by adding a warm ethanolic solution of lanthanide⁸⁻⁹ nitrates to warm ethanolic solution of KCNS. The precipitate of KNO₃ rapidly settle down which was removed. After reducing the volume by heating on steam bath and on concentration, solid precipitate, which was used for further studies.

The Schiff base was prepared by condensation of A solution of aromatic aldehyde (1 mole) in methanol (30 ml) was mixed with 4-amino antipyrine (1.0 mole) in the same solvent and the mixture was refluxed for 3- hours on water bath, on cooling, a yellow crystalline product appeared, which was filtered washed with methanol and ether and crystallized from ethanol and dried under vacuum in desiccators.

PREPARATION AND ISOLATION OF COMPLEXES

The complexes [Ln (NCS)₃. nEBAAP (n=2, Ln=La and Pr;n=3, Ln=Nd, Sm, Gd, Tb and Dy (EBAAP - C₂₀H₂₁N₃O₂)]

A solution (25 ml) of lanthanide (III) isothiocyanate (1.0 mmol) in ethanol was mixed with 40 ml of an ethanolic solution of ligand (3mmol) and refluxed for three hours on water bath. The whole content partially concentrated on a water bath to get a greenish-yellow precipitate. It was filtered, and washed with ethanol and ether crystallized and dried over P₄O₁₀ in vacuum desiccators.

CHARACTERIZATION, IDENTIFICATION AND CONFORMATION OF STRUCTURES OF THE COMPLEXES.

Lanthanide salts reacts with 4 [N-4-ethoxy benzalidene) amino] antipyrine (C₂₀H₂₁N₃O₂), resulting complexes of the general composition Ln(NCS)₃.2 C₂₀H₂₁N₃O₂ where Ln = La ,Pr, Ln(NCS)₃.3 C₂₀H₂₁N₃O₂ where Ln=Nd ,Sm, Gd, Tb and Dy.

Chemical analysis of the isolated compounds are given in Table-1

Table 1: Analytical, conductivity and molecular weight data of lanthanide(III) isothiocyanate complexes of 4[N-4-(Ethoxy benzalidene) amino] antipyrine (C₂₀H₂₁N₃O₂)

S. No.	Complex	Found (calc. %)					Ω M (ohm ⁻¹ cm ² mole ⁻¹)	Electrolytic nature	Average Mol. Wt.	Formula Weight
		Metal	C	N	H	Anion				
1	La (NCS) ₃ . 2 (C ₂₀ H ₂₁ N ₃ O ₂)	(14.13)	(52.50)	(12.82)	(4.27)	(17.70)	3.87	Non-electrolyte	975	982.9
		14.00	52.40	12.70	4.15	17.60				
2	Pr (NCS) ₃ . 2 (C ₂₀ H ₂₁ N ₃ O ₂)	(14.31)	(52.39)	(12.79)	(4.26)	(17.67)	4.23	Non-electrolyte	980	984.9
		14.20	52.20	12.60	4.16	17.50				
3	Nd (NCS) ₃ .3 (C ₂₀ H ₂₁ N ₃ O ₂)	(10.90)	(57.13)	(12.70)	(4.76)	(13.15)	2.33	Non-electrolyte	1318	1323.2
		10.80	57.0	12.60	4.60	13.50				
4	Sm (NCS) ₃ .3 (C ₂₀ H ₂₁ N ₃ O ₂)	(11.31)	(56.87)	(12.63)	(4.74)	(13.09)	3.54	Non-electrolyte	1320	1329.4
		11.10	56.70	12.50	4.60	12.00				
5	Gd (NCS) ₃ . 3 (C ₂₀ H ₂₁ N ₃ O ₂)	(11.77)	(56.57)	(12.57)	(4.71)	(13.02)	4.22	Non-electrolyte	1330	1336.3
		12.60	56.40	12.48	4.60	12.94				
6	Tb(NCS) ₃ .3 (C ₂₀ H ₂₁ N ₃ O ₂)	(11.88)	(56.51)	(12.56)	(4.71)	(13.01)	3.72	Non-electrolyte	1330	1337.9
		11.70	56.40	12.40	4.60	12.90				
7	Dy (NCS) ₃ .3 (C ₂₀ H ₂₁ N ₃ O ₂)	(12.11)	(56.35)	(12.52)	(4.70)	(12.97)	4.16	Non-electrolyte	1335	1341.5
		12.00	56.20	12.40	4.57	12.80				

Complexes are stable under ordinary conditions and can be kept for a sufficient long time without decomposition. Complexes are soluble in acetone, alcohol, acetonitrile, and nitrobenzene as well as in dimethyl formamide and dimethyl sulfoxide. On heating the complexes upto 120-130°C, no changes in loss in weight of the complexes are noticed showing the absence of Lattice or coordinated held water molecule. The molar conductance ¹⁰⁻¹² of the complexes in nitrobenzene shows their non electrolytic nature.

The magnetic susceptibility measurements were made by Gouy's method¹³⁻¹⁴ using a semi-micro Mettler balance and electromagnetic field of 8.5 x 10³ Gauss. All the observations are made at room temperature.

The magnetic behavior of the Lanthanides widely differs from that of transition metal ions. The magnetic moment values observed in the present studies are given in Table 2

Show that lanthanum complexes are diamagnetic in nature, as expected from its closed shell electronic configuration and absence of unpaired electrons However all other tripositive Lanthanide ions are paramagnetic due to the presence of 4f electrons, which are effectively shielded by 5s² 5p⁶ electrons.

These complexes show a little deviation from the Van Vleck values¹⁵ although they obey simple curie equation. This was to be expected as the crystal field splitting of the f- orbitals was of the order of 100 cm⁻¹ a value quite inadequate to bring about electron pairing or even an altered magnetic moment due to thermal population of excited states whose degenerate¹⁶⁻²¹ levels have been split by the crystal field.

The assignments of the IR- absorption frequencies of the synthesized compound and their complexes have been made by comparing their spectra with allied compounds like pyrazoles²² mono substituted benzene ring²³ antipyrine, 4 -amino antipyrine ²⁴⁻²⁸ substituted 4- amino antipyrine ²⁹⁻³⁴ in all the complexes carbonyl and azomethine group frequencies considerably reduced showing their involvement in chelation. In the present ligands

it has been observed in the region (1620-1600) cm^{-1} in complexes this absorption frequency suffer a negative shift showing it involvement in chelation. The high negative shift in the carbonyl frequency may be attributed to the greater flow of electrons from the carbonyl group to the lanthanide (III) atom due to greater delocalization of positive charge on the nitrogen atom.

Table 2 : Permanent magnetic moments (B.M.) of Lanthanide ions and their complexes with 4-[(N-4-Ethoxy benzalidene) amino] antipyrine(C₂₀H₂₁N₃O₂) at room temperature

S. No.	Ln ³⁺	Theoretical			Measured
		Hund	Van Vleck	R ₂ (SO ₄) ₃ .8H ₂ O	NCS ⁻
1	La	0.00	0.00	0.00	0.56
2	Pr	3.60	3.62	3.48	3.66
3	Nd	3.62	3.68	3.52	3.62
4	Sm	0.84	1.55	1.53	1.58
5	Gd	7.94	7.94	7.81	7.92
6	Tb	9.70	9.70	9.40	9.16
7	Dy	10.60	10.60	10.30	10.72

- (I) Ln (C₂₀H₂₁N₃O₂)₂ (NO₃)₃
 (II) Ln (C₂₀H₂₁N₃O₂)₃ (NCS)₃
 (III) Ln (C₂₀H₂₁N₃O₂)₄ (ClO₄)₃

Ln = La, Pr, Nd, Sm, Gd, Tb, Dy

Another important band occurs in the range 1600-1605 cm^{-1} attributed to (C=N) mode. In spectra of all the complexes this band is shifted to lower wave number and appears at 1570-1500 cm^{-1} respectively indicating the involvement of N-atom of the azomethine group in coordination³⁵. These observations are in conformity with the earlier reported work on lanthanide(III) and dioxouranium (VI) complexes of schiff bases obtained from 4- amino antipyrine and hydroxy aldehydes³⁶.

Five membered heteroaromatic compounds are found to give two strong bands near 1560 and 1490 cm^{-1} which are considered to be characteristic of five membered. Several other absorptions associated with C-H out-of-plane deformation modes appear in the range 920-720 cm^{-1} in the present ligands. In the far infrared region, an absorption at ca. 660 cm^{-1} has been assigned to C=O in-Plane bending in the free ligands³⁷⁻³⁹. This shows a positive shift on complexation. Other absorptions given in Tables 5.1-5.9 do not show any significant change on complexation. Some new medium and weak bands are observed in the far infrared range 430-380 cm^{-1} in these complexes where the ligands have no absorptions vibration. These new non ligands bands are assigned to (Ln-O) and (Ln-N) modes observed for several other lanthanide(III) complexes⁴⁰⁻⁴³.

For lanthanide (III) nitrate complexes the occurrence of two strong absorption at ~ 1525 – 1480 cm^{-1} and 1320 – 1285 cm^{-1} region is attributed to ν_4 and ν_1 modes of vibration of the covalently bonded nitrate group respectively suggesting that the nitrate groups lie inside the coordination sphere.

Since according to Lever et al.⁴⁴ bidentate coordination involves a greater distortion from D_{3h} symmetry than unidentate coordination therefore, bidentate complexes should show a large separation of ($\nu_1 + \nu_4$). Nevertheless we have tried to apply this method to the present lanthanide (III) nitrate complexes. Thiocyanate anion can coordinate either through the nitrogen or the sulphur atom to the metal ion.

Table 2 shows the IR absorption C-N stretching (ν_1), C-S stretching (ν_3) and N-C-S bending (ν_2) are identified. These frequencies are associated with the terminal N-bonded. Isothiocyanate ions⁴⁵⁻⁴⁶.

ELECTRONIC SPECTRAL STUDIES OF LANTHANIDE COMPLEXES

The electronic absorption spectra of the lanthanide complexes have been measured many times in solids as well as in aqueous and non aqueous solutions, and are characterized by a number of sharp bands with low intensities ($\epsilon \leq 10$). The crystal fields splitting for the tervalent lanthanides are so small that the spectra of the compounds closely resemble with those of the free ion⁴⁷. The electronic spectra of Pr (III), Nd (III), Sm (III) and Dy (III) complexes show bands at lower energies as compared to those in the aqua metal ions⁴⁸. This may be attributed to lowering of the interelectronic repulsion parameter on complexation⁴⁹.

In the UV- region of the electronic spectra of the complexes an intense band appears at 280nm due to the ($\pi - \pi^*$) transition. The 4f transitions are normally forbidden but are followed when degeneracy in the 4f orbitals is lifted due to external crystal field^{50, 51}. The spectra show a shift of the band towards lower energy compared with those of the aqua ions owing to nephelauxetic effect⁵². The bonding parameter ($b_{1/2}$) and the covalence parameter (β) are less than unity while sinhas parameter (δ) is positive indicating a moderate covalent character for the bond between⁵³.

The metals and ligands and

$$\bar{S} = \frac{(\text{complex})}{(\text{aquo})}; b_{\frac{1}{2}} = \left[\frac{1}{2} (1 - \bar{S}) \right]^{\frac{1}{2}}$$

$$u = \frac{100 (1 - \bar{S})}{S}$$

The hypersensitive bands of the Nd (III) complex resemble that of nine and eight coordinate complexes reported by Karrakar⁵³ suggesting a coordination number of nine and eight around the metal ion in the complexes⁵⁴⁻⁶⁶.

The electronic spectral data are shown in Table 3

TABLE 3 : ELECTRONIC SPECTRAL DATA (CM-1) AND RELATED BONDING PARAMETERS OF LANTHANIDE(III) ISOTHIOCYANATE COMPLEXES OF 4[N-4- ETHOXY BENZALIDENE AMINO)] ANTIPYRINE (C₂₀H₂₁N₃O₂)

Complexes	Ln(NCS) ₃ Electronic Spectral Bands	Complex Electronic Spectral Bands	Energy levels	(1-β)	β	b ^{1/2}	δ%
1	2	3	4	5	6	7	8
Pr(NCS) ₃ (C ₂₀ H ₂₁ N ₃ O ₂) ₃	22400	22220	³ H ₄ ³ P ₂	6.008 04	0.9919 6	0.06339	0.8105 1
	21230	21020	³ P ₁	0.009 89	0.9901 1	0.07032 6	0.9988 7
	20800	20600	³ P ₀	0.009 62	0.9908 3	0.06934	0.9709
	16900	16710	¹ D ₂	0.011 24	0.9887 6	0.07498	1.1367 7
Nd(NCS) ₃ (C ₂₀ H ₂₁ N ₃ O ₂) ₃	1940	19210	⁴ I _{9/2} ² G _{9/2}	0.009 79	0.9902 1	0.06998	0.9886 7

	17400	17190	$^2G_{5/2}$ $^2G_{7/2}$	0.012 07	0.9879 3	0.7768	1.2217 4
	13400	13220	$^2S_{3/2}$ $^4F_{7/2}$	0.013 43	0.9865 7	0.8195	1.3612 8
	12500	12210	$^4F_{5/2}$ $^4H_{9/2}$	0.023 2	0.9868	0.10770	2.3751

THERMAL STUDIES ON THE LANTHANIDE COMPLEXES

Thermal behavior of lanthanides complexes of Schiff base 4[N-4-(ethoxy benzalidene)amino] antipyrine have been reported. Thermal data shows that the complexes are stable up to 330°C revealing there by absence of water molecule in lattice or coordination sphere.

On the basis of above studies the following structure of the complexes have been assigned.

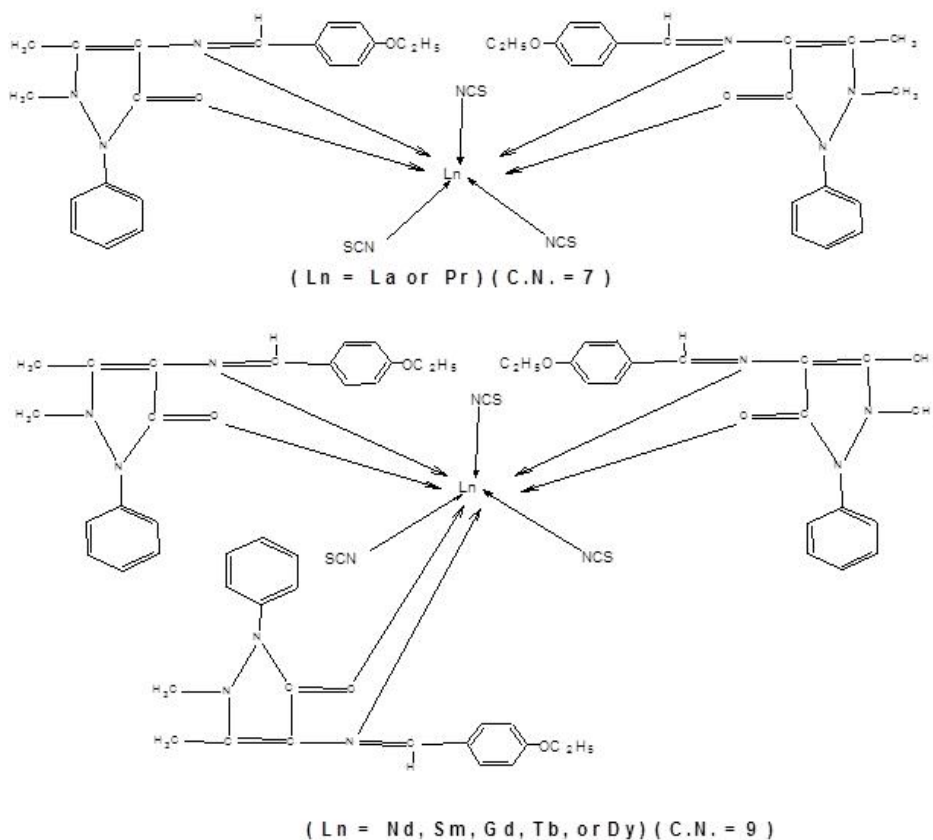


Fig. Structure of lanthanide (III) isothiocyanates complexes of 4[N-4-Ethoxy benzalidene) amino] antipyrine (C₂₀H₂₁N₃O₂)

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