Research Article

Synthesis, Characterization, and Physicochemical Studies of Mixed Ligand Complexes of Inner Transition Metals with Lansoprazole and Cytosine

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Few complexes of inner transition metals [Th(IV), Ce(IV), Nd(III), Gd(III)] have been synthesized by reacting their metal salts with lansoprazole, 2-([3-methyl-4-(2,2,2-trifluoroethoxy)pyridin-2-yl]methylsulfinyl)-1*H*-benzoimidazole and cytosine. All the complexes were synthesized in ethanolic medium. The yield percentage ranges from 80 to 90%. The complexes are coloured solids. The complexes were characterized through elemental analyses, conductance measurements, and spectroscopic methods (FT IR, FAB Mass, ^1H NMR and UV). An IR spectrum indicates that the ligand behaves as bidentate ligands. The metal complexes have been screened for their antifungal activity towards *Aspergillus niger* fungi. The interaction of inner transition metals with lansoprazole, in presence of cytosine, has also been investigated potentiometrically at two different temperatures $26 \pm 1^\circ\text{C}$ and $36 \pm 1^\circ\text{C}$ and at 0.1 M (KNO_3) ionic strength. The stability constants of ternary complexes indicate the stability order as $\text{Th(IV)} < \text{Ce(IV)} < \text{Gd(III)} < \text{Nd(III)}$. Log K values obtained are positive and suggest greater stabilization of ternary complexes. The values of thermodynamic parameters (free energy (ΔG), enthalpy (ΔH), and entropy (ΔS)) are also calculated.

1. Introduction

Inner transition metal complexes are of continuing interest mainly due to their structural and catalytical properties and their application in diagnostic pharmaceutical and laser technology [1–3]. They have been found to exhibit anticancer and fungicidal properties also [4].

Investigations are going on the formation of metal complexes with benzimidazole ring containing ligands because benzimidazole and its derivatives play an important role in analysis and in several biological reactions [5]. Considering the importance of drugs and their complexes it has been desired to synthesize and characterize some ternary complexes of inner transition metal [Th(IV), Ce(IV), Gd(III), Nd(III)] with a Benzimidazole derivative, lansoprazole, and cytosine. Lansoprazole being an antiulcer drug reduces gastric acid secretion and has successfully been used to heal and relieve symptoms of gastric or duodenal ulcers and gastroesophageal reflux [6–9].

As the interaction of metal ions with nucleobases is of great interest because of their relevance to the essential,

medical or toxic bioactivity of metal, where nucleobase molecule can coordinate as exogenous ligands in metalloproteins, function as cofactors in the enzymatic systems. Thus, cytosine is selected as the secondary ligand for the formation of ternary complexes. Its chemical name is 4-amino-1*H*-pyrimidine-2 one [10].

2. Experimental

All the chemicals used throughout the course of experiments were either of BDH or E merck quality. Spectroscopic grade solvents were employed for recording the spectra.

2.1. Preparation of the Complexes. The solid complexes were prepared by mixing the aqueous solution of metal salts [$\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$, $\text{Ce}(\text{SO}_4)_2 \cdot x\text{H}_2\text{O}$, $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$] with ethanolic solution of lansoprazole and cytosine in molar ratio 1 : 1 : 1. The resulting mixtures were then refluxed for 4–5 hours to give the precipitate. After cooling at room temperature the solid complexes were filtered as fine precipitates. These precipitates were washed

TABLE 1: Stability constants of ternary complexes of Lanso (L) and Cyto (C) at $26 \pm 1^\circ\text{C}$ and $36 \pm 1^\circ\text{C}$.

Metal complexes	$\log K_{\text{MLC}}^{\text{M}}$	
	At temp. $26 \pm 1^\circ\text{C}$	$36 \pm 1^\circ\text{C}$
Th	5.50	5.35
Ce	6.5	6.4
Gd	7.5	7.1
Nd	8.3	8.1

TABLE 2: Ligation free energy, enthalpy, and entropy change of mixed ligand complexes of M-Lanso-Cyto at $26 \pm 1^\circ\text{C}$ and $36 \pm 1^\circ\text{C}$ and at $\mu = 0.1\text{ m}$ (KNO_3).

Metal complexes	$-\Delta G$ (K.cal./mole)		$-\Delta H$ (K.cal./mole)		$-\Delta S$ (K.cal./mole)	
	$26 \pm 1^\circ\text{C}$	$36 \pm 1^\circ\text{C}$	$26 \pm 1^\circ\text{C}$	$36 \pm 1^\circ\text{C}$	$26 \pm 1^\circ\text{C}$	$36 \pm 1^\circ\text{C}$
[Th-Lanso-Cyto-4H ₂ O]NO ₃ ·xH ₂ O	1.012	1.029	313.01	307.93	31.19	30.69
[Ce-Lanso-Cyto-4H ₂ O]SO ₄ ·xH ₂ O	1.112	1.139	343.68	340.83	34.25	33.96
[Gd-Lanso-Cyto-4H ₂ O]NO ₃ ·xH ₂ O	1.197	1.203	369.95	359.89	36.87	35.86
[Nd-Lanso-Cyto-4H ₂ O]NO ₃ ·xH ₂ O	1.257	1.284	388.568	384.090	38.73	38.28

twice with water. Then they were dried and stored in a desiccators containing dry calcium chloride. The compounds obtained were stable coloured solids.

2.2. Physical Measurement. The melting point was recorded on Labotech instrument. Elemental analysis was performed on a Carlo Erba mod 1108 elemental analyzer. The Mass spectra was done on a Jeol SX-102 spectrometer using argon as the FAB gas Elico and SL191 double beam uv-vis spectrophotometer is used for recording uv-vis spectra. The ¹H NMR spectra were recorded on Bruker DRX-300. The FT IR spectrum was recorded on Varian 1000 FTIR using KBR Pallets. The antifungal activity is studied by paper disk method and data was recorded after 48 hours of incubation.

2.2.1. Ligand-Metal Ratio. The metal-ligand-ligand ratio was confirmed by conductometric titration method.

2.2.2. Stability of Complexes. Stepwise and overall proton ligand stability constants were computed by Bjerrum clavin pH titration technique as adapted by Irving and Rossotti. The extension of this titration technique to ternary system, as suggested by Chidambaram and Bhattacharya [11] has been applied to determine the stability constants of 1 : 1 : 1 ternary complexes at $26 \pm 1^\circ\text{C}$ and $36 \pm 1^\circ\text{C}$.

The proton ligand stability constant of the drug lansoprazole and cytosine has been calculated at $26 \pm 1^\circ\text{C}$ and $36 \pm 1^\circ\text{C}$ and at 0.1 M (KNO_3) ionic concentration, utilizing the Irving Rossotti pH titration technique [12].

2.3. Thermodynamic Parameters. Thermodynamic parameters computed for the complexation reactions studied in this investigation are free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) changes [13].

The reaction will go in the direction written, when ΔG is negative. These have been calculated using the Vant Hoff isotherm, Vant Hoff equation, and the Gibbs-Helmholtz

equations, respectively, at 26°C and 36°C and at ionic strength of 0.1 M with KNO_3 :

$$\Delta G = -2.303 RT \log_{10} K,$$

$$\Delta H = 4.576 \frac{T_1 \times T_2}{T_2 - T_1} \log_{10} K, \quad (1)$$

$$\Delta S = \frac{\Delta H - \Delta G}{\Delta T}.$$

3. Result and Discussion

3.1. Stability of Complexes. The $\Delta \log K$ values obtained in the present study (recorded in Table 1) are positive indicating greater stabilization (greater degree of chelation) of ternary complexes.

The stability order obtained in the present investigation is shown below:

$$(\text{M-LANSO-CYTO})$$

$$\text{Th} < \text{Ce} < \text{Gd} < \text{Nd} \quad \text{at } 26 \pm 1^\circ\text{C}, \quad (2)$$

$$\text{Th} < \text{Ce} < \text{Gd} < \text{Nd} \quad \text{at } 36 \pm 1^\circ\text{C}.$$

3.2. Thermodynamic Parameters. The values of changes in free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) recorded in Table 2, accompanying the formations of the ternary complexes, using the standard equations are as in [14]. The negative values of ΔG show that the driving tendency of the complexation reaction is from left to right and the reaction tends to proceed spontaneously.

4. Analytical Data of Complexes

The reaction of the inner transition metal with lansoprazole and cytosine was afforded in good yield (85–90%) of stable solid compound. The compounds prepared were coloured, soluble in ethanol, 1, 4 dioxane, DMF, DMSO and

TABLE 3: Analytical data of synthesized mixed ligand complexes of M-Lanso-Cyto.

Serial no.	Complex	Color	Melting point	Molar conductance (Λ° / S cm ² mol ⁻¹)
1	[Th-Lanso-Cyto-4H ₂ O]NO ₃ ·xH ₂ O	Light brown	322°C	96.1
2	[Ce-Lanso-Cyto-4H ₂ O]SO ₄ ·xH ₂ O	Light brown	319°C	89.6
3	[Gd-Lanso-Cyto-4H ₂ O]NO ₃ ·xH ₂ O	Orange	300°C	94.2
4	[Nd-Lanso-Cyto-4H ₂ O]NO ₃ ·xH ₂ O	Black	320°C	80.2
5	[Sm-Lanso-Cyto-4H ₂ O]NO ₃ ·xH ₂ O	Black	319°C	79.2
6	[Ytt-Lanso-Cyto-4H ₂ O]NO ₃ ·xH ₂ O	Black	315°C	83.2

TABLE 4: Elemental analysis of mixed ligand complexes of Lanso and Cyto.

Metal complex	Found mass (calculated mass %)						
	C	H	N	O	F	S	Metal
[Th-Lanso-Cyto-4H ₂ O]NO ₃ ·xH ₂ O	30.26 (30.6)	3.4 (3.4)	10.59 (10.71)	12.1 (12.24)	7.18 (7.27)	4.03 (4.08)	32.44 (31.65)
[Ce-Lanso-Cyto-4H ₂ O]SO ₄ ·xH ₂ O	33.99 (34.6)	3.82 (3.9)	11.89 (12.13)	13.59 (13.5)	8.07 (8.23)	4.53 (4.64)	24.11 (22.55)
[Gd-Lanso-Cyto-4H ₂ O]NO ₃ ·xH ₂ O	34.13 (33.8)	3.84 (3.8)	11.94 (11.8)	13.65 (13.54)	8.1 (8.0)	4.55 (4.51)	23.79 (24.4)
[Nd-Lanso-Cyto-4H ₂ O]NO ₃ ·xH ₂ O	34.23 (34.4)	3.85 (3.87)	11.98 (12.06)	13.69 (13.7)	8.13 (8.1)	4.56 (4.5)	23.56 (23.03)

insoluble in water. The characterization of their molecular structure was made by elemental analysers conductivity and spectroscopy studies. The studied complexes of inner transition metal showed 1 : 1 : 1 (M : LANSO : CYTO) composition as indicated from elemental analyser and exhibited corresponding conductivities suggesting 1 : 1 : 1 electrolytic behaviour. The analytical data including yield percentage of the complexes are recorded in Table 3.

5. Elemental Analysis

The result of elemental analysis is recorded in Table 4.

5.1. FT IR Spectra. The relevant vibration bands of the free ligand and the complexes are in the region 4000–400 cm⁻¹ [15, 16]. The characteristic frequencies of the ligands and metal complexes are given in Table 5. In case of Lanso molecule the N–H (aromatic sec. amine) stretching occurs at 3050 cm⁻¹, whereas sulfoxide (S=O) stretching occurs at 1090 cm⁻¹. The band of C=N occurs at 1590 cm⁻¹ [17]. In free cytosine molecule, the C–N ring band is shown in 1276 cm⁻¹ and C=O is at 1700 cm⁻¹ [18].

In case of ternary complexes of M-lansoprazole-cytosine, all the complexes showed frequency of (N–H) at ~3050 cm⁻¹ showing that there is no involvement (N–H) group in complex formation. The frequency of (C=N) bands appears at different region in complexes, that is, lowered by ~40 cm⁻¹ indicating the coordination of nitrogen atom of (C=N) with metal, whereas sulfoxide stretching shifts to lower frequencies at ~50/60 cm⁻¹ due to coordination of the sulfonyl oxygen with metals in all the complexes. Thus, lansoprazole molecule chelates with metal ions using its (C=N) group and (S=O) group, acting as bidentate ligand.

The C=O bonding of cytosine at ~1700 cm⁻¹ shifts to lower frequency on coordination and change in C–N ring is also reported. Hence in these complexes cytosine also acts as

bidentate ligand coordinating through the nitrogen at N(3) and the oxygen of C=O. Additional bands in the complex in the region 740–765 cm⁻¹ compared with IR spectra of free ligand have tentatively been assigned to M–O frequency and new band appearing at 1380–1390 cm⁻¹ in the complexes might be due to chelate ring formation in the complexes. The appearance of strong band at ~820 cm⁻¹ and ~3380 cm⁻¹ in the spectra of all the ternary complexes indicates the presence of coordinated water.

5.2. Mass Spectra. In the present investigations, the mass spectrum of the lansoprazole shows the formation of molecular ion peak at M/Z 344 corresponding to the total molecular weight of the ligand. Data on the molecular weight of complexes are present in table along with the values calculated on the basis of established molecular formulae of the complexes as shown in Table 6.

5.3. ¹H NMR Spectra. To confirm the coordination of the ligands to the metal ion the complexes, ¹H NMR spectra were recorded for the ligands and its inner transition metal complexes. The important chemical shifts for the ligands and the complexes are given in the Table 7. The ¹H NMR spectra of the ligand have the expected characteristic signals. The CH₃ proton shows singlet at δ 2.16 and O–CH₃ proton at δ 3.69 ppm and the peak observed at δ 4.71 is attributed to CH₂ protons. In addition multiplet peak at δ 6.8–8.2 may be due to aromatic protons and peak at δ 13.2 is observed due to NH proton of benzimidazole ring.

In case of ternary complexes of lansoprazole-cytosine, the chemical shifts occur at low field; that is, deshielding of proton occurs in methylene group proving the involvement of electron of S=O in bonding. Signals observed in the complexes at region of δ 8.18–8 due to the azomethine proton have either remained unaffected or shifted slightly to higher field with reference to those of the parent ligand, and the

TABLE 5: IR bands of mixed ligand complexes of M-Lanso-Cyto.

Metal complexes	ν (S=O) cm^{-1}	ν (C=N) cm^{-1}		ν (C=O) cm^{-1}	ν (C-N) RING cm^{-1}	ν (M-O)	ν (coordinated H_2O) cm^{-1}	
		Stretching	Bending				Stretching	Bending
Lanso	1090	1590	547	—	—	—	—	—
Cyto	—	—	—	1700	1276	—	—	—
[Th·Lanso·Cyto·4H ₂ O]NO ₃ ·xH ₂ O	1077 1035 (s)	1578 (s)	529	1636	1240 (m)	759	3428	824
[Ce·Lanso·Cyto·4H ₂ O]SO ₄ ·xH ₂ O	1079	1550 (w)	525	1637	1232 (s)	745	3450	821
[Gd·Lanso·Cyto·4H ₂ O]NO ₃ ·xH ₂ O	1038 (s)	1573 (s)	520	1637 (s)	1255 (s)	764	3490	821
[Nd·Lanso·Cyto·4H ₂ O]NO ₃ ·xH ₂ O	1052 (w)	1554 (s)	520/576	1633 (s)	1242 (m)	740	3450	859
[Sm·Lanso·Cyto·4H ₂ O]NO ₃ ·xH ₂ O	1080	1560 (s)	520	1632 (s)	1250	740	3471	859

TABLE 6: Mass spectra of mixed ligand complexes of Lanso and Cyto.

Metal complex	Structure	Spectral mass
[Th·Lanso·Cyto·4H ₂ O]NO ₃ ·xH ₂ O	1 : 1 : 1 : 4H ₂ O	793
[Ce·Lanso·Cyto·4H ₂ O]SO ₄ ·xH ₂ O	1 : 1 : 1 : 4H ₂ O	706
[Gd·Lanso·Cyto·4H ₂ O]NO ₃ ·xH ₂ O	1 : 1 : 1 : 4H ₂ O	703
[Nd·Lanso·Cyto·4H ₂ O]NO ₃ ·xH ₂ O	1 : 1 : 1 : 4H ₂ O	701

FIGURE 1: Proposed Scheme and Structure of representative ternary complex (M-Lanso-cyto).

position of signal due to NH proton remains unaffected in the complexes. Rest of the chemical shift is more or less the same in the ligands and their complexes. These observations support the assigned structure to the complex.

5.4. Electronic Spectra. Typical spectral data of the metal salts, ligand and ternary complexes of inner transition metal complexes have been investigated in ethyl alcohol and are shown in Tables 8(a) and 8(b). The electronic spectra of the lansoprazole display absorption bands at 219, 301 which is assigned to $n-\pi^*$ and $\pi-\pi^*$ transition, respectively. The electronic spectra of the complexes show a shift towards lower frequency. This shift was attributed to the effects of the crystal field upon the inter electronic repulsion between the 4f electrons.

Some red shift or nephelauxetic effect is observed in the alcohol solutions of these complexes. This red shift is usually accepted as evidence of a higher degree of covalency than the presence of aqua compounds [13, 19]. In all the complexes, marked enhancement in the intensity of the bond has been observed. This red shift of the hypersensitive bands has been utilized to calculate the nephelauxetic effect (β) in these chelate complexes. From the β values the covalence factors ($b^{1/2}$), Sinha parameter ($\delta\%$) (metal-ligand covalency

percent), and the covalency angular overlap parameter (η) have been calculated using the following expressions [20]:

$$b^{1/2} = \frac{1}{2} \left[(1 - \beta)^{1/2} \right],$$

$$\delta (\%) = \left[\frac{(1 - \beta)}{\beta} \right] \times 100, \quad (3)$$

$$\eta = \left[\frac{(1 - \beta)^{1/2}}{\beta^{1/2}} \right].$$

The positive values for $(1 - \beta)$ and $\delta\%$ in these coordination compounds suggest that the bonding between metal and ligand is covalent compared with the bonding between the metal and an aqua ion. The values of parameter of bonding ($b^{1/2}$) and angular overlap parameter (η) were found to be positive, indicating covalent bonding. The mechanism of the formation and structure of representative ternary complex can be given in Figure 1.

6. Antifungal Activity

The antifungal activity of the ligand, metal salts and the corresponding complexes was assayed simultaneously against

TABLE 7: ^1H NMR signals of the ligands and mixed ligand complexes of M-Lanso-Cyto.

Serial no.	kind of proton Lanso	$[\text{Th}\cdot\text{Lanso}\cdot\text{Cyto}\cdot 4\text{H}_2\text{O}]\text{NO}_3\cdot x\text{H}_2\text{O}$	$[\text{Ce}\cdot\text{Lanso}\cdot\text{Cyto}\cdot 4\text{H}_2\text{O}]\text{SO}_4\cdot x\text{H}_2\text{O}$	$[\text{Gd}\cdot\text{Lanso}\cdot\text{Cyto}\cdot 4\text{H}_2\text{O}]\text{NO}_3\cdot x\text{H}_2\text{O}$	$[\text{Nd}\cdot\text{Lanso}\cdot\text{Cyto}\cdot 4\text{H}_2\text{O}]\text{NO}_3\cdot x\text{H}_2\text{O}$
1	Aromatic benzimidazole	7.35–7.63	7.33–7.69	7.25–7.70	7.38–7.64
2(a)	Aromatic pyridine	8.18	8.20	8.30	8.2
(b)	Aromatic pyridine	6.98	6.90	6.94	6.5
3(a)	Methylene- CH_2 -	4.81	4.7 (sharp)	4.7 (sharp)	4.6 (sharp)
4	Methyl- CH_3	2.20	2.26	2.24	2.39
Cyto					
6	N(1) -H	10.7	10.52	—	—

TABLE 8: (a) Electronic spectral data of mixed ligand complexes of Lanso-Cyto. (b) Electronic spectral data and related bonding parameter of ternary complexes of Lanso-Cyto.

(a)						
Serial no.	Metals complexes	λ max (nm)	ABS	ϵ max ($\text{Lmol}^{-1}\text{cm}^{-1}$)	Assignment	
1	[Th·Lanso·Cyto·4H ₂ O]NO ₃ ·xH ₂ O	221	0.2057	2057	n- π^*	n- π^*
		293	0.0913	913	π - π^*	π - π^*
2	[Ce·Lanso·Cyto·4H ₂ O]SO ₄ ·xH ₂ O	218	0.4268	4268	n- π^*	n- π^*
		298	0.3822	3822	π - π^*	π - π^*
3	[Gd·Lanso·Cyto·4H ₂ O]NO ₃ ·xH ₂ O	225	0.7008	7008	n- π^*	n- π^*
		295	0.5243	5243	π - π^*	π - π^*

(b)							
Serial no.	Complex	Lanthanide salts (cm^{-1})	Complex band (cm^{-1})	β	1- β	$b^{1/2}$	$\delta\%$
1	[Th·Lanso·Cyto·4H ₂ O]NO ₃ ·xH ₂ O	47619	44248	0.9292	0.0708	0.13304	7.61945
		43290	35461	0.81914	0.18086	0.21263	22.0792
2	[Ce·Lanso·Cyto·4H ₂ O]SO ₄ ·xH ₂ O	47169	45455	0.96366	0.03634	0.09531	3.77103
		43859	35461	0.80852	0.19147	0.21878	23.6824
3	[Gd·Lanso·Cyto·4H ₂ O]NO ₃ ·xH ₂ O	47846	45248	0.94570	0.0543	0.11651	5.7417
		39525	34965	0.88462	0.11538	0.16983	13.0428
4	[Nd·Lanso·Cyto·4H ₂ O]NO ₃ ·xH ₂ O	47169	45454	0.96364	0.03636	0.09534	3.7737
		42553	38610	0.90733	0.09267	0.15220	10.2134

TABLE 9: Sensitivity test of lansoprazole, cytosine and their complexes against *Aspergillus niger* culture.

Serial no.	Metal ion	Inhibition Diameter (cm)			
		Lanso	Cyto	M-Lanso-Cyto	
1	Th	1.1	0.6	0.5	1.1
2	Ce	0.7	0.6	0.5	1.3
3	Gd	0.8	0.6	0.5	1.6

Aspergillus niger fungus by paper disk method [21] at room temperature. The pure metal salts, and lansoprazole drug showed activity in *Aspergillus niger*. The zones of inhibition against microorganism were measured (in cm) after 48 hours of incubation as shown in Table 9. The mixed ligand complexes showed higher inhibition zone as compared to parent drug.

7. Conclusion

The studied ternary complexes of inner transition metals showed 1:1:1 (M:LANSO:CYTO) composition as indicated from elemental analyser and exhibited corresponding conductivities suggesting 1:1:1 electrolytic behaviour. The IR data reveals that all the ligands function as bidentate ligands. Lansoprazole molecules chelate with the metal ions using their C=N group and S=O group and the cytosine acts as a chelating ligand binding through its N(3) and the oxygen of C=O. The ^1H NMR spectra of nonequivalent proton of lansoprazole in complex exhibit chemical shift towards lower field due to complexation with metals.

The complexes may be formulated ($\text{L}_{\text{Lanso}} \cdot \text{M} \cdot \text{L}_{\text{cyto}} \cdot 4\text{H}_2\text{O}$) $\text{X} \cdot n\text{H}_2\text{O}$ where X is SO_4^{2-} or NO_3^{2-} . The result of antifungal activity indicates that the complexes are more active than free ligand (lansoprazole drug). The possible general structure of these representative ternary complexes is shown in Figure 1.

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