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SYNTHESIS AND PHYSICO-CHEMICAL STUDIES OF NEWLY FORMED TERNARY COMPLEXES OF INNER TRANSITION METLAS WITH A BENZIMIDAZOLE DERIVATIVE AND CYTOSINE

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ABSTRACT

Few complexes of inner transition metals have been synthesized by reacting their metal salts with a benzimidazole derivative, omeprazole (5-methoxy-2-{{(4-Methoxy-3,5-dimethy-1-pyridiny) methyl} sulfinyI}-IH-benzimidazole) and cytosine. All the complexes were synthesized in ethanolic medium and refluxed in reaction medium. The interaction of Inner transition metals (Th, Ce, Nd, Gd) with Omeprazole, in presence of cytosine has been investigated potentiometrically at two different temperatures 26 ± 1°C and 36 ± 1°C and at 0.1 M (KNO_3) ionic strength. The stability constants of ternary complexes indicates the stability order as Th < Nd < Ce < Gd. Log K values obtained are positive and suggest greater stabilization of ternary complexes. The calculated values of thermodynamic parameters indicate that the interactions are enthalpy characterized. The complexes are characterized through elemental analyses, conductance measurements, spectroscopy (FT IR, Mass, ^{1}H NMR and U.V). An IR spectrum indicates that the ligands behave as bidentate ligands. The metal complexes have been screened for their antifungal activity towards aspergillus niger fungi.

Key words: Spectroscopy, Conductance, Thermodynamic parameters and Antifungal activity.

INTRODUCTION

Metal ions affect the well-being of human in various ways. Several of these elements are in dispensable for life and nature governs their uptake metabolism and excretion consequently their concentrations in a human body are compartmentalized and well defined. The inner transition metal ions are known to have the small radii and variable coordination number ranging from 3 to 12, which make them excellent spacers in assembling fascinating metal organic frameworks. Inner transition metal complexes are of continuing interest mainly due to their structural and catalytical properties and their application in diagnostic

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pharmaceutical and laser technology[1-6]. They have been found to exhibit anticancer and fungicidal properties also[7].

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[8]. Considering the importance of drugs and their complexes it has been desired to synthesize and characterize some ternary complexes of Inner transition metals [Th (ll), Ce (ll), Gd (ll), Nd (ll)] with a benzimidazole derivative, omeprazole and cytosine. Omeprazole is used for the treatment in acid induced inflammation conditions and ulcers of the stomach and duodenum, gastro esophageal reflux disease which are all caused by stomach acid[9-13]. By blocking the enzyme, the production of acid is decreased and this allows the stomach and esophagus to heal. Its chemical name is (5-methoxy-2-{{(4-Methoxy-3,5-dimethy-1-pyridiny) methyl} sulfinyI}-IH-benzimidazole)[14].

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-1H-pyrimidine-2 one[15].

EXPERIMENTAL

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

Ligand-metal ratio

Before the synthesis of complexes, we need to confirm metal-ligand-ligand ratio by conductometric titration method. 0.01 M solution of omeprazole drug and cytosine was prepared in 80 : 20 mixture of ethanol and distilled water. Similarly, solution of metal salts were prepared in the same solvent of 0.02 M concentration. 20 mL of ligand solutions were diluted to 200 mL. The ligands were titrated against metal salt solutions and conductance was recorded after each addition of metal salt solution. From the graph between corrected conductance and volume of titrant added, it was concluded that the complex formation has taken place.

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[16] have

been applied to determine the stability constants of 1 : 1 : 1 ternary complexes at 26 ± 1°C and 36 ± 1°C.

For pH titrations the following thermostated mixtures were titrated with a carbonate free 0.1M NaOH, keeping total volume 50 mL.

(a) 5 mL of 0.01M HNO_3

(b) Mixture (a) + 10 mL 0.002M OME

(c) Mixture (a) + 10 mL U002M CYTO

(d) Mixture (b) + 5 mL 0.01M metal

(e) Mixture (c) + 5 mL 0.01M metal

(f) Mixture (a) + 5 mL 0.01M metal + 5 mL 0.002M OME + 5 mL 0.002M CYTO

The ionic strength of above solutions were maintained to 0.1M by adding required quantity of 1.0M KNO_3 solution and the total volume of solution to be titrated was made 50 mL by the addition of required volume of millipore water.

Stability constants of the mixed ligand complex, metal-OME-CYTO (1 : 1 : 1) was obtained by utilizing the Irving Rossotti equations as applicable to ternary systems.

The proton ligand stability constant of the drug omeprazole and cytosine have been calculated at 26 ± 1°C and 36 ± 1°C and at 0.1 M (KNO_3) ionic concentration, utilizing the Irving Rossotti pH titration technique[17].

Thermodynamic parameters computed for the complexation reactions studied in this investigation are free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) changes[18].

Preparation of the complexes

The solid complexes were prepared by mixing the aqueous solution of metal salts with ethanolic solution of ligands in molar ratio 1 : 1 : 1. The resulting mixtures were than 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 twice with water. Then they were dried and stored in a desiccators containing dry calcium chloride.

Physical measurement

The melting point was recorded on labotech instrument. The mass spectra was done on a jeol SX-102 spectrometer using argon as the FAB gas. Elico, SL191 double beam UV-Vis spectrophotometer is used for recording UV-Vis spectra. Elemental analysis was

performed on a Carlo erba mod 1108 elemental analyzer. The FT IR spectrum was recorded on varian 1000 FTIR using KBr Pallets. The ^{1}H NMR spectra was recorded on bruker DRX-300. The antifungal activity is studied by paper disk method and data was recorded after 48 hours of incubation.

RESULTS AND DISCUSSION

The reaction of the inner transition metal ions with omeprazole and cytosine afforded in good yield (85%) of stable solid compound. The compounds prepare were brown colour, soluble in ethanol, 1, 4 dioxane, DMF, DMSO and 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 : OME : CYTO) composition as it is indicated from elemental analyser and exhibit corresponding conductivities suggesting 1 : 1 : 1 electrolytic behaviour .

Table 1(a): Stability constants of binary and ternary complexes of OME (l) and CYTO (c) at 26 ± 1°C

S. No.	Metal complexes	log K^M_{ML}	log K^M_{MLC}	$\Delta \log K$ $K = [K^M_{MLC} - K^M_{ML}]$
1	Th	5.05	5.2	0.15
2	Ce	6.1	6.6	0.5
3	Gd	6.6	7.6	1.1
4	Nd	5.8	5.9	0.1

Table 1(b): Stability constants of binary and ternary complexes of OME (l) and CYTO (c) at 36 ± 1°C

S. No.	Metal complexes	log K^M_{ML}	log K^M_{MLC}	$\Delta \log K$ $K = [K^M_{MLC} - K^M_{ML}]$
1	Th	4.5	5.0	0.5
2	Ce	5.95	6.5	0.55
3	Gd	6.2	7.40	1.2
4	Nd	5.5	5.70	0.2

The Δ log K values obtained in the present study are positive indicating greater stabilization (greater degree of chelation) of ternary complexes.

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

(M-OME-CYTO)

Th < Nd < Ce < Gd at 26 ± 1°C

Th < Nd < Ce < Gd at 36 ± 1°C

The values of changes in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) accompanying the formations of the ternary complexes, using the standard equations are recorded in Table 2[18]. 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.

Table 2: Ligation free energy, enthalpy and entropy change of ternary complexes of M-OME-CYTO at 26 ± 1°C and 36 ± 1°C and at μ = 0.1 m (KNO_3)

S. No.	Metal complexes	-ΔG (K.cal./mole)		-ΔH (K.cal./mole)		-ΔS (K.cal./mole)	
		26 ± 1°C	36 ± 1°C	26 ± 1°C	36 ± 1°C	26 ± 1°C	36 ± 1°C
1	[Th.Ome.Cyto.4 H_2O]SO_4.xH_2O	0.979	0.988	302.71	295.51	30.17	29.45
2	[Ce.Ome.Cyto.4 H_2O]SO_4.xH_2O	1.121	1.149	346.48	343.68	34.53	34.25
3	[Gd.Ome.Cyto.4 H_2O]SO_4.xH_2O	1.2051	1.229	372.39	367.49	37.11	36.62
4	[Nd.Ome.Cyto.4 H_2O]SO_4.xH_2O	1.054	1.068	325.90	319.56	32.48	31.85

The analytical data including yield percentage of the complexes are recorded in Table 3.

I.R. Spectra

The relevant vibration bands of the free ligand and the complexes are in the region 4000-400 cm^{-1} [19,20]. The characteristics frequencies of the ligands and metal complexes are

given in Table 2. In case of Omeprazole molecule the N-H (aromatic sec. amine) stretching occurs at 3050 cm^{-1}, where as sulfoxide (S = O) stretching occurs at 1076 cm^{-1}. The aromatic tertiary amine (C = N) occurs at 1660 cm^{-1} in Omeprazole[21]. In free cytosine molecule, the C-N ring band is shown in 1276 cm^{-1} and C = O is at 1700 cm^{-1} [22]. In case of ternary complexes of M-Omeprazole-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, where as sulfoxide stretching shifts to lower frequencies at ~ 50/60 cm^{-1} due to coordination of the sulfonyl oxygen with metals in all the complexes. The frequency of (C = N) bands appears at different region in complexes i.e lowered by ~ 40 cm^{-1} indicating the coordination of nitrogen atom of (C = N) with metal. Thus, Omeprazole molecule chelates with metal ions using its (C = N) group and(S = O) group, acting as bidentate ligand.

Table 3: Analytical data of synthesized ternary complexes of M-OME-CYTO

Metal complexes	Yield (%)	Color	Melting point (^oC)	Solubility	Molar conductance (^/S cm^2 mol^{-1})
[Th.Ome.Cyto.4 H_2O]SO_4.xH_2O	85.5	Light Brown	327	Freely soluble in DMF, DMSO, Ethanol,1,4 Dioxane, Nitric acid cold water and partially in hot water. Insoluble in acetone and methanol	89.9
[Ce.Ome.Cyto.4 H_2O]SO_4.xH_2O	83	Brown	303	Freely soluble in DMF, DMSO, Ethanol,1,4 Dioxane, Nitric acid cold water and partially in hot water. Insoluble in acetone and methanol	86.5
[Gd.Ome.Cyto.4 H_2O]SO_4.xH_2O	84.8	Light Brown	307	Freely soluble in DMF, DMSO, Ethanol,1,4 Dioxane, Nitric acid cold water and partially in hot water. Insoluble in acetone and isopropanol	85.6

The C = 0 bonding of cytosine at ~1700 cm^{-1} shifts to lower frequency on coordination and also 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 binary complexes indicates the presence of coordinated water.

Table 4: IR bands of ternary complexes of M-OME-CYTO

S. No.	Ligands and metal complexes	N (S=O) cm^{-1}	N (C = N) cm^{-1}		ν (C=O) cm^{-1}	N (C-N) Ring cm^{-1}	ν (-O) cm^{-1}	ν (Coordinated H_20) cm^{-1}	
			Stretch-ing	Bend-ing				Stretch-ing	Bend-ing
1	Omeprazole	1076	1660	547	-	-	-	-	-
2	Cytosine	-	-	-	1700	1276	-	-	-
3	[Th.Ome.Cyto.4 H_2O] $SO_4.xH_2O$	1066 (s)	1610(s)	530	1610	1207 (w)	758	3390	816
4	[Ce.Ome.Cyto.4 H_2O] $SO_4.xH_2O$	1038	1637(s)	538	1637	1260 (w)	740	3356	819
5	[Gd.Ome.Cyto.4 H_2O] $SO_4.xH_2O$	1079	1635(s)	548	1635	1203	762	3390	817

^{1}H NMR Spectra

To confirm the coordination of the ligands to the metal ion the complexes, ^{1}H NMR spectra was 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 5. The ^{1}H NMR spectra of the ligand has the expected characteristic signals. The CH_3 proton shows singlet at δ 2.16 and O-CH_3 proton at δ 3.69 ppm the peak observed at δ 4.71 is attributed to CH_2 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 omeprazole- cytosine, the chemical shifts occurs at low field i.e. 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 are either remained unaffected or shifted slightly to higher field with reference to those of the parent ligand and the position of signal due to NH proton remain unaffected in the complexes. Rest of the chemical shift is more or less same in the

ligand and their complexes. These observations support the assigned structure to the complex.

Table 5: ^{1}H NMR signals of the ligands and ternary complexes of M-OME-CYTO

S. No.	Kind of proton omeprazole	Atom No.	Omepra-zole	[Th.Ome. Cyto.4H_2O] SO_4.xH_2O	[Ce.Ome. Cyto.4H_2O] SO_4.xH_2O	[Gd.Ome. Cyto.4H_2O] SO_4.xH_2O
1	Aromatic Benzimidazole	6,7,9	6.8-7.9	6.87-7.7	6.7-7.67	6.9-7.8
2	Aromatic pyridine	17	8.22	8.29	8.2	8.17
3	Methylene-CH_2-	14	4.71-4.75	4.18 (weak)	4.4/4.6 (weak)	4.7 (sharp)
4(a)	Methoxy-0-CH_3	13	3.69	3.5	3.6 (sharp)	3.5
(b)	-0-CH_3	23	3.81	3.82	3.83	3.83
5(a)	Methyl-CH_3	24	2.16	2.1	2.1	2.1
(b)	Methyl-CH_3	21	2.5	2.57	2.48	2.58
	CYTO					
6	N(1)-H	1	10.7	10.5 (weak) 12.8	10.5 (weak) 12.6	10.2 (weak) -

Mass spectra

In the present investigations, the mass spectrum of the omeprazole shows the formation of molecular ion peak at M/Z 344 corresponds to the total molecular weight of the ligand. The mass spectra of the cerium and thorium shows the molecular ion peaks at M/Z 669 and 761, respectively supporting the composition of the complexes. 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.

Electronic spectra

Typical spectral data of the metal salts, ligand and ternary complexes of inner transition metal complexes have been investigated in alcohol and is shown in Table 5. The electronic spectra of the omeprazole displays absorption bands at 219, 301 which is assigned

to n- π* and π - π* transition, respectively. The electronic spectra of the complexes shows 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.

Table 6: Molecular mass C, H, N values of Omeprazole and its binary complexes

S. No.	Metal complexes	Structure	Cal. mass	Spec. mass	Found mass (Calculated mass %)					
					C	H	N	O	S	Metal
1	[Th.Ome.Cyto.4 H_2O]SO_4.xH_2O	1 : 1 : 1 : 4H_2O	760	759	33.2	4.21	11.06	16.86	4.21	30.46
					(33.15)	(4.21)	(11.05	(16.84)	(4.21)	(34.75)
2	[Ce.Ome.Cyto.4 H_2O]SO_4.xH_2O	1 : 1 : 1 : 4H_2O	743	740	34.05	4.32	11.35	17.29	4.32	28.67
					(33.9)	(4.4)	(11.3)	(15.07)	(4.3)	(28.83)
3	[Gd.Ome.Cyto.4 H_2O]SO_4.xH_2O	1 : 1 : 1 : 4H_2O	665	663	38	4.52	12.63	16.89	4.81	23.15
					(37.8)	(4.5)	(12.6)	(16.8)	(4.8)	(23.3)

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[23,24]. In all the complexes, marked enhancement in the intensity of the bond has been observed. This red shift of the hyper sensitive bands has been utilized to calculate the nephelauxetic effect (β) in these chelate complexes. From the β values the covalence factors ($b^{½}$), Sinha parameter (δ %) (metal-ligand covalency percent) and the covalency angular overlap parameter (η) have been calculated using the expressions[25] below -

$$b^{½} = ½[(1- \beta)^{½}]$$

$$\delta (\%) = [(1- \beta)/ \beta] \times 100$$

$$H = [(1- \beta)^{½}/ \beta^{½}]$$

The positive values for (1- β) and δ% 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 ($b^{½}$) 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 Fig. 1.

Table 7(a): Electronic spectral data of ternary complexes of OME-CYTO

S. No.	Metals complexes	λ_{max} (nm)	ABS	Wave number (cm^{-1})	ε_{max} ($Lmol^{-1}cm^{-1}$)	Assign-ment
1	$[Th.Ome.Cyto.4H_2O]SO_4.xH_2O$	221	0.2057	45249	2057	$n–\pi^*$
		293	0.0913	34130	913	$\pi–\pi^*$
2	$[Ce.Ome.Cyto.4H_2O]SO_4.xH_2O$	218	0.4268	45872	4268	$n–\pi^*$
		298	0.3822	3357	3822	$\pi–\pi^*$
3	$[Gd.Ome.Cyto.4H_2O]SO_4.xH_2O$	225	0.7008	44444	7008	$n–\pi^*$
		295	0.5243	33898	5243	$\pi–\pi^*$

Table 7(b): Electronic spectral data and related bonding parameter of ternary complexes of OME - CYTO

S. No.	Metal complexes	Lantha-nide salts (cm^{-1})	Complex band (cm^{-1})	B	1 - β	b½	δ%	η
1	$[Th.Ome.Cyto.4H_2O]SO_4.xH_2O$	47619	45249	0.95023	0.04977	0.11146	5.2376	0.02457
		43290	34130	0.78800	0.21200	0.23021	26.9035	0.09969
2	$[Ce.Ome.Cyto.4H_2O]SO_4.xH_2O$	47169	45872	0.972503	0.02749	0.08291	2.82744	0.01365
		43859	3357	0.76511	0.23489	0.242327	30.7001	0.10959
3	$[Gd.Ome.Cyto.4H_2O]SO_4.xH_2O$	47846	45248	0.94570	0.05430	0.11651	5.7417	0.05430
		39525	34965	0.88462	0.11538	0.16983	13.0428	0.11538

Antifungal activity

The antifungal activity of the ligand, metal salts and the corresponding complexes were assayed simultaneously against Aspergillus niger fungus by paper disk method[26] at room temperature. The pure metal salt and Omeprazole 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 8. The complexes of Th, Gd, Ce with omeprazole also showed higher inhibition zone as compare to omeprazole.

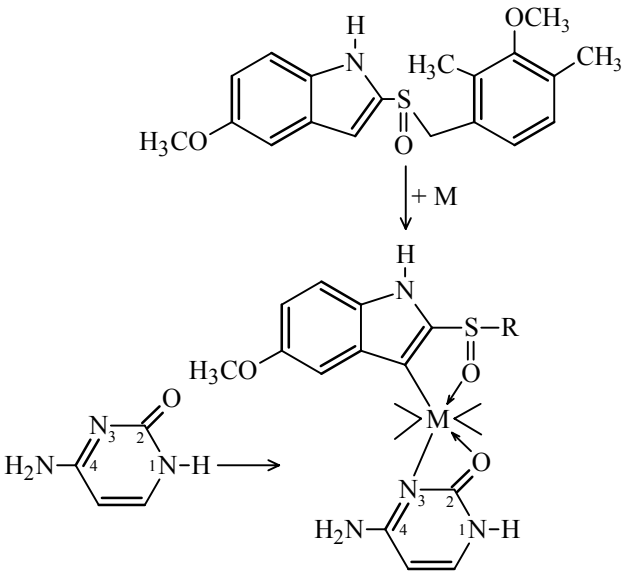

Fig. 1: Proposed scheme and structure of representative ternary complex (M-LANSO-URA).

Table 8: Sensitivity test of Omeparazole, Cytosine and their complexes against aspergillus niger culture

S. No.		Inhibition Diameter (cm)				
		Metal ion	OME	CYTO	M-OME	M-OME-CYTO
1	Th	1.1	0.5	0.5	1	1.3
2	Ce	0.7	0.5	0.5	1	1.2
3	Gd	0.8	0.5	0.5	1.1	1.5

The result indicates that the complexes are more active than free ligand. Increased activity of the complexes can be explained on the basis of chelation theory. If the orbital of each metal ion overlaps the ligand orbital increases which enhances the lipophilicity of complexes due to delocalization of electron in the chelate.

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REFERENCES

1. J. Nishikido, M. Kamishima, H. Matsuzawa and K. Mikami, Tetrahedron, **58**, 8345 (2002).
2. A. Y. Louie, Nat. Biotechno., 18321-325 (2000).
3. R. Reisfeld and C. K. Jorgensen, Lasers and Excited States of Rare Earths, Springer-Verlag, Berlin Heidelberg, New York (1977).
4. F. A. Cotton, Advance Inorganic Chemistry, 6th Edition, John Wiley, New York (1999).
5. C. Picard, N. Geum, I. Nasso and B. Mestre, P. Tisnès, Laurent and R. N. Muller, L. V. Elst, Bioorganic & Medicinal Chem. Lett., **16**, 5309-5312 (2006).
6. S. Aime, S. G. Crich, E. Gianolio and G. B. Giovenzana, L. Tei and E. Terreno, Co. Chem. Rev., **250**, 1562-1579 (2006).
7. S. J. Franklin, Current Opinion in Chem. Biol., **5**, 201-208 (2001).
8. J. Sluka, J. Navakand and Z. Budesinsk, Coll. Czech. Chem. Com., **41**, 3628 (1976).
9. L. S. Welage and R. R. Beradi, Evalution of Omeprazole, Lansoprazole, Pantoprazole and Rabeprazole in the Treatment of Acid Related Diseasea, J. Am. Pharma Assoc., **40**, 52 (2000).
10. J. P. Reilly, Safety Profile of the Proton Pump Inhibitors, Am. J. Health Syst. Pharm., **56**, 11 (1999).
11. T. G. Franko and J. E. Richter, Proton Pump Inhibitors for Gastric Acid Related Disease, Cleve. Clin. J. Med., **65**, 27 (1998).
12. S. J. Spechler, GRED and its Complications, Mt. Sinai J. Med., **67**, 106 (2000).
13. K. R. De Vault and D. O. Castell, Updated Guidelines for the Diagnosis and Treatment of Gastroesophageal Reflux Disease, the Practice Parameters Committee of the American College of Gastroentrology, Am. J. Gastroenterol, **94**, 1434 (1999).
14. E. Carlsson, P. Lindberg and S. Vanunge, Chem. Brit., **38**, 42 (2002).
15. O. P. Agarwal, Chemistry of Organic Natural Products, **2**, (2008).

16. M. V. Chidambaram and P. K. Bhattacharya, J. Inorg. Nucl. Che., **39**, 2471 (1970).

17. H. Irving and H. S. Rossotti, J. Chem. Soc., 1954, 2904, 1953, 3397, 1955, 1176.

18. E. Uusitalo, Ann. Acad. Sci. Tenn., **87** (1957).

19. R. M. Silverstein, Spectrophotometric Identification of Organic Compounds, John Wiley, New York (2009).

20. J. R. Dyer, Application of Absorption Spectroscopy of Organic Compounds, Prentice Hall of Ind. Pvt. Lt., (2009).

21. M. Gehad, J. Coord. Chem., **62**, 645-654 (2009).

22. A. Sarkar and S. Mandal, Metal-Based Drugs, **7**, No. 3 (2000).

23. C. Jørgensen, C. K. Pappalardo R., and Ritterhaus, Naturforsch, Z. Inorg. Nucl. Chem., **19a**, 424 (1964).

24. S. P. Sinha, J. Inorg. Nucl. Chem., **33**, 2205 (1971).

25. M. Mohan, J. P. Tandon and N. S. Gupta, Inorg. Chim. Acta., **111**, 187 (1986).

26. A. W. Bauer, W. M. M. Kirby, J. C. Sherris and M. Truck, J. Clin. Pathol., **45,** 493 (1966).

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