Oriental Journal of Chemistry Vol. **25**(1), 133-136 (2009)

Synthesis and characterisation of Y(III), La(III), Pr(III), Nd(III), Sm(III) and Dy(III) complexes with 2-(2'-hydroxy-5'-chloroacetophenyl)- 4, 6- dimethylbenzothiazolyl hydrazone

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(Received: December 23, 2008; Accepted: January 31, 2009)

ABSTRACT

Complexes of Y (III), La (III), Pr (III) , Nd (III) , Sm (III) , and Dy (III) with 2-(2'- hydroxy-5'-chloroacetophenyl)-4,6-dimethylbenzothiazolyl hydrazone (HCAPDMBTH) have been synthesized and characterized by elemental analytical, molar conductance, thermogravemetric, UV-visible and IR spectral data. Spectral data reveal that the ligand coordinates with the metal ion in a bidentate fashion through azomethine nitrogen and phenolic oxygen giving the complexes of the type [MLCl $(H_2 0)_3$] Cl_2 . The ligand and its complexes exhibit antibacterial activity

Key words: Hydrazones, bidentate, antibacterial, complexes.

INTRODUCTION

Hydrazones and their metal complexes have been extensively used in many biological processes as antitubercular[1,2] anti-inflammatory[3], anticancerous[4], and pharmacological[5,6]agents. Considering the facts and in continuation of our previous work[7] we therefore report here the synthesis and characterization of some rare earth metal complexes with hydrazone containing O, N, and S donor atoms.

EXPERIMENTAL

The ligand 2-(2' hydroxy-5'-chloroacetophenyl)-4,6- dimethylbenzothiazolyl hydrazone (HCAPDMBTH) was synthesized in three steps. First 2 - amino – 4, 6 – dimethylbenzothiazole (m.p.140°C) was prepared by a reported method[8].Then it is converted to 2-hydrazino-4,6-dimethyl benzothiazole (m. p. 175° C) by refluxing with hydrazine hydrate in an oil bath at 160°C for about 2 and 1/2 hours in presence of concentrated HCl and ethylene glycol. In step third equimolar quantities of 2-hydrzino-4, 6 – dimethylbenzothiazole and 2-hydrxy-5-chloroactophenone in ethanol were refluxed on water bath for one hour and allowed to cool. The solid obtained was filtered and recrystalised from ethanol. Methanol, ethanol and ether were purified by standard procedures.

Pure metal oxides were obtained from Indian Rare Earth Ltd., Kerala. Metal chlorides were prepared by dissolving the respective oxide in minimum quantity of hydrochloric acid and evaporating the solution on steam bath. The solid obtained washed with distilled water 3-4 times to remove excess acid. The complexes were prepared by following the method of Rao et. al[9]. To a weighed amount of metal chloride in ethanol, a calculated amount of ligand (1:1.5 stoichiometric ratio) in required volume of ethanol was added. PH of the solution adjusted to 5.8 by the addition of alcoholic ammonia. The solution was concentrated on steam bath, the solid complex separated. The complex was washed with ether to remove excess of the ligand and dried on anhydrous calcium chloride for 48 h.

The metal percentages were determined by igniting a weighed amount of the complex in a platinum crucible and weighing the residual oxide. Estimation of nitrogen in representative complexes was done by micro- kjeldahl method. Chlorides were estimated by Mohr's method[10]. UV – Visible spectra were recorded on UV-Visible–160 A spectrophotometer at SGGS College of Engineering and Technology, Nanded. The IR spectra were recorded on Jasco. FTIR-5300 spectrophotometer as KBr disc at University of Hyderabad. TGA was carried out up to 900ºC at the heating rate of 15ºC/min using Perkin – Elmer TGA-2 at RSIC, Nagpur. Molar conductances determined in methanol (10^{-3}M solution) using Elico CM 82 T Conductivity Bridge. The ligand and some complexes were tested for their antibacterial and antifungal activities.

RESULTS AND DISCUSSION

Physical properties and analytical data of the complexes are given in Table 1. The analytical data indicate that 1: 1 (M: L) complexes are formed having general composition [MLCl(H2O)3] $C1_2$ where M = Y(III), La(III), Pr.(III) Nd(III), Sm(III), and Dy(III); L = 2—(2'–hydroxy–5'–chloroacetophenyl) – 4 , 6 – dimethylbenzothiazolyl hydrazone. UV spectra were recorded in methanol. The ligand exhibits two bands maxima at 224.5 nm (log ε = 4.96) and 367nm (log ε = 4.41). The ligand band at 224.5 nm was found shifted to a region of longer wavelength by 3-4 nm in all complexes with the reduction in its intensity (log ε = 3.57-4.05.). The band at 367 is unaffected in the coplexes. The non-ligand band at 310 nm is observed in all the complexes. The shifting, intentisification, alteration[11,12] and appearance of new bands indicate the involvement of ligand in complex formation with metal ions.

A sharp strong band at 3353 cm^{-1} with a shoulder at 3400 cm^{-1} is observed in IR spectra of the ligand which can be assigned to phenolic hydroxyl group[13-15] . In all the complexes this band is broaden in the region 3000-3378 cm^{-1} indicating the coordination through the oxygen of phenolic group. It is further confirmed by the splitting and broadening of ligand band at 1480 cm^{-1} in all the complexes[14,15]. A non-ligand absorption band is observed in the region 3400-3600 cm^{-1} in the complexes shows the presence of coordinated water[13,16,17]. The presence of water further supported by thermal studies. IR spectra of ligand includes a sharp strong band at 1620 cm^{-1} attributed to C=N

Table 1: Physical and analytical data of the complexs

Complex (Colour)	M.P. (°C)	% M found (calc.)	% N Found (calc.)	% Cl found (calc.)	Molar conductance ohm $^{-1}$ cm^2 mole $^{-1}$
$[YLCl(H_2O)_3]Cl_2$	>300	15.75	7.16	24.60	137.6
(light yellow)		(14.94)	(7.06)	(23.87)	
$[LaLCl(H_2O)_3]Cl_2$	250	21.54	6.60	21.06	138.6
(light yellow)		(21.54)	(6.51)	(22.02)	
$[PrLCl(H_2O)_3]Cl_2$	-	21.64	6.8	21.86	158.4
(light yellow)		(21.79)	(6.49)	(21.95)	
$[Nd\ LCl(H_2O)_3]\ Cl_2$	—	22.58	-	21.76	148.5
(greenish yellow)		(22.19)	-	(21.84)	
$[Sm\ LCl(H_2O)_3]\ Cl_2$	257	22.55	-	22.00	178.2
(light yellow)		(22.94)	-	(21.67)	
$[Gd\ LCl(H_2O)_3]\ Cl_2$	>300	24.69	5.98	21.05	178.0
(light yellow)		(23.71)	(6.33)	(21.41)	
$[Dy\ LCl(H_2O)_3]\ Cl_2$	269	24.15	6.50	20.84	178.2
(light yellow)		(24.31	(6.28)	(21.24)	

(azomethine) stretching vibration[13,17-19]. In all the complexes this band is slightly shifted to higher frequency indicating the involvement of azomethine nitrogen in coordination[17,18,20]. A sharp strong band at 1572 cm^{-1} assigned to C=N stretch of thiazole ring[13,14,21] and a broad band in the region 772 - 864 cm^{-1} attributed to C-S-C stretch[14,15,22,23]. These bands are found unaffected in the complexes suggesting non-involvement of nitrogen and sulphur of thiazole moiety in complexation. Details of IR spectral data are given in Table 2.

Table 2: IR spectral data (cm $^{-1}$) of ligand and complexes

Ligand	Y(III) Complex	La(III) Complex	Pr(III) complex	Nd(III) complex	Sm(III) complex	Gd(III) complex	Dy(III) Complex	Assignment
		3600bs	3567	3571	3567			-OH Stretch
			3547	3560	3542			(water)
3400sh	3353bs	3378ss	3353ss	3353ss	3353ss		3353ss	-OH str
	3130bs	3100bs	3140bs	3138bs	3131bs		3120bs	(Phenolic)
3353ss	3000sh	3000sh	3044bs					
1620ss	1625ss	1626ss	1628ss	1624ss	1624sw	1620sw	1626ss	C=N Str.
					1601sw	1601sw		(azome-
					1625ss			thine)
1572ss	1572ss	1568ss	1572sm	1572ss	1572ss	1572ss	1572ss	C=N Str.
								(Ring)
1480sm	1480sm	1480sh	1480sb	1480sb	1402bs	1404bs	1480sh	C-O Str.
	1404bs	1406bs	1406bs	1404bs	1480sh		1406bs	(Phenolic)
					1404bs			
864sw	864		864sw	864bw	864bw		864sw	C-S-C
841	820	818sm	841sm	828sm	828sm	824sw	828sm	Str.
841sm	831	772sw	754bm			754bm	772sw	vibrations
772sw	772sw							

An examination of TG and DTG curves of Y^{3+}, Sm^{3+} and Dy^{3+} complexes show that all of them contain three coordinated water molecules which loss at 215, 200 and 207°C respectively. In all the complexes loss occurs in two steps.

Molr conductance of the complexes are in the range 137-178 ohm^{-1} cm^{2} mole^{-1} suggest that the complexes are 1:2 electrolytes[24,25].

Biological activity

The ligand and its Pr^{3+}, Nd^{3+} , and sm^{3+} complexes have been screened for their antibacterial and antifungal activities against *staphylococcus aureus, Escherichia coli* and *Aspergillus niger, Helminthosporium orazae.* It is observed that the ligand and complexes are active against s. aureas. Nd^{3+}complex are more active (inhibition zone 13 mm) compared to *gentamycin* (12mm) and *streptomycin* (10 mm). They are less active (6-9 mm) against *E. coli* compared to *getamycin* (32 mm) and streptomycin (25). Ligand and its complexes do not exhibit antifungal activity.

REFERENCES

1. Mokhtar H . M.; *Pharmazie*, **34**: 150 (1971).
2. Albert Q; *Nature*, **9**: 370 (1973).
3. Maknurva V .T ; Farm Zh. (*Vikrainkiv*), **5**: 55 (1985).
4. Sharma R.C., Mohan G., Tripathi S. P. and Srivastava R.K., *Indian Drugs*, **23**: 490 (1986).
5. Boucher L. J. and Coe C. G., *Inorg. Chem.,* **14**: 1289 (1975)
6. Skyes A. G. and Well J. A.Prog. *Inorg. Chem.,* **13**: 1 (1970)
7. Sontakke N. M. , Munde D. R. and Bansode A. S.*, Oriental J. Chem*., **23**(1): 349 (2007).
8. Adams Roger 'Organic reactions' volume III P 256, John Wiley and Sons,Inc, PNew York (1956).
9. Ramchandra Rao V., Brunetti A.P., Clarke G.A. and Marinsky J.A. , Progress report , Dept. of Chem. , SUNY at Buffalo, N. Y. A. E. C. contract No. At (30-D), 2269 (1964).
10. Vogel A.I., A Textbook of Quantitative Inorganic Analysis, 3rd Edn., Longman, London (1969).
11. Vaidya Pallavi V., Deshpande V.D. and Ramchandran Rao Y., *Asian J. Chem.,* **3**: 13 (1991).
12. Pande M.V. and Ramchandran Rao V., *Asian J. Chem*., **5**(3): 530 (1993).
13. Shina A. I. P. and Manju Bala, *Asian J. Chem.,* **3**(1): 49 (1991).
14. Dash D. C., Behara P. K., (Miss) Sen M. and Meher F. M., *J. Indian Chem. Soc.,* **68**, 663 (1991)
15. Singh R. V. and Tandon J. P., *Indian J. of Chem*., **19**(a): 602 (1980).
16. Sinha S. P., *spectrochim, Acta*, **20**: 879 [1664]
17. Revankar V. K., Arali V. H. and Mahale V. B., *Indian J. Chem.,* **29**(A): 892 (1990).
18. Garb A. A., *Asian J. Chem*., **3**(2): 216 (1991).
19. More P. G. and Pawar T.N., *J. Indian Chem. Soc*., **70**: 155 (1993).
20. Srivastav Shekar, *Asian J. Chem.* **5**: 259 (1993).
21. Colthup et. al., "Introduction to IR and Raman spectroscopy." P. 409 , Academic press, New York (1964).
22. Mishra R. P., Mohapatra B. B. and Guru S., *J. Indian Chem. Soc.,* **56**: 832 (1979).
23. Sharma A., Jain L., Sharma S.,Kacchwah G R., Jangid S. and Mehata R. K., *Asian J. Chem.,* **5**: 162 (1993).
24. Rao Thatavarthi R. and Singh Genda., *Asian J. Chem.,* **2**: 114 (1990).
25. Geary W. J., *Coord. Chem. Rev.,* **7**, 81 (1971).