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Synthesis and Characterization of Lanthanide(III) Ion Complexes with 2-Methoxy-4-amino-5-chloro-N-[2-(diethylamino)ethyl]benzamide

MANOHAR LOKHANDE*, SHARAD TAJANE† and RAMESH YAMGAR‡

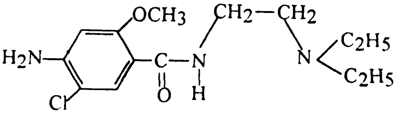
Department of Chemistry, Sathaye College, Mumbai-400 057, India

Complexes of 2-methoxy-4-amino-5-chloro-N-[2-(diethylamino)ethyl]benzamide with lanthanide(III) ions of the type of $[ML_3 \cdot 3H_2O]Cl_3$ (M = La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, Tb^{3+} and Dy^{3+} and L = 2-methoxy-4-amino-5-chloro-N-[2-diethylamino)ethyl]benzamide) have been synthesized and characterized on the basis of elemental analysis, IR, electronic spectral studies, molar conductance, magnetic moment and thermal analysis. Except La^{3+} complex, all other metal complexes are paramagnetic in nature. The coordination number of the central metal ion in the present complexes is found to be nine.

Key Words: Lanthanide(III), Complexes, 2-Methoxy-4-amino-5-chloro-N-[2-(diethylamino)ethyl]benzamide.

INTRODUCTION

Literature survey shows that much more is known about pharmaceutical activity of metoclopramide (2-methoxy-4-amino-5-chloro-N-[2-(diethylamino)-ethyl]benzamide)[1, 2] (Fig. 1). m.f. $C_{14}H_{22}N_3O_2Cl$, m.w. 299.81, m.p. 145–147 °C. Analysis %, Found (Calcd.) C = 56.03 (56.06), H = 7.30 (7.33), N = 13.98 (14.02) and Cl = 11.78 (11.84).



Metoclopramide

Fig. 1

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†Department of Chemistry, Bhavan's College, Mumbai-400 058, India.

‡Department of Chemistry, Patker College, Mumbai-400 063, India.

EXPERIMENTAL

The lanthanide(III) chlorides from Indian Rare Earth Limited, India were used for the preparation of complexes. The ligand was made available by Biochem. Pharma, Mumbai. The solvents were purified using standard procedure. The metal contents were estimated by decomposing the organic matter by successive treatment with aqua regia by using standard solution of ethylene diamine tetraacetate volumetrically and chlorine was estimated by Mohr's method[3]. Molar conductivity measurements were carried out on Equitronic digital conductivity bridge. The infrared spectra were recorded using KBr pellets on Perkin-Elmer Paragon-500 FTIR spectrophotometer at UDCT, Mumbai. Electronic spectra were recorded on Cintra-500 UV-Vis spectrophotometer at UDCT, Mumbai. Magnetic susceptibility measurements were carried out on Faraday electro Gouy balance using $Hg[Co(CNS)_4]$ as calibrated at Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad. The thermal data were recorded in the range 25–1000°C at 10°C/min using Mettler Toledo star system at C-MET, Pune.

Preparation of complexes

0.01 M of respective metal chloride solutions and ligand solution were prepared in ethanol. The metal chloride solutions and ligand solution were mixed in 1 : 3 molar ratio by adding a few drops of ethanolic solution of ammonia (0.001 M). This mixture was refluxed for 3 h. After complete refluxing the complexes were filtered, washed with ethanol and dried at 60°C in an oven.

RESULTS AND DISCUSSION

The analytical data of elemental analysis, decomposition points, colour of complexes, molar conductance and magnetic susceptibilities are given in Table-1. The complex decomposes in the range 245–270°C. The molar conductance values of complexes (10^{-3} M solution) were found to be in the range 145–165 ohm^{-1} cm^2 mol^{-1}. The molar conductivity values are in consistent with 1 : 3 electrolytic behaviour of the complexes[4]. The complexes are insoluble in ethanol, acetone, pyridine, acetophenone, acetonitrile, esters and chloroform but these are soluble in dimethyl sulfoxide and dimethyl formamide.

Infrared spectra

Important infrared bands of ligand have been studied. The ligand contains –N–C–C–N< system. In this ligand both nitrogens are important as binding sides. In the spectra of ligand bands at 2910 cm^{-1} for ν(C—H), 2900–2870 cm^{-1} for ν(CH_3) or amide-I, 1690, 1610, 1600 and 780 cm^{-1} are assigned by ν(N—CO) or ν(C—N) and ν(C—Cl) respectively[5, 6]. The band at 1530 cm^{-1} is assigned to amide-II frequency. In the complexes the two bands in 3360–3340 and 3290–3260 cm^{-1} region for secondary amine >NH also show negative shift to single band at 3210–3190 cm^{-1}, which indicates the coordination through imino nitrogen ν(NH)

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF LANTHANIDE(III) COMPLEXES WITH BENZAMIDE-2-METHOXY-4-AMINO-5-CHLORO-N-[2-(DIETHYLAMINO)ETHYL]BENZAMIDE

S.No.	Complexes	Decomp. temp. (°C)	Colour (yield %)	Analysis %, Calcd. (Found)					μ_{eff} (B.M.)	Ω (ohm^{-1} cm^2 mol^{-1})
				C	H	N	Cl	M		
1.	$[La(C_{14}H_{22}N_3O_2Cl)_3 \cdot 3H_2O]Cl_3$	256–259	Light pink, (68.00)	42.04[a] (41.92[b])	6.50 (6.42)	10.51 (10.44)	17.76 (17.22)	11.57 (11.40)	Diamag.	158
2.	$[Ce(C_{14}H_{22}N_3O_2Cl)_3 \cdot 3H_2O]Cl_3$	248–251	Light yellow, (63.00)	41.99 (41.78)	6.49 (6.47)	10.49 (10.38)	17.74 (17.24)	11.67 (11.49)	3.44	164
3.	$[Pr(C_{14}H_{22}N_3O_2Cl)_3 \cdot 3H_2O]Cl_3$	258–261	Light green, (58.40)	41.97 (41.79)	6.49 (6.34)	10.48 (10.35)	17.73 (17.38)	11.72 (11.58)	2.48	162
4.	$[Nd(C_{14}H_{22}N_3O_2Cl)_3 \cdot 3H_2O]Cl_3$	249–252	Light purple, (59.00)	41.85 (41.67)	6.47 (6.31)	10.46 (10.32)	17.68 (17.35)	11.97 (11.76)	3.58	146
5.	$[Sm(C_{14}H_{22}N_3O_2Cl)_3 \cdot 3H_2O]Cl_3$	254–257	Light orange, (62.50)	41.64 (41.57)	6.44 (6.29)	10.41 (10.29)	17.60 (17.39)	12.42 (12.26)	1.52	152
6.	$[Gd(C_{14}H_{22}N_3O_2Cl)_3 \cdot 3H_2O]Cl_3$	246–249	Colourless, (64.20)	41.41 (41.32)	6.41 (6.37)	10.35 (10.22)	17.50 (17.24)	12.90 (12.74)	7.92	163
7.	$[Tb(C_{14}H_{22}N_3O_2Cl)_3 \cdot 3H_2O]Cl_3$	262–265	Light brown, (61.50)	41.37 (41.26)	6.40 (6.25)	10.34 (10.24)	17.48 (17.26)	12.99 (12.82)	9.61	158
8.	$[Dy(C_{14}H_{22}N_3O_2Cl)_3 \cdot 3H_2O]Cl_3$	255–258	Colourless, (57.50)	41.24 (41.12)	6.38 (6.24)	10.31 (10.18)	17.43 (17.18)	13.77 (13.52)	10.54	149

or amide-II. The ν(N—H) at 3340–3270 and 3250–3180 cm^{-1} appear in the propylene complexes[7] with Ni^{2+} and Cu^{2+}. Out of several bands appearing in the range 3060–2790 cm^{-1} in the free ligand, the sharp one, which appears in the range 2810–2790 cm^{-1}, may be attributed to ν(N—CH_2) or combination of ν(C—NH_2). Further, the bands in the range 1470–1450 cm^{-1} are assigned for ν(C—N) and bands at 1430–1420 cm^{-1} indicate ν(C—NH_2). These bands show shift to 2770–2750, 1650–1440 and 1400–1370 cm^{-1} in the complexes showing that tertiary nitrogen of $N(C_3H_5)_2$ participates in the coordination to the lanthanide metal ions. In the far infrared region ν(M—N) has been assigned at 485–455 cm^{-1}, Murthy and Ligaiah[8, 9] reported ν(M—N) at just lower frequencies, *i.e.*, ν(M—N) at 390–360 cm^{-1} in benzimidazole complexes with transition metal ion complexes. The sharp band in the range 3580–3560, 3480–3470 and 3420–3380 cm^{-1} for the coordinated water molecules. The sharp medium band at 550–520 cm^{-1} for ν(M—O) has been suggested in these complexes.

Studies of magnetic moments of these complexes at room temperature show that the lanthanum(III) complex is diamagnetic, while other metal complexes are paramagnetic in nature; magnetic susceptibilities of all other complexes except those of samarium(III) complex show little deviation from Van Vleck values[10] and indicate participation of 4*f* electrons in bonding. The relatively high values obtained in case of Sm(III) complex are due to low J-J separation, which leads to thermal population of high energy levels and shows magnetic susceptibilities due to a first order of Zeeman effect[11].

The electronic spectra of the Pr^{3+}, Nd^{3+} and Sm^{3+} complexes are recorded in dimethyl formamide[8]. The spectral data and various parameters calculated are given in Table-2.

TABLE-2
ELECTRONIC SPECTRA AND THEIR ASSIGNMENTS
FOR Pr(III), Nd(III) AND Sm(III) COMPLEXES

Complexes	B	δ (%)	$b^{1/2}$
$[Pr(C_{14}H_{22}N_3O_2Cl)_3 \cdot 3H_2O]Cl_3$	0.9804	1.999	0.070
$[Nd(C_{14}H_{22}N_3O_2Cl)_3 \cdot 3H_2O]Cl_3$	0.9846	1.564	0.055
$[Sm(C_{14}H_{22}N_3O_2Cl)_3 \cdot 3H_2O]Cl_3$	0.9879	1.224	0.055

The slight red shift in these complexes clearly indicates the interaction of metal ion with the ligand. Jorgensen[12] attributed these shifts to the effect of the crystal field upon the interelectronic repulsion among the 4*f* electron, *i.e.*, to the lowering of the interelectronic repulsion parameter (β) in the complex. The bonding parameter ($b^{1/2}$) and Sinha's parameter (δ) have also been calculated using literature produced[13]. Pr^{3+} complex with respect to the free ion or aquo ions[14]. In the range 22520–16790 cm^{-1} numerous bands appear, for which we are unable to make any definite assignments at present. The spectral data of the Nd^{3+} complex have been compared with calculated values of their aquo ions and the benzamide complex. The levels observed for Sm^{3+} in $LaCl_3$ host have been also identified in the Sm^{3+} complex under investigation, and in addition, the ^6P term is also located. The numerous weak bands in this complex, not assigned at present, appear between 20750 cm^{-1} and 21460 cm^{-1}. These value indicate that there is weak covalent bonding between the metal ions and the ligand[15, 16].

Thermogravimatric and differential thermal analysis results of Gd^{3+} and Dy^{3+} complexes with 2-methoxy-4-amino-5-chloro-N-[2(diethylamino)ethyl]benzamide are reported in Table-3.

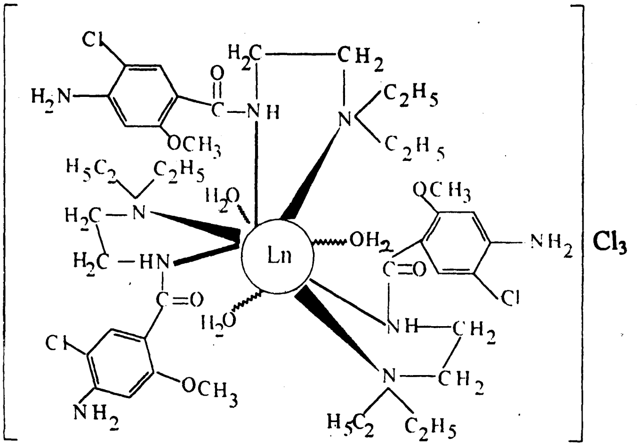
TABLE-3
THERMAL ANALYSIS

Temperature range (°C)	Theor.	Expt.	Eliminated groups
$[Gd(C_{14}H_{22}N_3O_2Cl)_3\cdot 3H_2O]Cl_3$			
90–180[a]	1.47	1.51	H_2O
190–280[a]	11.25	11.60	$2H_2O, OC_5H_{13}$
300–450[b]	18.07	18.86	$C_2H_4ON_2$
480–560[b]	42.72	43.08	$C_{13}H_{24}, N_3O_2Cl$
620–940[a]	69.37	70.27	Gd_2O_3
$[Dy(C_{14}H_{22}N_3O_2Cl)_3\cdot 3H_2O]Cl_3$			
90–190[a]	2.94	3.14	$2H_2O$
210–270[a]	15.13	16.02	H_2O, OC_4H_{13}
310–440[b]	20.62	21.18	C_9H_{14}, N_2O_3
450–560[b]	45.09	45.92	$C_{15}H_{25}, ClN_2O_3$
630–930[a]	69.50	70.20	Dy_2O_3

a = endothermic, b = exothermic.

The thermal losses are due to exo- and endothermic processes[17–18]. The complexes are thermally stable at room temperature[19]. The decomposition of both the complexes involved five steps.The experimental percentage loss is matched with the theoretical percentage loss of the complexes[20, 21]. In the first stage the complex loses the water molecule. In the second stage water molecule and some organic part of the complex is lost. In the third and fourth stages the major organic part of the complex is decomposed. In the last stage the complex decomposes and it is converted into stable metal oxide[19].

On the basis of the foregoing evidences, we propose the following tentative structure for the present complexes:



Proposed structure of Lanthanide (III) complexes with Benzamide-4-amino-5-chloro-[2-(diethylamino)ethyl]-2-methoxy (Ln = La, Ce, Pr, Nd, Sm, Gd, Tb or Dy)

Fig. 2

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