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Synthesis and Characterization of Lanthanide(III) Complexes with 2[(2,6-dichlorophenyl) amino] benzene acetic acid

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Lanthanide(III) complexes with 2[(2,6-dichlorophenyl) amino] benzene acetic acid (DPABA) with the general composition [$Ln(DPABA)_3 \cdot 2H_2O$] were prepared and characterized by IR, NMR, TGA, DTA, elemental analysis, X-ray diffraction, molar conductance and magnetic moment. The spectral studies suggest that ligand behaves as bidentate. The study indicates that the coordination number is eight of the central metal ion. There is slight participation of 4f electron in bonding.

Key Words: Lanthanide, Complexes, 2[(2,6-Dichlorophenyl) amino] benzene acetic acid, IR, NMR, TGA, DTA, XRD.

INTRODUCTION

A perusal of literature shows much more knowledge about pharmacological activity of 2[(2,6-dichlorophenyl) amino] benzene acetic acid] (DPABA) (Fig. 1). The coordinating ability of DPABA has been investigated toward Co^{2+}, Ni^{2+} and Cu^{2+} ions[1–3].

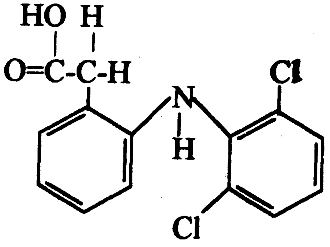

Fig. 1. Structure of ligand

The present communication reports the synthesis and characterization of the complexes of DPABA with La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, Tb^{3+} and Dy^{3+} metal ions.

EXPERIMENTAL

Lanthanide(III) chlorides were available from Indian Rare Earths Ltd. (India).

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Lanthanide(III) chlorides were available from Indian Rare Earths Ltd. (India). The reagents were used of AR grade; the solvents were purified using standard procedure, the ligand were available from Bio-Chem Pharma.

The complexes were prepared by mixing ethanoic solution of lanthanide(III) chloride and DPABA with 1 : 3 stoichiometric ratio; this mixture solution was refluxed for *ca.* 3 h using water condenser and the pH of the reaction mixture was adjusted at 6.0 to 6.5. After refluxing the solid product was obtained; this product was cool-washed with absolute alcohol and dried at 60°C in oven. The elemental analysis was carried out in micro-analytical laboratory using a micro-analyser. The metal contents were determined by complexometric titrations. The chlorides were estimated by Mohr's method[4].

RESULTS AND DISCUSSION

The analytical data and physical data are given in Table-1. It indicates that the complexes formed by DPABA with La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, Tb^{3+} and Dy^{3+} have the general composition $[Ln(DPABA)_3 \cdot 2H_2O]$. These complexes were insoluble in water, ethanol, methanol, acetone, esters, toluene, benzene and acetonitrile but they are soluble in DMF, DMSO. They were decomposed in the range between 258–329°C. The complexes have low conductance value in DMF at 10^{-3}m concentration, which indicates the non-electrolytic nature of the complexes.

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF $[Ln(DPABA)_3 \cdot 2H_2O]$

Complexes (Colour, yield %)	Decomp. temp. (°C)	% Analysis, Calcd. (Found)					μ_{eff} (B.M.)
		C	H	N	Cl	M	
$La(C_{42}H_{30}N_3O_6Cl_6) \cdot 2H_2O$	326–329	47.55	2.83	3.96	20.09	13.10	Diamag
(Light pink, 68)		(46.94)	(2.75)	(3.92)	(19.88)	(12.94)	
$Pr(C_{42}H_{30}N_3O_6Cl_6) \cdot 2H_2O$	308–311	47.46	2.81	3.95	20.05	13.26	3.57
(Light green, 65)		(46.92)	(2.62)	(3.89)	(19.82)	(13.03)	
$Nd(C_{42}H_{30}N_3O_6Cl_6) \cdot 2H_2O$	288–291	47.31	2.78	3.91	19.99	13.54	3.64
(Purple, 62)		(46.88)	(2.59)	(3.64)	(19.72)	(13.40)	
$Sm(C_{42}H_{30}N_3O_6Cl_6) \cdot 2H_2O$	273–276	47.08	2.75	3.87	19.88	14.03	2.11
(Light pink, 51)		(46.97)	(2.64)	(3.66)	(19.68)	(13.89)	
$Gd(C_{42}H_{30}N_3O_6Cl_6) \cdot 2H_2O$	268–271	46.74	2.70	3.82	19.75	14.38	7.95
(Light pink, 53)		(46.34)	(2.52)	(3.17)	(19.12)	(14.05)	
$Tb(C_{42}H_{30}N_3O_6Cl_6) \cdot 2H_2O$	263–265	46.67	2.66	3.78	19.71	14.51	9.64
(Light buff, 55)		(46.12)	(2.38)	(3.69)	(19.24)	(14.36)	
$Dy(C_{42}H_{30}N_3O_6Cl_6) \cdot 2H_2O$	258–261	46.51	2.61	3.74	19.65	14.99	10.56
(Cream, 58)		(46.18)	(2.24)	(3.62)	(19.08)	(14.78)	

between 4000–500 cm^{-1}. In the IR spectra, the $Ln(DPABA)_3 \cdot 2H_2O$ complexes have one double hump at 3480–3200 cm^{-1} [5,6] the bands between 3392–3332 cm^{-1} for >NH followed by the sharp peaks in 1600–1580 cm^{-1} and 840–830 cm^{-1} assignable to off-stretching bending and rocking vibrations respectively, indicating the presence of coordinated water molecule. In the complexes the ligand bands at 3485 cm^{-1}(>NH) and 1585 cm^{-1} (>C=O) shifted (±)35–40 cm^{-1}in the complexes indicating the coordination through these groups. In the far-IR region, the chelate shows new bands at 480–440 cm^{-1} and 435–425 cm^{-1} comparable with ν(M—N) and ν(M—O) respectively,[7] which indicates that the bonding of ligand is through oxygen carboxylate ion and nitrogen of amino group with central metal ion. The NMR spectra were recorded on Bruker 500 MHz at TIFR, Mumbai. δ 6.2, δ 8.0 to δ 6.5 and δ 2.5 for the carboxylate proton, NH, aromatic ring and aromatic proton of —CH_2 group respectively. In the complexes Pr(III) and Nd(III) the shift of δ 11.3 were disappear and >NH at δ 6.3 to δ 6.1 and the aromatic shifts for proton at δ 8.0 to 6.5 and CH_2 proton at δ 2.5 were found.

The magnetic susceptibility was carried out on Gouy electrobalance using $[HgCo(CNS)_4]$ as a calibrant. The $La(DPABA)_3 \cdot 2H_2O$ is diamagnetic in nature, while other complexes paramagnetic at room temperature. The values of magnetic moment are shown in Table-1. The magnetic values are slightly deviating from Van Vleck[8] which indicates that there is slight participation of 4f electrons in bonding. The relative high value obtained in Sm(III) complexes is due to j-j separation which leads to thermal population of high energy levels shows susceptibility to Zeeman's effects[9].

TGA/DTA was carried out in the range between 25–1000°C at the rate 10°C/min at IICT, Hyderabad. The TGA/DTA study of $Gd(DPABA)_3 \cdot 2H_2O$ complex shows some losses of volatile and decomposed material through endothermic and exothermic process. It decomposes in three stages. The weight losses start at 160°C corresponding to the beginning of the dehydration process that takes place in the temperature range 160–190°C. The decrease of mass connected with the loss of two water molecules of crystallization water in one step: theoretical, 6.63% and found, 6.61%, is connected with endothermic peak seen on DTA curve. In this range, the TGA curve gains a constant level, which is indicative of the anhydrous complex formation. Subsequently the rapid mass loss indicates the decomposition of organic matter in the range 320–350°C: theoretical 33% and found 33.79%. The strong inflection of TGA curve is seen and the exo-effect appears on DTA curve. The TG curve attains a constant level at 700°C, which suggests formation of Gd_2O_3. Further, a small weight loss in the range at 740°C is observed and after 750°C the TG curve again attains a constant level due to Gd_2O_3 formation. This indicates that the two water molecules are forming a coordinate linkage with central lanthanide (III)metal ion and satisfies the coordination number.

The powder diffraction data was obtained on Joel-8030 goniometry X-ray diffractometer using CuKα radiation. In order to estimate the external powder forms of the complexes, their X-ray powder diffraction measurements were carried out. The diffractogram analysis suggests that they are polycrystalline compounds with low symmetry. 2,4-dichlorophenyl-amino benzeneacetic acid[10] carried out. The diffractogram analysis suggests that they are polycrystalline compounds with low symmetry. 2,4-dichlorophenyl-amino benzeneacetic acid[10] of La(III), Sm(III), Nd(III), seem to be isostructural, The complexes may have different structures, but this has not been determined because no single crystal of these compounds has been obtained.

The electronic spectra in liquid state were recorded on Cintra-500 UV-Visible spectrophotometer at UDCT, Mumbai. The electronic f-f transition bond normally shows weak perturbation due to complexation; an increase in intensity shifts to the red region and shifting of some bands are observed at complex formation. The portion and shape of electronic spectral bands of Pr^{3+} and Nd^{3+} complexes in DMSO were recorded.

This suggests that the complexes maintain the same stereochemistry also in solution phases. While the La^{3+} and Gd^{3+} complexes are not observed in the visible region, the other complexes have shown various bands appearing at lower energies as compared to those in aqua complexes. The magnetic effect of the bathochromic shift of the bands in each case indicates a meagre nephelauxetic effect at complex forxnation.[11] The nephelauxetic effect (β), the bonding parameters ($b^{1/2}$) and Sinha's parameter (δ) have been calculated[12, 13]. The bonding parameter $b^{1/2}$ reflects the extent of participation of 4f crystal in complexation; greater the magnitude of the parameter greater is the contribution of 4f-orbitals[13]. The $b^{1/2}$ values obtained for the present complexes indicate a decreasing order of 4f-orbitals participation in the series Pr(III) and Nd(III). The average value of the Sinha's parameter (δ) obtained in each case is positive and smaller than unity, indicating the presence of a weak covalent bonding character in the complex. (Table-2).

TABLE-2

Electronic SPECTRA OF Pr^{3+} and Nd^{3+} Complexes of DPABA

Complex	Band maxima (cm^{-1})	Assignments	Spectral parameters
$Pr(DPABA)_3 \cdot 2H_2O$	16949	$^3H_4 \rightarrow {}^1D_2$	$\beta = 0.0986$
	20833	$\rightarrow {}^3P_0$	$\delta\,\% = 1.4100$
	21413	$\rightarrow {}^3P_1$	$b^{1/2} = 0.0830$
	22831	$\rightarrow {}^3P_2$	
$Nd(DPABA)_3 \cdot 2H_2O$	12468	$^4F_{5/2}$	$\beta = 0.9870$
	13368	$^4F_{7/2}$	$\delta\,\% = 1.3100$
	14619	$^4F_{9/2}$	$b^{1/2} = 0.0806$
	17123	$^2G_{7/2}, {}^4G_{5/2}$	
	19083	$^4G_{7/2}$	
	19531	$^4G_{9/2}$	
	20920	$^2G_{11/2}$	
	23364	$^2P_{1/2}$	

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