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SYNTHESIS AND CHARACTERIZATION OF DIGLUCAMINE AND DI-SODIUM SALTS OF Sm (III) AND La (III) METAL COMPLEXES OF DIETHYLENETRIAMINE PENTAACETIC ACID LIGAND

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ABSTRACT

The synthesis of diethylenetriamine pentaacetic acid, its metal complex with Sm (III), and La (III) and its different salts have been synthesized and characterized by chemical analysis, Mass confirmation, HPLC analysis, infrared electronic spectra studies, ^{1}H NMR, magnetic susceptibility measurements and thermogravimetric analysis. The results suggest octahedral coordination in which the central metal ion is bonded to DTPA. The complexes of diethylenetriamine pentaacetic acid, Sm (III) and La (III) and its salts have been assigned the formula [Sm(DTPA)], [Sm(DTPA)]Na_2, [Sm(DTPA)]$Glucamine_2$, [La(DTPA)], [La(DTPA)]Na_2 and [La(DTPA)]$Glucamine_2$.

Key words: Glucamine, Samarium, Lanthanum, Complexes, Diethylenetriamine pentaacetic acid (DTPA).

INTRODUCTION

The metal complexes and their salts are very important class of organic/inorganic compounds. The coordination compounds are very much useful in magnetic resonance images. This is because the coordination ligands are biologically more active than the non-coordinated compound[1-5]. The studies of metal complexes of polydentate ligand containing amide group have been reported[6-8]. The complexes of di-ethylenetriamine pentaacetic acid with ion metal ion and N---O donor ligand have been isolated and characterized. The present work describes the synthesis and characterization of diethylenetriamine pentaacetic acid complexes with samarium and lanthanum, its sodium and glucamine salts.

Medicinally, ethylenediamine tetraacetic acid metal complex has been used in MRI[9]. The EDTA and metals complex salts have long been used in Magnetic Resonance Imaging (MRI). Magnetic resonance imaging agents improve the resolution of MRI image by increasing the brightness in various part of body where the agent reside. Most of the MRI agent that have been approved for human use that metals, which have paramagnetic species. Thus species, which have unpaired electrons are mostly used in MRI. Hexamethylene triamine is used in agriculture as a fertilizer[10,11] and it gives distinctive microscopic test for several metals[12,13] and are also used as an anticorrosion agent[14,15]. Now in this paper, we report the

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synthesis, characterization and magnetic resonance image activity of diethylenetriamine pentaacetic acid complex of Sm (III) and La (III).

EXPERIMENTAL

Synthesis of the ligand and complexes

All laboratory chemicals were of reagent grade and were used without further purification. All solvents used were dried and distilled according to standard method. Diethylenetriamine (0.08 mol, 1.0 g), Chloroacetic acid (0.32 mole, 27 g) and potassium carbonate (2.0 g) were mixed and stirred for 2 hr at 20^o – 25^oC. Then DM water (25 mL) was slowly added, diethylenetriamine pentaacetic acid (DTPA) precipitates out as white solid. It is stirred for one hr filtered and washed out with water; then methanol. After that, it is dried under vacuum at 50^o – 60^oC for 5 hr. Compound is purified by hot water and ethanol solvent. Complexes of samarium and lanthanum with the ligand were synthesized using chloride, nitrate and perchlorate salts of the metals.

The ligand and metal salts were mixed in equimolar ratio in water-methanol mixture and then refluxed for 5-6 hr. During the complex synthesis, metal chloride and bromide product precipitates out on refluxing, which was isolated by filtration. Normally the solvent are distilled out under vacuum at 50^o – 60^oC in reaction mixture to obtain a pasty mass, which was solidified by successively washing with acetone and ethanol solvent. The complexes were filtered and washed with suitable solvent and dried at 70^o – 80^oC under vacuum and kept in anhydrous phosphorous pentoxide.

Element analysis for carbon, hydrogen and nitrogen were carried out by Hitachi CHN-O rapid analyzer. The anions present in complexes were estimated by analytical standard method[16]. The ^1H NMR analysis was done with Varien-300 nuclear magnetic resonance instrument using benzene/DMSO $–d_6$ as solvent. Infrared spectra were measured in the range 4000-400 cm^{-1} with Schimadzu FTIR -8101 spectrophotometer. Electronic spectra were recorded using Hitachi-2000 spectrophotometer. The samarium and lanthanum were determined by Gouy method using as mercury tetrathiocynateocobaltate as calibrant[17] at room temperature. Diamagnetic correction were calculated from Pascal's constants[17]. The effective magnetic moment, μ_{eff} was than calculated from the expression :

$$\mu_{eff} = 2.83\sqrt{X_A T} \qquad \ldots(1)$$

where X_A is the magnetic susceptibility per gram atom and T is the Kelvin temperature.

RESULTS AND DISCUSSION

The physical and analytical data like colors, magnetic susceptibilities, molar conductivities and melting points obtained for the complexes are shown in Table 1. The complexes are stable and soluble in DMF and DMSO solvent. The molar conductivity in DMF solution showed that all except one behave as non-electrolytes indicating the coordinated nature of the anions.

Characterization of ligand

The ^1H NMR spectrum of the ligand DTPA in DMSO-d_6 shows that peak at 3.5 ppm, which was assigned to the azo methane type proton and singlet at 4.3 ppm was assigned to the methyl protons, while peak at 13.5 ppm was assigned to acid group. All peaks were observed in aliphatic region only.

Table 1: General properties and micro analytical data of complexes

Complex	Colour	M.P. (°C)	Yield (%)	Elemental analysis			
				Found		Calculated	
				% C	% H	% N	% Metal
Sm (DTPA)	Green brown	210	0.9	37.43 (37.32)	6.18 (6.20)	8.85 (8.80)	15.32 (15.34)
Sm (DTPA) Na_2	Offwhite greenish white	196	1.1	46.12 (46.08)	5.75 (5.74)	7.99 (8.0)	9.44 (9.40)
Sm (DTPA) Glucamine$_2$	Greenish white	235	2.0	37.96 (37.84)	5.48 (5.50)	9.12 (9.06)	11.20 (11.16)
La (DTPA)	Pink brown	194	1.0	38.86 (38.80)	5.58 (5.50)	9.65 (9.60)	8.68 (8.74)
La (DTPA) Na_2	Orange brown	146	1.1	44.32 (44.28)	4.86 (4.90)	8.56 (8.48)	12.24 (12.20)
La (DTPA) Glucamine$_2$	Pink pale red	220	1.7	39.78 (39.76)	5.66 (5.60)	8.95 (8.90)	9.98 (9.90)

The IR bands of ligand DTPA at 3423.41 and 3387 cm^{-1} were assigned to –OH and –NH stretch, The bands at 2862.48 and 2832.68 cm^{-1} were assigned to the C-H stretching, The bands present at 1600 and 1556 cm^{-1} were assigned to C-N. The bands present at 1436.87 and 1406.02 cm^{-1} were assigned to C-H bending, while stretch at 1091.63 and 1031.65 were due to C=O group of acid (Table 3). The element analysis and spectral data for Ligand are consistent with the formula $C_{14}H_{23}O_{10}N_3$ and the structure given in Fig. 1.

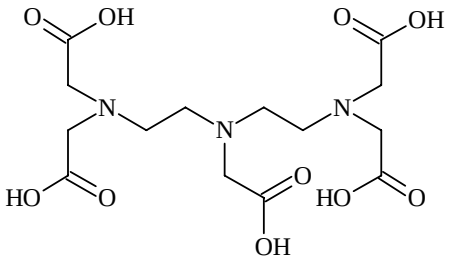

Fig. 1: Diethylenetriamine pentaacetic acid (DTPA)

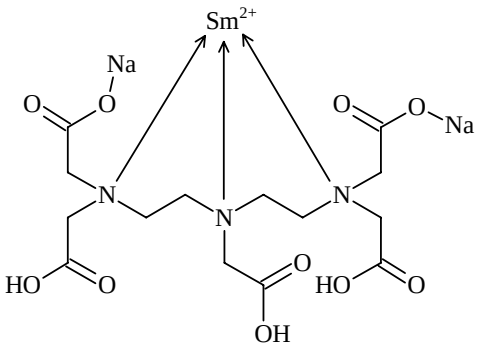

Fig. 2: Disodium DTPA-Sm complex

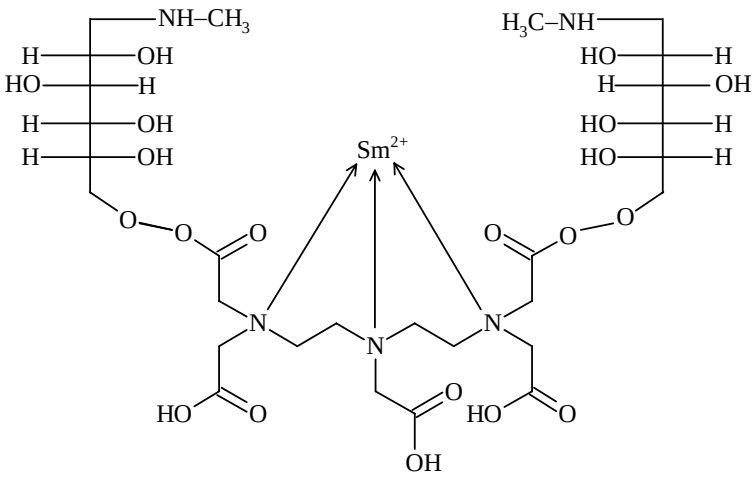

Fig. 3: Di -glucamine DTPA -Sm complex

Characterization of complexes

The complexes of samarium and lanthanum with ligand (DTPA) and its different salts with sodium and N-methyl glucamine. The molar conductivities of the DTPA complexes in water are given in Table 2. The sodium and glucamine salts gave positive tests.

Table 2: Molar conductivity data of metal complexes

Complex	Eff (B.M.)	Am (Ohm^{-1} cm^2 mol^{-1})
Sm (DTPA)	3.96	133.11
Sm (DTPA) Na_2	4.50	85.32
Sm (DTPA) $Glucamine_2$	4.11	35.23
La (DTPA)	4.66	18.64
La (DTPA) Na_2	5.20	33.64
La (DTPA) $Glucamine_2$	5.10	52.12

In the IR spectra of ligand, complexes and its salts, the band in all complexes at 678-498 are assigned to (M-N)[19-21], while bands in region of 3356-3478 is due to – OH; 2896-2821 cm^{-1} is due to -CH_2; 1211-1278 cm^{-1} is due to -CN and 1098-1011 cm^{-1} is due to –CO were also observed.

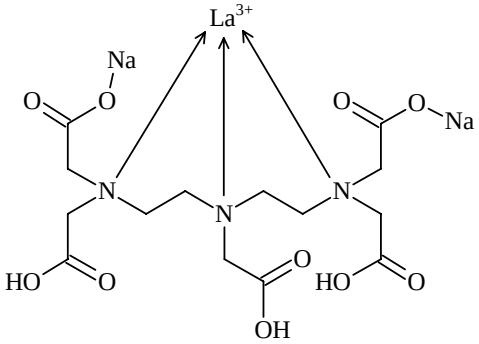

Fig. 4: Disodium DTPA-La complex

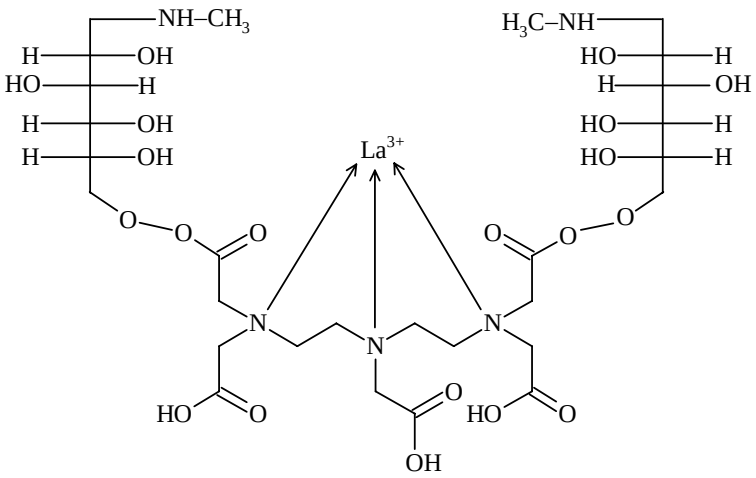

Fig. 5: Diglucamine DTPA -La complex

Table 3: IR Absorption bands (cm^{-1}) of DTPA and complexes

Complex	$\nu_{(O-H)}$	$\nu_{(CH_2)}$	$\nu_{(C-N)}$	$\nu_{(C=O)}$	$\nu_{(M-N)}$
Sm (DTPA)	3415.12	2821.26	1246.32	1042.87	622
Sm (DTPA) $Glucamine_2$	3455.36	2896.48	1211.38	1033.75	678
La (DTPA)	3406.96	2852.26	1278.78	1012.87	652
La (DTPA) $Glucamine_2$	3356.32	2832.24	1233.48	1054.12	612

^{1}H NMR data of complex show single peak at 3.51 ppm, which implies that hydrogen atom are in same environment[22,] However, the ^{1}H NMR spectra for the complexes show peak at 2.95 and 3.00 ppm indicating that the free ligands are attributed to the coordination of the DTPA to the metal ions.

The magnetic moments data and electronic spectral data of complexes are shown in Table 2. The magnetic moment for the Sm is 5.34 B.M. This value is higher than spin-only moment of 3.87 B.M. due to the large orbital contribution for Sm ion. The La complex magnetic moment data (3.16 to 3.40), usually have a magnetic moment in the range 2.9-3.40 B.M.[23]

CONCLUSION

DTPA ligand, samarium and lanthanum complexes and their salts have been synthesized and characterized. The shift in IR band position from 1236 to 1242 cm^{-1} and chemical shift of ^{1}H NMR from 3.60 ppm to 2.99 ppm suggest that DTPA is coordinated to the metal center.

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