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Original Research Article

PREPARATION OF MIXED LIGAND COMPLEXES OF LANTHANIDE METAL, THEIR CHARACTERIZATION AND ANTIBACTERIAL STUDY

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Abstract:

The new mixed ligand complexes of the Cerium metal are obtained by using (2Z)-2-(N-hydroxyimino)-1, 2-diphenylethan-1-ol as a primary ligand and various amino acids like L-Arginine, L-Glutamine, L-Asparagine as a secondary ligand .The analysis of synthesized complexes has been carried out on the basis of elemental analysis, magnetic susceptibility measurements, electrical conductance details, UV-Visible and IR spectrophotometric measurements, TG DTA studies. All new complexes are formed in the ratio of 1:2:1 which is finalized by elemental analysis. Paramagnetic nature of the new synthesized Ce (III) complexes has been confirmed by magnetic susceptibility measurements. Electrical conductance studies clears their non-electrolytic nature. FTIR spectra shows that the Cerium(III) metal ion is bonded to primary ligand and secondary ligand through donor atoms which are N and O atomes present in the given ligands, while intra ligand and LCMT transitions are proved by electronic absorption spectra of the complexes. The thermal studies of complexes reveal the presence of coordinated H2O molecules, metal ion and primary as well as secondary ligand in the synthesized complexes. Antibacterial activity of all the complexes studied against selective microorganisms S. typhi, P. aeruginosa, S. aureus, C. diphtheriae by Tube dilution and Agar cup methods exposes that the complexes have moderate activity against the chosen microorganism strains.

Key Words: *Lanthanide Complexes, Characterization, Ligand, Antibacterial Study.*

Introduction:

Many researchers studied the mixed ligand complexes synthesized from transition metals using amino acids. These metal complexes exhibit antibacterial activity, ant tuberculosis activity, antimicrobial activity and behave as potential therapeutic agents. The mixed ligand complexes also have biological importance. Antifungal activity as well as cytotoxic activity are also reported by mixed ligand complexes of Ce (III) metal [1]. Many cerium compounds are utilized as a catalyst and express their vital role in water-gas shift reaction [2]. It was therefore determined to synthesize the mixed ligand complexes of cerium, the lanthanide series element with (2Z)-2-(N-hydroxyimino)-1, 2-diphenylethan-1-ol (ND) as primary ligand and different amino acids (HL) like L-Arginine, L-Glutamine, L-Asparagine.

Material and Methods:

Materials:

All the chemicals used for the research work are of analytical grade. The Cerium chloride heptahydrate, (2Z)-2-(N-

Hydroxyimino)-1, 2-diphenylethan-1-ol (ND) and L-Arginine, L-Glutamine, L-Asparagine used for the research work were of analytical grade and purified solvents were used for the research work.

Instrumentation:

The elemental analysis of all complexes has been carried out for determination of C, H and N by using Thermo Finnigan Elemental Analyser. The conductance was recorded on an Equiptronics Digital Conductivity Meter using DMSO as solvent. Shimadzu UV/VIS spectrophotometer was employed to record the electronic absorption spectra. The FTIR spectra of all compounds obtained from Shimadzu FTIR spectrophotometer in the region 4000-400 cm^{-1}. Perkin Elmer Diamond TG-DTA instrument has been employed for thermal study. Gouy's method was used note the the magnetic susceptibility.

Preparation of mixed ligand complexes:

cerium metal complexes were synthesized by utilizing cerium chloride heptahydrate, (2Z)-2-(N-hydroxyimino)-1,2-diphenylethan-1-ol (ND) and various amino acids like L-Arginine, L-Glutamine, L-Asparagine Initially the aqueous solution of cerium chloride heptahydrate (372 mg, 1mmol) of 10 ml quantity was prepared and then to this aqueous solution of cerium chloride heptahydrate, 20 ml alcoholic solution of (2Z)-2-(N-hydroxyimino)-1,2-diphenylethan-1-ol (2 mmol, 454.52 mg) was added constant stirring. The reaction mixture was placed in a boiling water bath for 10-15 minutes. After to this hot reaction mixture, the previously prepared 10 ml aqueous solution of amino acids (1 mmol) was mixed drop wise with constant stirring. Then the whole reaction mixture was again kept in a boiling water bath for 15 minutes. Then the reaction mass is removed from the boiling water bath and allowed to cool. In this cooled solution, dilute ammonia solution drop by drop is added to increase the pH of the solution. The precipitation of complex has been observed at pH 7. The resultant complex was filtered through a Buckner funnel and washed by water and then ethyl alcohol.

Results and Discussion:

Characterization of metal complexes

Synthesis reaction of mixed ligand cerium (III) can be represented as follow

$CeCl_3 \cdot 7H_2O + 2HND + HL \rightarrow [Ce(ND)_2(L) \cdot 2H_2O] + 3HCl + 5H$

Where ND is (2Z)-2-(N-hydroxyimino)-1, 2-diphenylethan-1-ol and HL is an amino acid.

The elemental analysis data shown in Table 3 and molar conductance value obtained in DMF at 10^{-3} M concentration.

Table 1: Empirical Formula, Colour and Molecular Weight

Complex	Empirical Formula	Color	Molecular weight
$[Ce(ND)_2(Arg)\cdot 2H_2O]$	$CeC_{34}H_{41}O_8N_6$	Light yellow	801.11
$[Ce(ND)_2(Glu)\cdot 2H_2O]$	$CeC_{33}H_{37}O_9N_4$	Light yellow	773.00
$[Ce(ND)_2(Asp)\cdot 2H_2O]$	$CeC_{32}H_{35}O_9N_4$	Light yellow	759.00

Where ND is (2Z)-2-(N-hydroxyimino)-1, 2-diphenylethan-1-ol, Arg is arginine, Glu is glutamine and Asp is asparagine.

Table 2: pH and Decomposition Temp.

Complex	pH	Decomposition temperature (^oC)
$[Ce(ND)_2(Arg)\cdot 2H_2O]$	6.90	258
$[Ce(ND)_2(Glu)\cdot 2H_2O]$	7.00	249
$[Ce(ND)_2(Asp)\cdot 2H_2O]$	6.86	242

Table 3: Elemental Analysis and Molar Conductance of Cerium (III) Complexes

Complex	Elemental Analysis Found (Calculated)				Molar Conductance (Mhos cm^2 mol^{-1})
	% M	% C	% H	% N	
$[Ce(ND)_2(Arg)\cdot 2H_2O]$	21.18 (22.10)	50.57 (49.55)	04.70 (04.63)	07.30 (07.35)	0.0020
$[Ce(ND)_2(Glu)\cdot 2H_2O]$	20.24 (19.25)	49.38 (51.32)	03.98 (03.90)	07.56 (07.32)	0.0024
$[Ce(ND)_2(Asp)\cdot 2H_2O]$	20.19 (20.17)	52.70 (48.65)	04.58 (04.45)	07.44 (07.30)	0.0017

.Magnetic Studies

The Gouy balance has been used to measure effective magnetic moments of complexes using diamagnetic corrections. The novel complexes are found to paramagnetic in nature.

Table 4: Magnetic susceptibility values of Cerium (III) complexes (-10^{-6} c.g.s. units)

Complex	Xg	Xm	μeff (B.M.)
$[Ce(ND)_2(Arg)\cdot 2H_2O]$	$- 2.10 \times 10^{-6}$	1.14×10^{-3}	1.92
$[Ce(ND)_2(Glu)\cdot 2H_2O]$	$- 2.34 \times 10^{-6}$	1.28×10^{-3}	1.80
$[Ce(ND)_2(Asp)\cdot 2H_2O]$	$- 2.28 \times 10^{-6}$	1.33×10^{-3}	1.74

Electronic Absorption Spectra analysis

Electronic spectra of the synthesized complexes has been recorded in DMF. This information confirms the bonding between the ligands with cerium metal ion through transition of electron [3]

Table 5: Electronic Spectral data of Cerium complexes

Complex	λ (nm)	ν (cm^{-1})	Proposed Assignments
$[Ce(ND)_2(Arg)\cdot 2H_2O]$	280	35714	π→π*
	341	29326	n →π*
	380	26316	Charge-transfer
$[Ce(ND)_2(Glu)\cdot 2H_2O]$	286	34965	π→π*
	345	28986	n →π*
	378	26455	Charge-transfer
$[Ce(ND)_2(Asp)\cdot 2H_2O]$	272	36765	π→π*
	340	29412	n →π*
	400	25000	Charge-transfer

Infra-red spectral details

The infrared spectra recorded by utilizing the FTIR spectrophotometer in the range of 4000-400 cm^{-1}. Band at ~3400 cm-1in the spectra of complex was absent which mainly occur due to free OH group in ND ligand due to the O-H stretching vibration confirming the deprotonation of the hydroxyl group of ND ligand and occurance of bond in complex between metal and ligand. Complexes also gives weak bands for C=N stretching at 1570-1490 cm^{-1} and the free ND ligand shows the same band at 1640 cm^{-1}. This confirms the bonding between nitrogen of ND ligand with metal ion. The broad peak between 3170-3200 due to O-H stretching vibrations and also the a peak arises in the range of 1500-1564 cm^{-1} due to the H– O–H bending vibrations which finds mainly due to presence of water molecules in complex [4].The peak obtained at ~3030 and ~2946 cm^{-1}, respectively due to the N-H asymmetric and N-H symmetric vibrations in the free amino acids are goes to higher wavenumbers 3148-3055 cm^{-1} and 3052-3048 cm^{-1}, respectively which shows the amino acids are coordinated through nitrogen atom with cerium metal. The COO- group peak in the range of 1560 to 1587 cm^{-1} shifted to higher wavenumber in the range of 1628-1646 cm^{-1} in the spectra confirming bonding takes through the oxygen atom of hydroxyl group of amino acids used to cerium metal ion.

Thermal information

TG and DTA methods has been employed for study of the thermal behaviour of the complexes. The information obtained has been summarized in the following Table No.7

Table 7: Thermal Data

Complex	Temp. Range (^oC)	Loss in Weight due to loss of	Weight loss (%)
$[Ce(ND)_2(Arg)\cdot 2H_2O]$	135-179	Two H_2O molecules	6.30
	249-410	Amino acid	15.48
	646-863	Two ND molecules	56.68
$[Ce(ND)_2(Glu)\cdot 2H_2O]$	146-180	Two H_2O molecules	6.63
	251-415	Amino acid	22.18
	640-858	Two ND molecules	64.25
$[Ce(ND)_2(Asp)\cdot 2H_2O]$	138-176	Two H_2O molecules	7.00
	253-418	Amino acid	20.30
	634-874	Two ND molecules	61.28

Therefore the proposed structure of the complexes on the basis of above study are as follows-

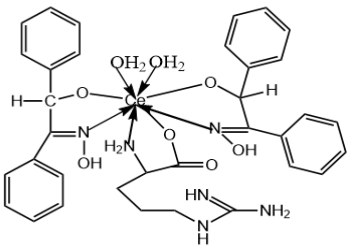

Fig. 1: Proposed Structures of $[Ce(ND)_2(Arg)\cdot 2H_2O]$

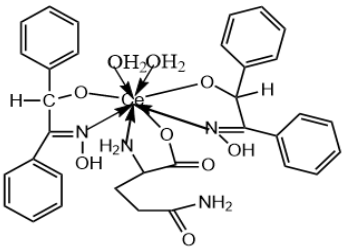

Fig. 2: Proposed Structures of $[Ce(ND)_2(Glu)\cdot 2H_2O]$

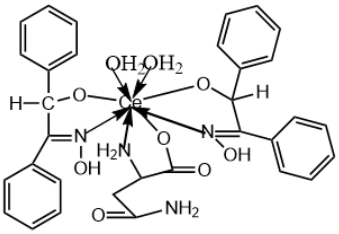

Fig. 3: Proposed Structures of $[Ce(ND)_2(Asp)\cdot 2H_2O]$

Agar cup and Tube dilution method are employed to study the antibacterial activity of the synthesized complexes. The MIC of metal salts and ligand lies in between 110 to 213 µg/mL while that of metal complexes lies in between 45 to 220 µg/mL. Metal complexes exbit higher antibacterial activity than ligands used for research work and metal salts. For the bacterial strain S. aureus and C. diphtheria, complexes produces more activity than *S. typhi* and *P. aeruginosa.* Chelation in complexes increases their activity. Chelation lowers polarity of metal ions so that hydrophobic property of complexes increases making its permeation via lipid layer of microorganisms.

Table 8: Antibacterial Activity (mm) of the Complexes by Agar Cup method.

Complex	Antibacterial Activity (mm) complexes with bacterial strain			
	C. diphtheria	S. aureus	P. aeruginosa	S. typhi
$[Ce(ND)_2(Arg)\cdot 2H_2O]$	14	19	08	09
$[Ce(ND)_2(Glu)\cdot 2H_2O]$	18	15	07	10
$[Ce(ND)_2(Asp)\cdot 2H_2O]$	10	13	09	08
Tetracycline	26	28	15	26

Conclusions:

The elemental analysis of the cerium complexes proposes the general proportion of 1:2:1 for synthesized complexes.

Thermal analysis of complexes confirms strong metal-ligand bonding while magnetic study clears that the metal complexes are paramagnetic in nature. The complexes are also found to be non-electrolytic nature. Intra ligand and charge transfer transitions are found from electronic absorption spectra of the complexes. FTIR spectra confirmed the bonding of metal and ligand molecules in the complexes. Thermal study shows the presence of metal ion, ligands as well as two coordinated water molecule in the complexes. So that the coordination number to synthesized complexes can be 8. Antibacterial investigations recommends that complexes are more active against C. diphtheria and S. aureus.

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