SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF SOME RARE EARTH METAL ION CHELATE WITH PHENYLGLYCINE

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ABSTRACT:

The complexes of the 2-amino-2-phenyl acetic acid with some rare earth metal ion were prepared in ethanol solution the ligand (L) and its metal complexes have been characterized by elemental analysis IR, UV, Visible spectra the suggesting M:L ratio is 1:3 octahedral geometries were proposed for La, Ce and Nd metal ion chelate.

INTRODUCTION:

The ligand phenylglycine (2-amino-2-phenyl acetic acid) has molecular formula C₁₈H₁₉NO₂ with molecular weight 151.2 g/mol. It is white crystalline powder and insoluble in common organic solvent and it is abbreviated as (PG). It is optically active, the ligand 1-3 containing –COOH, –NH₂ functional groups have important applications in analytical and biochemical reactions. Literature survey indicates that ligand 1-3 containing –COOH, –NH₂ functional groups have important applications in analytical and biochemical reactions. The formation, stabilities and reactivity of these chelate is a challenging field of research work. Many investigations have been under taken to learn interaction of metal ion with ligand containing oxygen, nitrogen donor atoms. The solid some rare earth metal ion chelates

Keywords:

2-Amino-2-phenyl acetic acid spectroscopic study: some rare earth metal ion chelate
Preparation Diaqua-tris(2-Amino2-phenyl acetic acid) La(III) chelate:

A weighed quantity of lanthanum chloride (3.713 gm) and ligand phenylglycine (1.5117 gm) were separately dissolved in 100 ml ethanol and 0.1 molar solutions were prepared. Clear solutions of metal salts and ligand were mixed in Stoichiometric ratio of 1:3 (by volume) Solutions. Solutions were mixed thoroughly with constant stirring and adjusted to a pH of 6.8 by adding alcoholic ammonia solution. Resultant mixture was heated under reflux for about three hours and allowed to cool. Dirty white colored mass precipitated obtained. It was separated after digestion for half an hour, washed with ethanol for three times and then dried in desiccators (yield = 75.08%).

EXPERIMENTAL:-

Preparation of Diaqua-tris(2-amino2-phenylacetic acid) Ce(III) chelate:

Molar solutions of phenylglycine (1.5117 gm) and cerium chloride (3.2758 gm) were prepared by dissolving 100 ml in ethyl alcohol. These solutions were mixed in to each other in 1:3 ratios and adjusted to a pH of 6.8 by adding alcoholic ammonia solution. Resultant mixture was heated under reflux for about three hours. At the end contents were allowed to cool, digested for half hour and filtered. Buff colored crystal was separated, dried in desiccators and stored in fresh bottle (yield = 75.77%).

Preparation of Diaqua-tris(2-amino2-phenyl acetic acid) Nd(III) chelate:

A weighted quantities of Nd(III) chloride (3.886 gm) and ligand PG (1.5117 gm) were prepared separately dissolved in 100 ml ethanol to prepare 0.1 molar solutions and clear solution were mixed in 1:3 ratio while constant stirring, by adding alcoholic ammonia pH of reaction mixture was adjusted to 6.8 and heated under reflux for about 3 hours. At the end contents were allowed to cool, digested for half hour and filtered white colored crystals were separated, dried in desiccators and stored in bottle (yield = 75.29%).

PHYSICAL CHARACTERIZATION OF PREPARED METAL CHELATES:

Synthesized metal chelates were subjected to physical characterization nature, colour and solubility was recorded. Decomposition point was measured by open capillary method and elemental analysis was carried out at IICT, Hyderabad. These observations are recorded in table No.1. Presence of lattice water was determined by heating known weight of metal chelate in the oven at 110°C.
Analytical data of La(III), Ce(III), Nd(III) metal chelate with 2-amino-2-phenyl acetic acid

RESULT AND DISCUSSION:

The ligand phenylglycine (PG) is used to prepare metal chelates of La(III), Ce(III), and Nd(III). These chelates are colored, but it is soluble in DMSO. Decomposition points of these metal ion chelates are very high suggesting good thermal stability.

UV – VISIBLE SPECTRAL STUDIES:

The electronic absorption data of the compounds in DMSO are given in the table no.2. In the spectrum of ligand, (Phenyl glycine) the band at 262 nm assigned is attributed to the $\pi \rightarrow \pi^*$ transition of the spectra of the ligand, bands at the 331 nm, 351 nm are assigned to the $n \rightarrow \pi^*$ transitions of the amine group. The electronic absorption spectra of the [La(PG)$_3$2H$_2$O]H$_2$O chelate have bands at 225 nm, 251 nm and 362 nm. These bands may be due to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of phenyl ring and amine group respectively. In the spectra of the chelate, the less instance band in the 421 nm due to the charge transfer $^{9-10}$LMCT (ligand to metal band) transition from the electronic lone pairs of the carboxylate charge transfer oxygen donor to metal ion. The electronic absorption spectrum of [Ce(PG)$_3$2H$_2$O]H$_2$O chelate have the bands 231 nm, 260 nm may be due to the $\pi \rightarrow \pi^*$ and transitions, the bands in the 342 nm 371 nm are assigned to the $n \rightarrow \pi^*$ transitions. In the spectra of the chelate, the less instance band in the 475 nm due to the charge transfer LMCT (ligand to metal band) transition [Nd(PG)$_3$2H$_2$O]H$_2$O chelate have bands at 225 nm, 298 nm and 355 nm, 365 nm. These bands may be due to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions $^{11-12}$ of phenyl ring and amine group respectively. In the spectra of the

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Chelates</th>
<th>Molecular weight</th>
<th>Empirical formula</th>
<th>Color</th>
<th>Decomposition point</th>
<th>Molar conductivity $\Delta n\Omega^{-1}cm^2$</th>
<th>yield %</th>
<th>M:L ratio</th>
<th>Elemental analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>[La(PG)$_3$2H$_2$O]H$_2$O</td>
<td>642.91</td>
<td>LaC$<em>{24}$H$</em>{30}$N$_3$O$_9$</td>
<td>Dirty white</td>
<td>187</td>
<td>11.50</td>
<td>75.08</td>
<td>1:3</td>
<td>C: 44.79, H: 4.66, N: 6.53, M: 21.60</td>
</tr>
<tr>
<td>2.</td>
<td>[Ce(PG)$_3$2H$_2$O] H$_2$O</td>
<td>644.12</td>
<td>CeC$<em>{24}$H$</em>{30}$N$_3$O$_9$</td>
<td>Buff</td>
<td>198</td>
<td>12.23</td>
<td>75.77</td>
<td>1:3</td>
<td>C: 44.71, H: 4.65, N: 6.52, M: 21.75</td>
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<td>3.</td>
<td>[Nd(PG)$_3$2H$_2$O] H$_2$O</td>
<td>648.24</td>
<td>NdC$<em>{24}$H$</em>{30}$N$_3$O$_9$</td>
<td>White</td>
<td>188</td>
<td>11.10</td>
<td>75.29</td>
<td>1:3</td>
<td>C: 44.52, H: 4.62, N: 6.47, M: 22.25</td>
</tr>
</tbody>
</table>
chelate, the band at the 420 nm due to the charge transfer LMCT (ligand to metal band) transition from the electronic lone pairs of the carboxylate charge transfer oxygen donor to metal ion.

### Table No. 2

**UV VISIBLE SPECTRAL DATA OF LANTHANIDE METAL CHELATES**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Ligand/ Metal Chelate</th>
<th>Absorbance</th>
<th>Transition</th>
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</thead>
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<tr>
<td></td>
<td></td>
<td>Nm</td>
<td>cm⁻¹</td>
</tr>
<tr>
<td>1.</td>
<td>Ligand (PG) (Phenylglycine)</td>
<td>262</td>
<td>381679</td>
</tr>
<tr>
<td></td>
<td></td>
<td>331</td>
<td>302114</td>
</tr>
<tr>
<td></td>
<td></td>
<td>362</td>
<td>276243</td>
</tr>
<tr>
<td>2.</td>
<td>[La(PG)₃.2H₂O].H₂O</td>
<td>225</td>
<td>444444</td>
</tr>
<tr>
<td></td>
<td></td>
<td>251</td>
<td>398406</td>
</tr>
<tr>
<td></td>
<td></td>
<td>362</td>
<td>276243</td>
</tr>
<tr>
<td></td>
<td></td>
<td>421</td>
<td>237552</td>
</tr>
<tr>
<td>3.</td>
<td>[Ce(PG)₃.2H₂O].H₂O</td>
<td>231</td>
<td>432900</td>
</tr>
<tr>
<td></td>
<td></td>
<td>260</td>
<td>384615</td>
</tr>
<tr>
<td></td>
<td></td>
<td>342</td>
<td>292397</td>
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<tr>
<td></td>
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<td>371</td>
<td>269541</td>
</tr>
<tr>
<td></td>
<td></td>
<td>475</td>
<td>210526</td>
</tr>
<tr>
<td>4.</td>
<td>[Nd(PG)₃.2H₂O].H₂O</td>
<td>225</td>
<td>444444</td>
</tr>
<tr>
<td></td>
<td></td>
<td>298</td>
<td>335570</td>
</tr>
<tr>
<td></td>
<td></td>
<td>355</td>
<td>281690</td>
</tr>
<tr>
<td></td>
<td></td>
<td>365</td>
<td>273972</td>
</tr>
<tr>
<td></td>
<td></td>
<td>420</td>
<td>238092</td>
</tr>
</tbody>
</table>

**Fig. No. 1:** UV spectra of 2-amino-2-phenyl acetic acid ligand
Fig. No. 2: UV spectra of [La (PG),2H₂O] H₂O

Fig. No. 3: UV spectra of [Ce(PG),2H₂O] H₂O
IR CHARACTERIZATION OF METAL CHELATES:

Studies of infrared spectra for the ligand and its metal ion chelates are recorded and presented in table no. 3 displays characteristic bands at (3349) cm\(^{-1}\). These bands were attributed to the (\(-\text{NH}_2\)) group. Also a weak band showed at 3298 cm\(^{-1}\) assigned to carboxylic (\(-\text{OH}\)) group. The band at 1631 cm\(^{-1}\) which shows \(\nu\) (C=O) group in ligand.

\([\text{La(PG)}_3\text{2H}_2\text{O}]\cdot\text{H}_2\text{O}\) chelate:

New broad band at 3505 cm\(^{-1}\) have appeared, this band indicated the presence of coordinated water molecule\(^{13}\). Further, the band observed at 3349 cm\(^{-1}\) due to \(-\text{NH}_2\) group in ligand and is shifted towards higher frequency at 3388 cm\(^{-1}\) attributed to involvement in coordinate bond\(^{14}\). IR band at 3298 cm\(^{-1}\) is observed in ligand due to (OH) stretching vibration\(^{15,16}\). This band is disappeared in the complex shows deprotonation.

Similarly band at 1350 cm\(^{-1}\) in ligand due to (OH) shifted at 1234 cm\(^{-1}\) indicates involvement in coordination.

The band at 1631 cm\(^{-1}\) which shows \(\nu\) (C=O) group in ligand, this frequency does not change in the spectra of metal chelate, indicates this group not involve for coordination. Appearance of new bands in the complex (M-N) at 447 cm\(^{-1}\) and (M-O) at 556 cm\(^{-1}\). This band not observed in the spectra of ligand.

\([\text{Ce(PG)}_3\text{2H}_2\text{O}]\cdot\text{H}_2\text{O}\) chelate:

The new band observed at 3510 cm\(^{-1}\) due to presence of coordinated water molecule\(^{18}\) in metal ion chelates which does not found in the IR spectra of ligand. A band at 3349 cm\(^{-1}\) is observed in ligand due to \(-\text{NH}_2\) stretching vibration. This band shifted to 3399 cm\(^{-1}\) indicates involvement in coordination\(^{19}\). IR band at 3298 cm\(^{-1}\) is observed in ligand due to (OH) stretching vibration. This band is disappeared in the chelate shows deprotonation\(^{20}\). Further the band at 1350 cm\(^{-1}\) in ligand due to (OH) shifted at 1282 cm\(^{-1}\) due to deprotonation indicates involvement in coordination.
The band at 1631 cm\(^{-1}\) which shows \(\nu (C=O)\) group in ligand, this frequency does not change in the spectra of metal chelate, indicates this group not involve for coordination The band due to M-Cl was not found because of instrumental limitation. Appearance of new bands in the chelate (M-N) at 461 cm\(^{-1}\) and (M-O) at 555 cm\(^{-1}\)\(^{21-22}\).

\[\text{Nd(PG)}_3\text{2H}_2\text{O}.\text{H}_2\text{O chelate:}\]

The IR spectrum of metal chelate is compared with IR spectra of ligand. The new band observed at 3515 cm\(^{-1}\) due to presence of coordinated water molecule\(^{23}\). The ligand exhibits stretching of -NH\(_2\) at 3349 cm\(^{-1}\) which on complexation shifted to higher wave number by 35 cm\(^{-1}\) suggesting that amino group are involved in coordination\(^{24}\). Further the band at 1350 cm\(^{-1}\) in ligand due to (OH) shifted by lower wave number at 1224 cm\(^{-1}\) due to deprotonation indicates involvement in coordination and underwent a shift confirms the participation of oxygen atoms in the C-O-M bond\(^{25}\). The band at 1631 cm\(^{-1}\) which shows \(\nu(C=O)\) group in ligand, this frequency does not change in the spectra of metal chelate, indicates this group not involve for coordination. The band due to M-Cl was not found because of instrumental limitation. The appearance of new bands in the spectra of metal ion complex at 445 cm\(^{-1}\) and 502 cm\(^{-1}\) due to new bonding i.e. (M-N) and (M-O)\(^{26}\).

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Ligand / Metal Chelate</th>
<th>(\text{H}_2\text{O}) cm(^{-1})</th>
<th>-NH(_2) cm(^{-1})</th>
<th>OH cm(^{-1})</th>
<th>C = O cm(^{-1})</th>
<th>C – O cm(^{-1})</th>
<th>M – O cm(^{-1})</th>
<th>M – N cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Ligand (PG) (Phenylglycine)</td>
<td>-</td>
<td>3349</td>
<td>3298</td>
<td>1631</td>
<td>1350</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>[\text{La (PG)}_3\text{2H}_2\text{O}] \text{H}_2\text{O}]</td>
<td>3505</td>
<td>3388</td>
<td>-</td>
<td>1635</td>
<td>1234</td>
<td>556</td>
<td>447</td>
</tr>
<tr>
<td>3.</td>
<td>[\text{Ce(PG)}_3\text{2H}_2\text{O}] \text{H}_2\text{O}]</td>
<td>3510</td>
<td>3399</td>
<td>-</td>
<td>1637</td>
<td>1282</td>
<td>555</td>
<td>461</td>
</tr>
<tr>
<td>4.</td>
<td>[\text{Nd(PG)}_3\text{2H}_2\text{O}] \text{H}_2\text{O}]</td>
<td>3515</td>
<td>3384</td>
<td>-</td>
<td>1635</td>
<td>1224</td>
<td>502</td>
<td>445</td>
</tr>
</tbody>
</table>
IR spectra of $[\text{La(PG)}_3\text{2H}_2\text{O}]\text{H}_2\text{O}$

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IR spectra of $[\text{La(PG)}_3\text{2H}_2\text{O}]\text{H}_2\text{O}$

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IR spectra of $[\text{Ce(PG)}_3\text{2H}_2\text{O}]\text{H}_2\text{O}$

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IR spectra of $[\text{Nd(PG)}_3\text{2H}_2\text{O}]\text{H}_2\text{O}$
Proposed structure of Diaqua-tris(2-amino 2-phenyl acetic acid) La (III) chelate

![Diagram of the proposed structure of Diaqua-tris(2-amino 2-phenyl acetic acid) La (III) chelate]

Molecular formula: $\text{LaC}_{24}\text{H}_{30}\text{N}_3\text{O}_9$  Mol. Weight: 642.91

Proposed structure of Diaqua-tris (2-amino 2-phenyl acetic acid) Ce (III) chelate

![Diagram of the proposed structure of Diaqua-tris(2-amino 2-phenyl acetic acid) Ce (III) chelate]

Molecular formula: $\text{CeC}_{24}\text{H}_{30}\text{N}_3\text{O}_9$  Mol. weight: 644.12

Proposed structure of Diaqua-tris-(2-amino-2-phenyl acetic acid) chelate

![Diagram of the proposed structure of Diaqua-tris-(2-amino-2-phenyl acetic acid) chelate]

Molecular formula: $\text{NdC}_{24}\text{H}_{30}\text{N}_3\text{O}_9$  Mol. weight: 648.24

REFERENCES: