MASS AND $^1$H NMR SPECTRA OF THE COMPLEX OF N-THIOTRITHIAZYL-o-THIOTRITHIAZYL PHENYLALANIANTE WITH Zn (II)

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ABSTRACT

The complex of Zn (II) with new ligand N-thiotrithiazyl-o-thiotrithiazyl phenylalaninate was prepared, and characterized by Mass, I.R. and $^1$H NMR spectral studies. The complex was found, having molecular formula ZnL$_2$. On the basis of IR, $^1$H NMR and mass spectra, it has been proved that the complex is quadridentately coordinated.

Key words: Mass, NMR, Zinc, Phenylalaninate, Thiotrithiazyl.

INTRODUCTION

S$_4$N$_3$Cl and its complexes have been used as chemical agents for microbials$^{1-3}$. N-thiotrithiazyl-o-thiotrithiazyl phenylalaninate (N-TTA-o-TTAPA) is obtained by the condensation of thiotrithiazyl chloride and phenylalanine, which formed number of complexes with metal ions, organic as well as inorganic compounds$^{4-9}$. The investigation of the complex, Zn (II)-bis-N-thiotrithiazyl phenylalaninate are being reported, herewith.

EXPERIMENTAL

Materials and methods

Phenylalanine, DMF and zinc oxide (B.D.H.) were used, S$_4$N$_3$Cl was prepared as reported earlier$^{10}$. The new ligand, N-TTA-o-TTAPA was obtained by refluxing S$_4$N$_3$Cl and phenylalanine in DMF for 6 h.

The light yellow product obtained, was filtered, washed subsequently with DMF, ether and alcohol; dried and stored in vacuum desiccator.
On the basis of quantitative estimation, mass, IR and $^1$H NMR spectra, the new ligand has been formulated as –

\[
\begin{align*}
C_6H_5CH_2 - CH & \quad \text{NHS}_3N_3 \\
& \quad \text{COOS}_2N_3
\end{align*}
\]

**Synthesis of Zn (II) complex**

1 mole of zinc oxide was dissolved in DMF and to this, 2 mol of ligands was added with constant stirring. This mixture was refluxed for 6 h. The light yellow powdered mass obtained, was subsequently washed with ether, dried and stored in vacuum desiccator.

M.P. $> 300^\circ\text{C}$ yield (65 %). The chemical data \%; found (cal.) Zn; 8.57 (8.60), S 35.00 (35.20), N; 15.22 (15.33), C; 29.44 (29.54), H 2.40 (2.46) and mol. wt. (730.5) 731 g/mol. The complex has been assigned structure as –

\[
\left( C_6H_5CH_2 - CH \quad \text{NHS}_3N_3 \right)^-Zn^{2+} \quad \text{COOS}_2N_3
\]

Mass, $^1$H NMR spectrum and IR spectrum were recorded on Jeol SX-102 (FAB) spectrometer, Bruker DRX-300 spectrometer and Shimadzu 8201 PC IR Hitachi spectrophotometer, respectively. Elemental analysis were obtained from Perkin-Elmer CHN microanalyzer.

Test for chloride was performed and it was found to be negative.

**RESULTS AND DISCUSSION**

Analytical data show that zinc has formed the 1 : 2 adduct with N-TTA-o-TTAPA. The complex obtained was stable at room temperature.

**Mass spectrum**

As an additional support, the recorded FAB mass spectrum of the complex shows the estimated molecular weight to be 731.5 g/mol for Zn (II) complex, which is in good agreement with the experimentally determined molecular weight (730.5) of the complex.
The mass pattern of the complex is explained by FAB fragmentation process as represented below -

\[ \text{C}_6\text{H}_5-\text{CH}_2-(\text{COO})\text{CH}-\text{NH-S}_4\text{N}_3 \]
\[ \rightarrow \text{Zn} \]
\[ \text{C}_6\text{H}_5-\text{CH}_2-(\text{COO})\text{CH}-\text{NH-S}_4\text{N}_3 \]
\[ \rightarrow \text{m/z} \ 731 \]
\[ \text{m/z} \ 559 \ (M + 1) \]

\[ \text{C}_6\text{H}_5-\text{CH}_2-(\text{COO})\text{CH}-\text{NH-S}_4\text{N}_3 \]
\[ \rightarrow \text{m/z} \ 664 \ (M - 3) \]

\[ \text{C}_6\text{H}_5-\text{CH}_2-(\text{COO})\text{CH}-\text{NH-S}_4\text{N}_3 \]
\[ \rightarrow \text{m/z} \ 633 \ (M - 2) \]

\[ \text{C}_6\text{H}_5-\text{CH}_2-(\text{COO})\text{CH}-\text{NH-S}_4\text{N}_3 \]
\[ \rightarrow \text{m/z} \ 601 \ (M - 2) \]

\[ \text{C}_6\text{H}_5-\text{CH}_2-(\text{COO})\text{CH}-\text{NH-S}_4\text{N}_3 \]
\[ \rightarrow \text{m/z} \ 559 \ (M + 1) \]
Thus, the mass lines for various fragments explained the ZnL\(_2\) complexes formation. The reaction between N-TTA-o-TTAPA and ZnO may be shown as –

\[
2(S_4N_3 - NH - CH - (COO)S_4N_3 - NH_2 - C_6H_5) + ZnO \rightarrow \text{DMF; 6 h}
\]

\[
(S_4N_3 NH - CH - (COO)CH_2 - C_6H_5)_2 Zn + (S_4N_3)_2O
\]

In the IR spectrum (Table 1) of the complex, the bands were observed at 465 (d, w), 617 (d, b), 1119, 1397, 1625 and 2359 cm\(^{-1}\), are for the O → M, N → M, new bonding N-S, S-S, S-N bonds of S\(_4\)N\(_3\) rings, NH and CO groups, respectively\(^{11,12}\).

The shifting of S-N free band toward lower frequency, suggests the coordination of S\(_4\)N\(_3\) ring through nitrogen atom, Lowering of the frequency of COO- groups also confirms its coordination to Zn (II) metal ion. Thus, the ligand, N-TTA-o-TTAPA has quadridentatively coordinated to Zn (II) through the oxygen atom of amino acid and N atom of S\(_4\)N\(_3\) ring.

\(^1\)H NMR spectrum was recorded and it is interpreted on the basis of available literature. The two sets of triplet signals at chemical shift, \(\delta\) 0.00 to 1.237 and \(\delta\) 6.908 to 7.325 ppm are due to the two S\(_4\)N\(_3\) rings present on opposite side along with the two sets of multiplet of signals in the range of chemical shift, \(\delta\) 2.502 – 3.320 ppm for the two phenylalanilate groups.
Table 1: IR spectral data of complex

<table>
<thead>
<tr>
<th>Vibrations</th>
<th>Band assigned</th>
<th>Free constant $K \times 10^5$ (dyn/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>465 (d, b)</td>
<td>O $\rightarrow$ M</td>
<td>10.77</td>
</tr>
<tr>
<td>617 (d, b)</td>
<td>N $\rightarrow$ M</td>
<td>18.96</td>
</tr>
<tr>
<td>1119 (sh)</td>
<td>N – S</td>
<td>18.96</td>
</tr>
<tr>
<td>1396 (sh)</td>
<td>S – N in $S_4N_3$ ring</td>
<td>62.37</td>
</tr>
<tr>
<td>1625 (b)</td>
<td>$\nu$ (C = O)</td>
<td>97.27</td>
</tr>
<tr>
<td>23.59 (sh)</td>
<td>$\nu$ (N – H)</td>
<td>277.18</td>
</tr>
</tbody>
</table>

The peaks at chemical shift $\delta$ 6.908 – 7.076 are due to excessive interaction of groups with CH$_2$ groups. The two triplets with chemical shift 7.206 – 7.408 are due to the two CH-CH$_2$ groups with in the complex. Two signals in the spectrum at chemical shift $\delta$ 7.907 and $\delta$ 7.964 are due to two phenyl groups present in the complex, while the two signals at chemical shift $\delta$ 8.344 and $\delta$ 8.372 are on account of two NH groups present in the complex.

The chemical shift change in the $^1$H NMR spectrum of the complex also suggest the complex formation.

These data suggest the following structure of the complex (Fig. 1).

![Figure 1: Structure of complex Zn (II) Bis (N-TTA-o-TTAPA)](image-url)
REFERENCES


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