SYNTHESIS AND CHARACTERIZATION OF AMINO ACID SUBSTITUTE CYCLOTRIPHOSPHAZENIDES

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ABSTRACT

The amino acid, lysine, substituted compound of (NPCl₂)₃ was synthesized. The complex was studied with the help of Mass, FT-IR and microanalysis assigning its molecular formula as -(PN)₃[OOC(CH₂)₅NH₂]₆

Key words: Phosphozenides, Amino acid, Lysine.

INTRODUCTION

Due to N atom (NPCl₂)₃ molecule has much coordinating property and hence, it has formed a large number of complexes with metals¹⁻⁶. On the other hand, there is six symmetric chlorine atoms, which perform substitution reaction with covalent compounds⁷. These substituted and adduct derivatives of (NPCl₂)₃ have industrial, pharmaceutical and biological importance such as, the complexes of (NPCl₂)₃ with Cu, Fe and Co were found bactericidal⁸⁻¹⁰.

Adducts of (NPCl₂)₃ with phenoxy substituted compound are hydraulic lubricant¹¹. Polyorganophosphazenes have fire proofing agents¹², plastics¹³ and biological properties,¹⁴ while polymethoxy, ethoxy, amino and aryl substituted polyphosphazene are bioactive¹⁵. Pt (II) complex of (NPCl₂)₃ has antitumor activities¹⁶. Polyaminophosphazenes were found good germicides¹⁷⁻²⁰. Water soluble cyclotriphos-phazenes (diamine) Pt (II) conjugated drugs were also found to have antitumor activity²¹.

EXPERIMENTAL

Methodology

Chemicals: Phosphorous pentachloride, amino acids (Lysine), ammonium chloride, chloro-
benzene, ether, alcohol, etc. doubly distilled were used.

**Preparation of hexachlorocyclotriphosphazene**

(NPCl₂)₃ was prepared by the refluxing an equimolar mixture of PCl₅ and NH₄Cl in chlorobenzene at 140-160°C for 7-8 hours. The unreacted NH₄Cl was removed by filtration and (NPCl₂)₃ was obtained, after distillation under reduced pressure.

**Preparation of amino acid (Lysine) substituted phosphazenides**

The compound of lysine with (NPCl₂)₃ was prepared by the refluxing a mixture of (NPCl₂)₃ and lysine (100 mg of each in 1 : 1) at 150-165°C for 7-9 hours using C₆H₅Cl as a solvent. A brownish precipitate was obtained, which was filtered, washed with chlorobenzene, ether and alcohol. Dried product was stored in vacuum desiccator over fused CaCl₂.

**Instrumental studies**

A Perkin-Elmer FT-IR spectrophotometer was used to record the IR spectrum (4000-500 cm⁻¹). The DART mass spectrum was recorded on a JEOL-Accutof JMS-T100lc Mass spectrometer having a DART source using helium lamp at 350°C. Microanalysis for constituent elements was carried out from CDRI, Lucknow. Molecular weight was determined by Rast’s method.

**Observation**

The newly synthesized compound was brownish in color, solid, soluble in water and having melting point 350-360°C.

![Fig. 1: IR Spectrum of compound](image-url)
Table 1: IR spectral data

<table>
<thead>
<tr>
<th>Frequency of band (cm(^{-1}))</th>
<th>Assigned bands</th>
<th>Force constants (Dyne/cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>3427.0 (b)</td>
<td>=NH</td>
<td>7.87 (\times) 10(^5)</td>
</tr>
<tr>
<td>2363.1 (s)</td>
<td>–P= N</td>
<td>6.5 (\times) 10(^5)</td>
</tr>
<tr>
<td>1651.9 (b,s)</td>
<td>CO</td>
<td>3.21 (\times) 10(^5)</td>
</tr>
<tr>
<td>1405.0 – 1466.2 (w,b)</td>
<td>PO</td>
<td>–</td>
</tr>
<tr>
<td>672.1 – 543.0 (b)</td>
<td>–PN–</td>
<td>–</td>
</tr>
</tbody>
</table>

Fig. 2: Mass spectrum of compound

Table 2: Mass spectral data

<table>
<thead>
<tr>
<th>m/z</th>
<th>Fragments</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>73</td>
<td>P(_2)N</td>
<td>(M-3)</td>
</tr>
<tr>
<td>103</td>
<td>P(_2)N(_3)</td>
<td>(M-3)</td>
</tr>
<tr>
<td>128</td>
<td>C(_3)H(_4)PN(_2)O(_2)</td>
<td>(M-3)</td>
</tr>
<tr>
<td>202</td>
<td>C(_6)H(_13)PN(_2)O(_2)</td>
<td>(M-3)</td>
</tr>
<tr>
<td>247</td>
<td>C(_6)H(_15)P(_3)N(_3)O(_2)</td>
<td>(M-3)</td>
</tr>
<tr>
<td>304</td>
<td>(CHCOO)(_3)N(_3)P(_3) (M-3)</td>
<td></td>
</tr>
<tr>
<td>533</td>
<td>(CHCOO)(_3)(NH(_2)CH(_2)COO)(_3)P(_3)N(_3) (M-3)</td>
<td></td>
</tr>
<tr>
<td>919</td>
<td>[NH(_2)(CH(_2))(_3)PCOO](_6)P(_3)N(_3) (M-3)</td>
<td>Parent peak</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

(i) On the basis of quantitative estimations, % found, are C-46.32, N-13.7, O-20.98 and H-7.86 and molecular weight is 915 mol\(^{-1}\). The compound may be assigned the structure (Fig. 3), which was supported by peak (m/z -919) in its mass spectrum and microanalysis.

(ii) This compound formation is supported by frequencies observed in its IR spectrum having the frequencies at 543.0-672.1 (b) \(^{22}\), 1405.0-1466.2 (w,b), 1651.9 (b,s), 2363.1 (s) and 3427.0 (b) (Table 1), corresponding to five \(-\text{P-N}\), P-O, CO, \(-\text{P = N}\) and NH bands. The occurrence of vibrations for P-O and C-O linked to P-O group indicates that P-Cl\(_2\) has reacted with COOH group of amino acid (lysine) through oxygen, due to affinity of phosphorous to oxygen. The value of force constant inferred the P-N and P = N groups

(iii) Mass spectroscopy of this compound has supported the structure of compound as \((\text{NP})_3[\text{OOC(CH}_2\text{)}_5\text{NH}_2]\)_6. The most probable fragments are given in Table 2.

The formation of adduct may be explained by the following reaction -

\[
P_3\text{N}_3\text{Cl}_6 + 6 \text{NH}_2(\text{CH}_2)_4\text{CH(NH}_2\text{)}\text{COOH} \rightarrow P_3\text{N}_3[\text{NH}_2(\text{CH}_2)_5\text{COO}]_6 + \text{N}_2 + 4 \text{NH}_3 + 6 \text{HCl}
\]

Hence, the structure of the adduct may be expressed as -

\[\text{H}_2\text{N(}\text{CH}_2\text{)}_3\text{OOC} - \text{P} - \text{N} \quad \text{OOC(}\text{CH}_2\text{)}_3\text{NH}_2
\]

\[\text{H}_2\text{N(}\text{CH}_2\text{)}_3\text{COO} - \text{P} - \text{N} \quad \text{OOC(}\text{CH}_2\text{)}_3\text{NH}_2
\]

\[\text{H}_2\text{N(}\text{CH}_2\text{)}_3\text{COO} - \text{P} - \text{N} \quad \text{OOC(}\text{CH}_2\text{)}_3\text{NH}_2
\]

Fig. 3: Proposed structure of the compound \(P_3\text{N}_3[\text{NH}_2(\text{CH}_2)_5\text{COO}]_6\)

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REFERENCES


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