



Spectral Characterization of the adduct of $[\text{NP}(\text{OH})_2]_3$ with Glutamic acid

Atul Gupta and S.P.S. Jadon*
Department of Chemistry,
S.V. College, Aligarh (U.P.) 202001, India

Abstract: The adduct of glutamic acid with hexahydroxycyclotriphosphazene, $[\text{NP}(\text{OH})_2]_3$ is formulated as $[\text{P}_3\text{N}_3(\text{OH})_2]_2 [\text{C}_{30}\text{H}_{46}\text{N}_6\text{O}_{24}]$, which is characterized on the basis of I.R., U.V., E.P.R., N.M.R., and X.R.D. spectra having linear structure.

Keywords: Triclinic, Geometry, Industrial Applications, Conductivity

I. Introduction

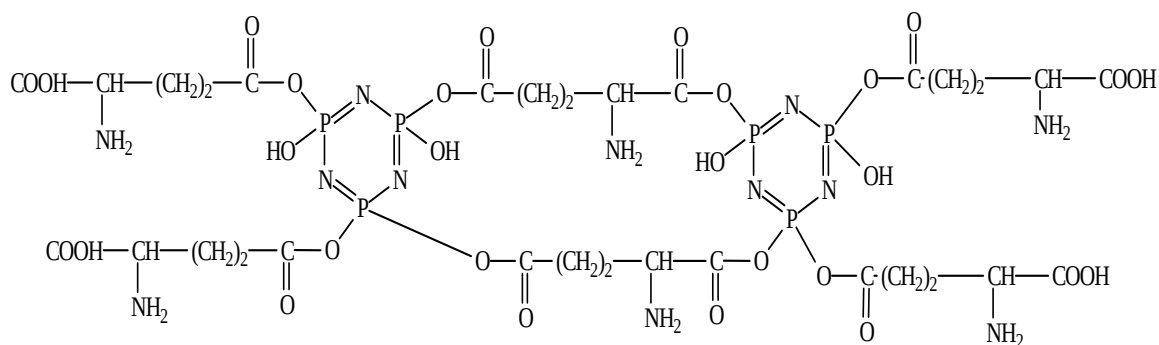
The adducts of $(\text{NPCl}_2)_3$ with various organic compounds have been found industrial, medicinal utilities.¹⁻⁸ Similarly the some adduct of $[\text{NP}(\text{OH})_2]_3$ with cinnamic acid, oleic acid, acrylic acid have been prepared and studied.⁹⁻¹⁰ The compounds with Hippuric acid, Salicylic acid, Nicotinic acid and Adipic acid have also been investigated and reported.¹¹⁻¹⁴ The studies of adduct of $[\text{NP}(\text{OH})_2]_3$ with Glutamic acid are being represented herewith.

II. Experimental

$[\text{NP}(\text{OH})_2]_3$, prepared¹⁵ by the reaction of NaOH with $[\text{NP}(\text{Cl})_2]_3$, were mixed with Glutamic acid in the ratio of 1:1, dissolved in alcohol, refluxed in presence of 1 ml concentration H_2SO_4 for 6 to 8 hours till the brownish black mass was precipitated out. The product, formed, was filtered, washed with alcohol and ether respectively, dried and stored in vacuum desiccators. For the spectral analysis, mass spectra on Jeol SX-102 (FAB), I.R. spectra on Shimadzu 8201 PC ($4000 - 500 \text{ cm}^{-1}$), U.V. on Perkin-Elmer Lambda - 15 spectrophotometer (200 - 800nm), E.P.R. on varian's X-E-4 band spectrometer, $^{13}\text{CNMR}$ & $^1\text{HNMR}$ on Bruker DRX-300, spectrometers were used at room temperature and X.R.D. were recorded on PW-1710 X-ray power diffractometer using $\lambda = 1.5418 \text{ \AA}$, ($\text{CuK}\alpha$, as source of radiation) in the 2θ range $0^\circ - 80^\circ$.

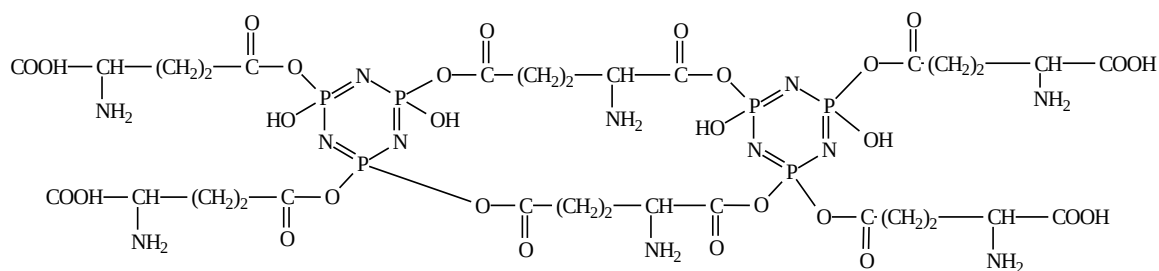
III. Results and Discussion

The brownish black adduct is soluble in DMSO. The analytical data; % found (Cal.), P 15.35 (15.34), N 13.87 (13.86), O 36.98 (36.96), C 29.72 (29.70), H 4.12 (4.12) and molecular weight 1211.4 (1212) gm. mol^{-1} , lead to formulated it as $[\text{P}_3\text{N}_3(\text{OH})_2]_2 [\text{C}_{30}\text{H}_{46}\text{N}_6\text{O}_{24}]$ which is supported by the prominent mass line m/z 1210 ($M - 2$), observed, in its mass spectrum (fig. 1).

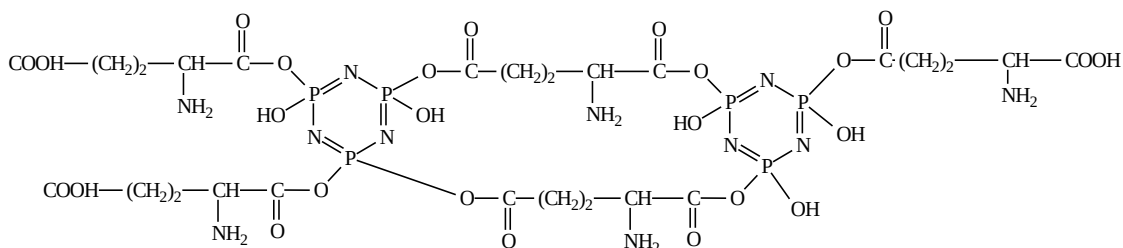


M/Z 1210 ($M - 2$)

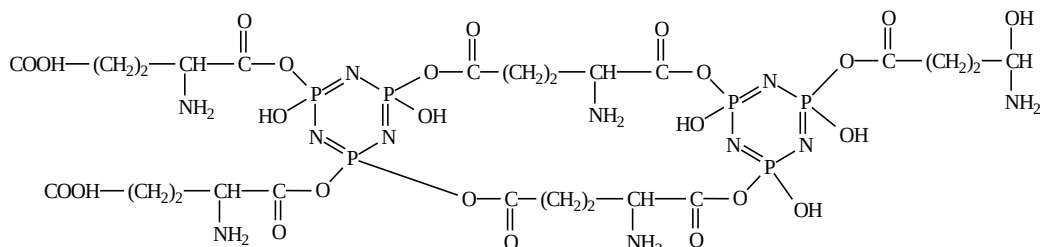
The appearance of the other mass lines may be explained by the FAB fragmentation process as:



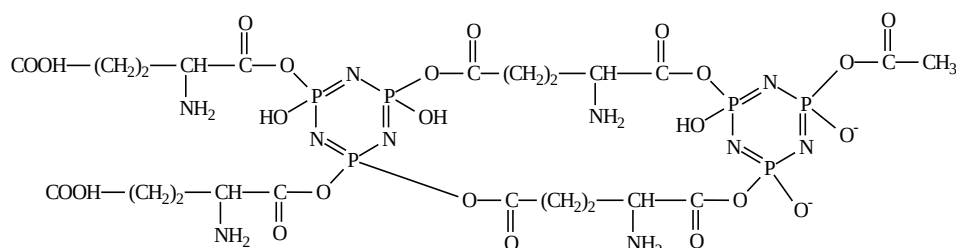
M/Z 1210 (M - 2)



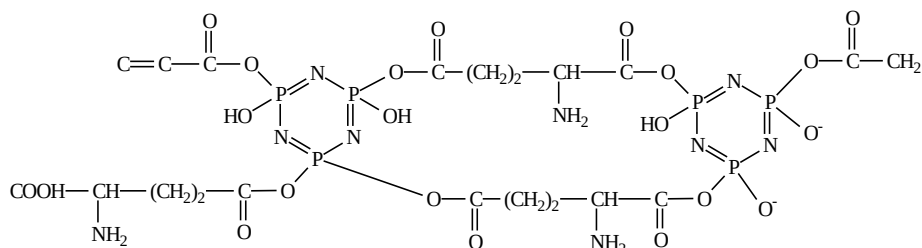
M/Z - 1080 (M - 3)



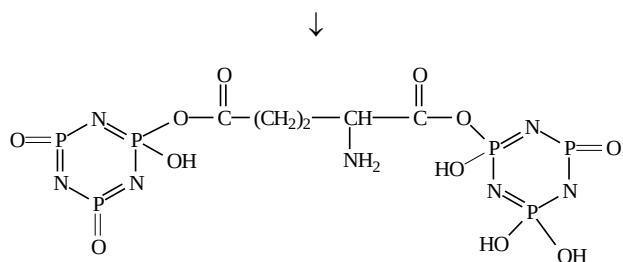
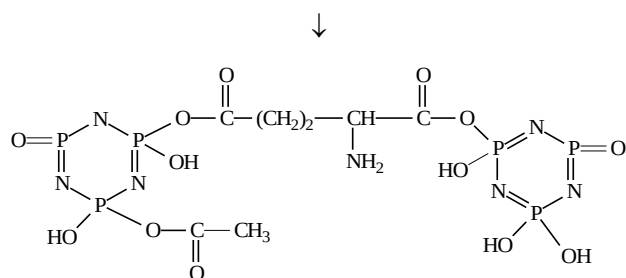
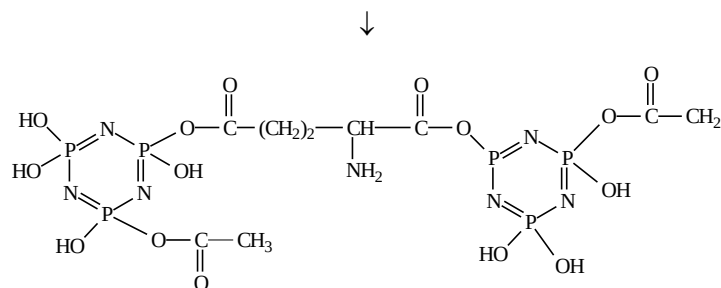
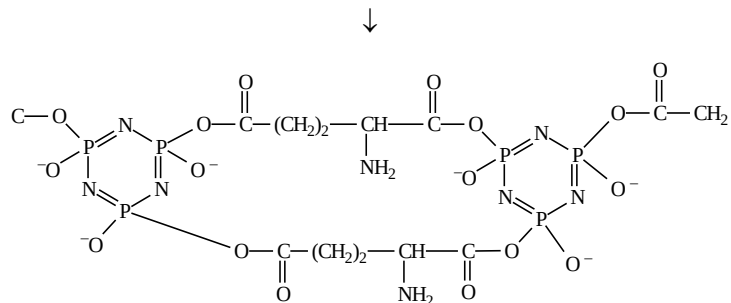
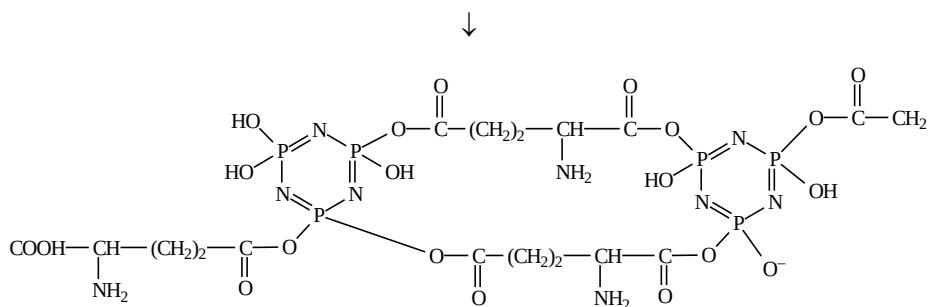
M/Z - 1056 (M + 1)

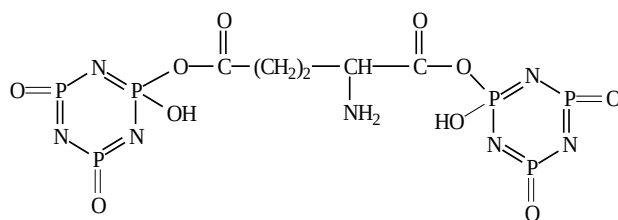


M/Z - 991 (M - 3)

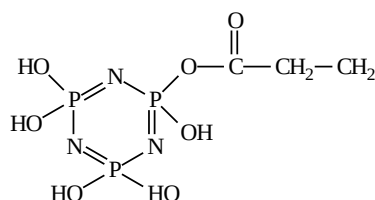


M/Z - 912 (M - 3)



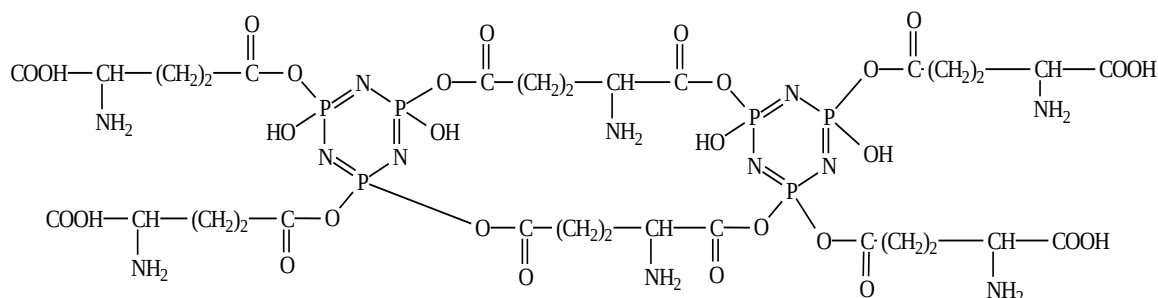


$M/Z - 514 (M + 1)$

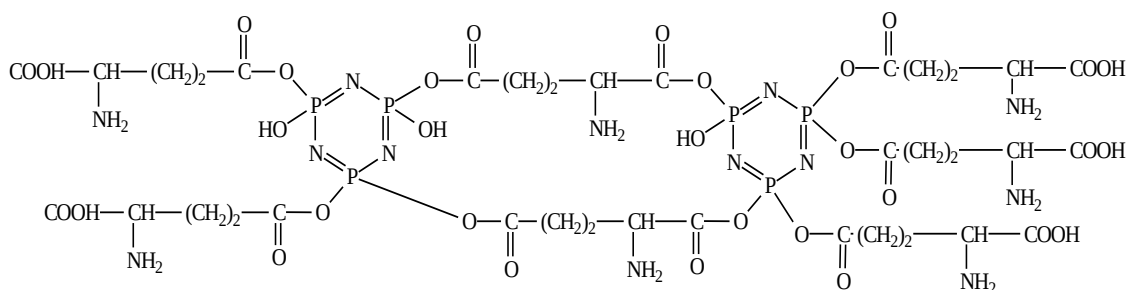
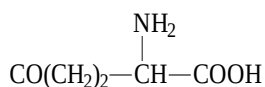


$M/Z - 290 (M - 2)$

The mass line observed at $m/z - 1345$ is on account of the combination of one molecule more of glutamic acid in presence of conc. H_2SO_4 .



$M/Z 1210 (M - 2)$



$M/Z 1345 (M+4)$

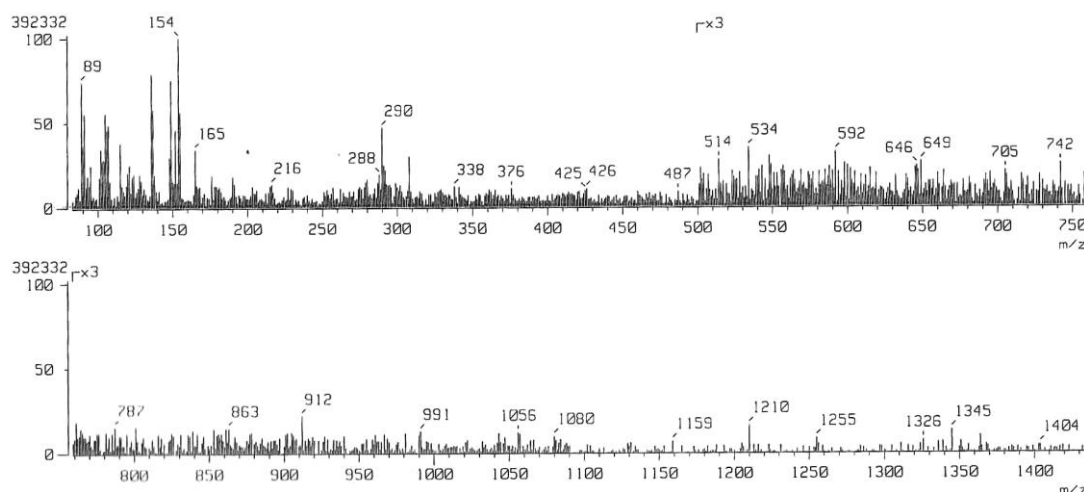


Fig. 1: Mass Spectrum of Compound

The vibration in lower region at 590.4, 770.0 and higher region at 2365.6 cm^{-1} (s) in its I.R. spectrum (fig. 2) are due to P – N bands of P_3N_3 ring. Frequency at 873.4 (s) is for P – OH group, a quadrate broad peak from 1058.9 – 1214.9 cm^{-1} is on account of P – O – C group¹⁶ present in the adduct. The peaks at 1376.6 and 1529.8 cm^{-1} (w) adjacent to quadrant band are due to CH_2 – C group linked to P – O – C band. The assignment at 1631.8 and 1728.7 cm^{-1} are due to O = C – O (carboxylic group) of the glutamic acid. The broad vibrations at higher region 2928.4 to 3414.5 cm^{-1} is on account of free CH_2COOH group of the glutamic acid in the adduct. Thus from the results it is evident that glutamic acid has reacted to $[\text{NP}(\text{OH})_2]_3$ through its one terminal CH_2COOH group with the elimination of H_2O molecule as shown below.

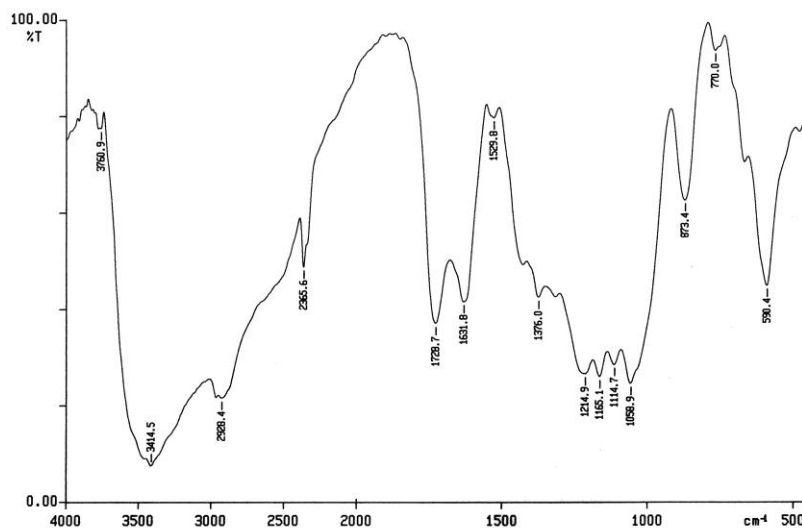
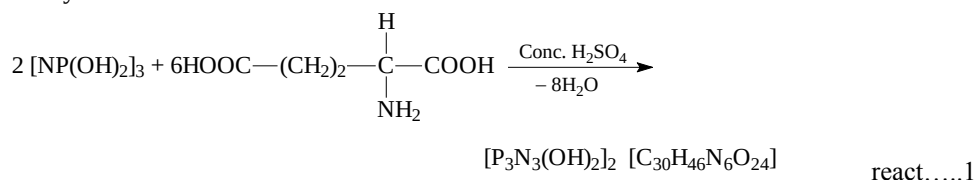


Fig. 2: I.R. Spectrum of Compound

The reaction may as follows:



The electronic spectrum (fig. 3) of the adduct consist two bands at 200 nm and 285 nm, out of which the former band equivalent to 6.2 eV energy showing ionic environment is due to the charge transfer transition¹⁷ while later band is according to $\pi \rightarrow \pi^*$ transition in the compound. The low value of band gap energy, $\Delta E_g = 0.925$ eV and high value of number of conducting electrons, $N_c = 2.7 \times 10^5$ expound the good conductivity of the adduct.

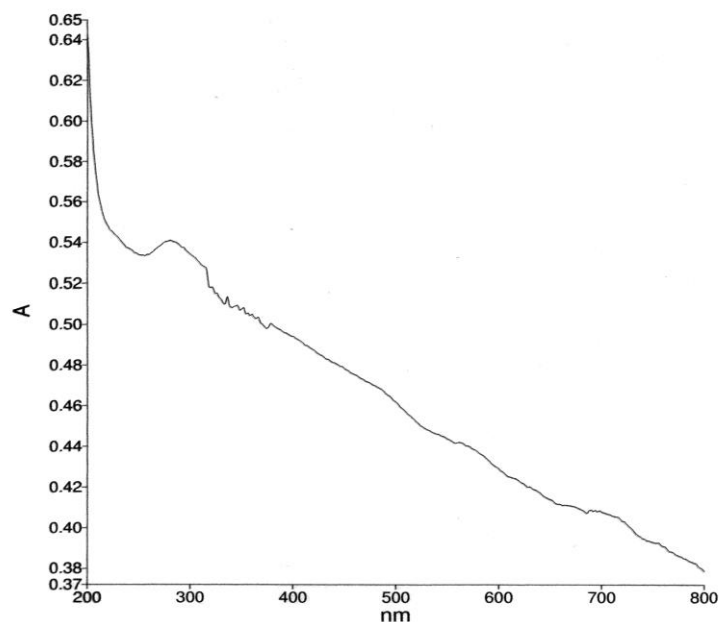


Fig. 3: U.V. Spectrum of Compound

A broad peak at 2659.58 Gauss is observed in its E.P.R. spectrum (fig. 4) indicating its paramagnetic character, which is confirmed by the values of magnetic moment $\mu_{\text{eff}} = 1.7931$ B.M. and low value of magnetic susceptibility, $\chi_A = 1.3400$ e.s.u. The value of magnetic moment is equivalent to one unpaired electron present in to adduct is supported by charge transfer transition.

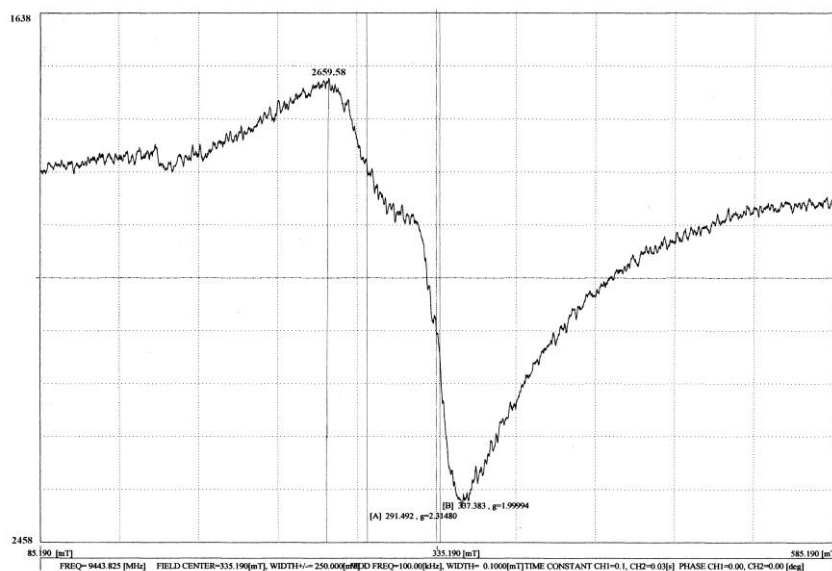


Fig. 4: E.P.R. Spectrum of Compound

^1H NMR spectrum: (fig. 5a) The five sets of signal in the range of chemical shift δ 1.081 – 2.227 ppm (broad quartet) is on account of free OH group while the signals at δ 1.9082 – 2.007 ppm is due to CH_2NH_2 group of glutamic acid. A set of signal of high intensity having the triplet signals to both side of the middle one in the range of chemical shift δ 2.296 – 2.720 ppm is corresponding to $(\text{CH}_2)_2\text{CH}=\text{C}$ group of glutamic acid linked to P_3N_3 ring through its (CH_2) CO group observed at the chemical shift δ 3.004 – 4.898 ppm. A set of signals in the range of chemical shift δ 8.053 – 8.552 ppm for P – N band of the P_3N_3 ring is found in ^1H NMR spectrum (Fig. 5a) of the compound exploring that one molecule of $[\text{NP}(\text{OH})_2]_3$ has reacted with three molecules of glutamic acid with the elimination of 8 H_2O molecule as expressed by the reaction no. 1 having the symmetric geometrical structure as represented by the fig. 6. This view is supported by the ^{13}C NMR spectrum (Fig. 5b) which consist four sets of signals, out of which one set is in lower region at the chemical shift δ 25.34 – 51.34 ppm, is due to the (CH_2) , CO group of the glutamic acid while the signals at chemical shift δ 127.07, 142.88 &

170.85 ppm are for CH – NH₂, HC – C and C = O group subsequently for different C atoms of glutamic acid linked differently to each other and N₃P₃ ring forming the adduct.

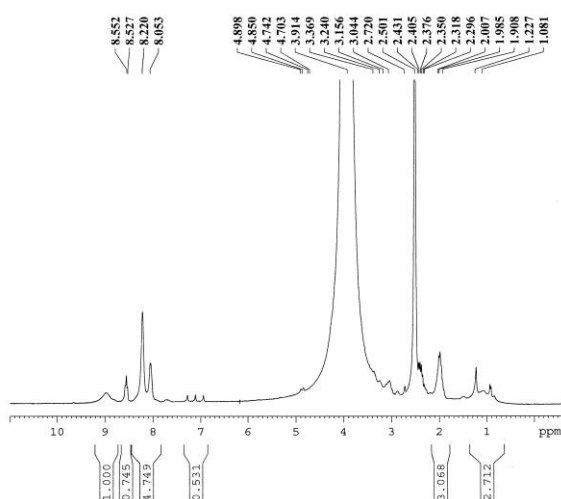


Fig. 5a: ¹H NMR Spectrum of Compound

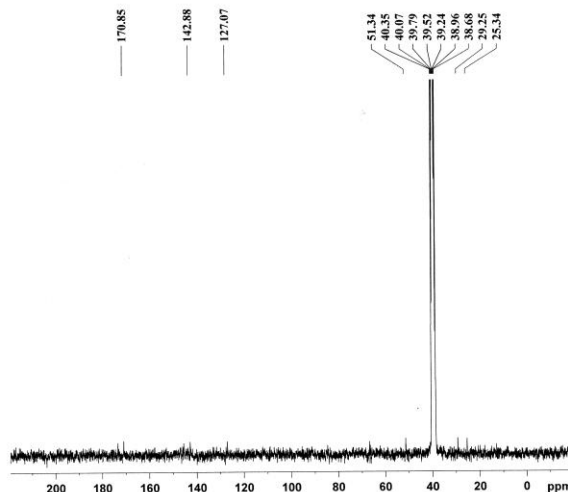


Fig. 5b: ¹³C NMR Spectrum of Compound

From the XRD spectrum the values of $\sin^2\theta$, hkl, and interplanar distance, 'd', calculated¹⁸ (Table-1) resembles with the theoretical once. The values of axial ratios and axial angles subsequently $a_0 = 1.7330$, $b_0 = 1.6527$, $c_0 = 1.1796$, $\alpha = 106.8^\circ$, $\beta = 114.09^\circ$, $\gamma = 135.02^\circ$ are according to the triclinic geometry of the compound.

Table-1: XRD Pattern of Compound

S. No.	2θ (degree)	$\sin^2\theta$	$q(h^2 + k^2 + l^2)$	hkl	d(Å)	
					Obs.	Theo.
1.	16.00	0.01936	0.01936 x (1)	100	5.5400	5.5346
2.	17.33	0.02269	0.02269 x (1)	100	5.1171	5.1126
3.	27.67	0.05718	0.01906 x (3)	111	3.2241	3.2211
4.	33.33	0.08224	0.02056 x (4)	200	2.688	2.6859
5.	38.00	0.10599	0.02119 x (5)	210	2.3679	2.3659
6.	48.33	0.16758	0.01862 x (9)	300	1.8832	1.8815
7.	54.00	0.20610	0.01873 x (11)	311	1.6982	1.6966
8.	59.00	0.24248	0.01865 x (13)	320	1.5655	1.5642
9.	70.67	0.33449	0.01967 x (17)	322	1.3329	1.3318
10.	72.33	0.34823	0.01934 x (18)	330	1.3063	1.3052

$$q_{\text{avg}} = 0.19787$$

$$a_0 = 1.7330 \text{ \AA}, b_0 = 1.6527 \text{ \AA}, c_0 = 1.1796 \text{ \AA}, \alpha = 106.8^\circ, \beta = 114.09^\circ, \gamma = 135.02^\circ$$

IV. Conclusion

From the analysis, the adduct synthesized and assigned as $[P_3N_3(OH)_2]_2 [C_{30}H_{46}N_6O_{24}]$ is good conductor having paramagnetic character and triclinic geometry confirming its structure as (fig. 6).

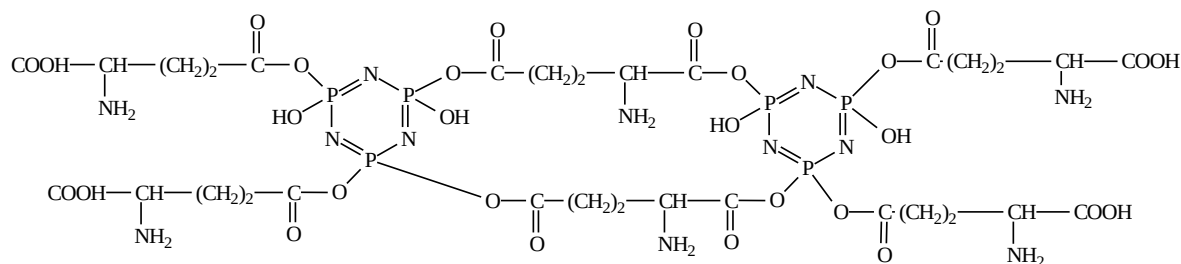


Fig. 6: Structure of the Adduct Dihydroxyphosphazene triglutamate

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