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Characterization of Hexahydroxycyclotriphosphazene Salicylate; EPR, NMR, XRD Spectra

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ABSTRACT

On the basis of the results of instrumental analysis, it may be predicted that the adduct is good conductor, paramagnetic in nature having triclinic geometrical packing of the molecule.

Key words: Paramagnetic, Conductor, Transition, Adduct.

INTRODUCTION

A few of the adducts of $[NP(OH)_2]_3$ with organic acids have been synthesized and reported.[1-6] U.V., E.P.R., ^{1}HNMR and XRD investigations of hexahydroxycyclotriphos-phazene salicylate are being reported herewith.

EXPERIMENTAL

$[NP(OH)_2]_3$ was prepared by the reaction of NaOH on $(NPCl_2)_3$ synthesized,[7] in non aqueous solvent. The white mass formed was refluxed with salicylic acid in presence of 1 ml conc. H_2SO_4 in alcohol used as solvent. Perken Elmer 15 PC (200 nm – 800 mn), Varian's X-E-4 band (RT), Bruker DRX-300 spectrometer (RT) were used to record subsequently for U.V., E.P.R. and ^{1}HNMR spectra. For XRD PW – 1710, X-ray powder differectometer was used (λ = 1.5418Å, CuK_α as source of radiation) in the 2θ range 0^o – 80^o.

RESULTS AND DISCUSSION:

Hexahydroxycyclotriphosphazene salicylate has been formulated as $P_3N_3[(CO)_3O_6(C_6H_4)_3]$, on the basis of its quantitative[8] estimation, mass and I.R. spectrum as reported (loc. cite). The three bands at 210, 225, 305 nm have appeared in its U.V. spectrum. The band at 210 nm = 5.9 ev is due to the ionic environment or charge transfer transition, while the remaining bands are corresponding to $\pi \rightarrow \pi^*$ transition[9] due to the double bond in adduct. The low values of band gap energy, ΔEg = 0.1965, 0.723 ev and high value of number of conducting electrons, Nc = 2.1931 x 10^5 and 4.3979 x 10^5 indicate the good conductive nature of the adduct.

Table 1: XRD Patter of the adduct

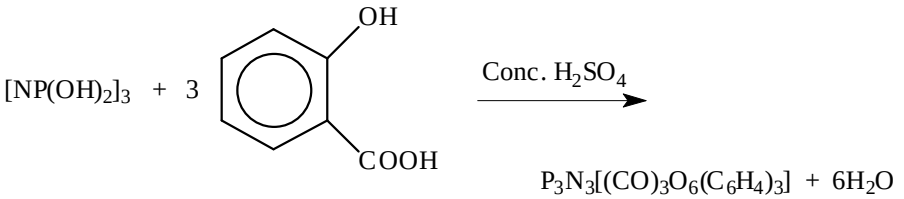
S. No.	2θ (degree)	$Sin^2\theta$	$q(h^2 + k^2 + l^2)$	hkl	d(Å)	
					Obs.	Theo
1.	7.67	0.00447	0.00447 x (1)	100	11.5317	11.516
2.	15.33	0.01779	0.00444 x (4)	200	5.7811	5.7748
3.	21.67	0.03533	0.00441 x (8)	220	4.1016	4.0974
4.	23.00	0.03974	0.00441 x (9)	221	3.8671	3.8635
5.	25.83	0.04995	0.00454 x (11)	311	3.4492	3.4462
6.	30.33	0.06843	0.00488 x (14)	321	2.9474	2.9443
7.	32.00	0.07597	0.00446 x (17)	322	2.7971	2.7944
8.	36.83	0.09979	0.00453 x (22)	332	2.4407	2.4382
9.	42.50	0.13136	0.00452 x (29)	432	2.1272	2.1252
10.	47.83	0.16220	0.00450 x (36)	442	1.9032	1.9000
11.	50.67	0.18310	0.00446 x (41)	443	1.8015	1.8000
12.	64.00	0.28081	0.00453 x (62)	732	1.4548	1.4535

$q_{avg} = 0.05415$

$a_0 = 3.3128$ Å, $b_0 = 1.5615$ Å, $c_0 = 9.6938$ Å, $\alpha = 108.44°$, $\beta = 153.44°$, $\gamma = 90.01°$

The hyperfine peaks in its E.P.R. spectrum[10] suggests the paramagnetic character of the adducts. The two prominent peaks (fig. 1) of high intensity selected for calculations. The values of $g_z > 2$ indicate the presence of covalent bonding alongwith the ionic bonding as referred by the low values of $g_x = g_y < 2$ as suggested by its the U.V. spectrum.

The values of magnetic moment, m_{eff} 1.6944, 1.6587 B.M. and magnetic susceptibilities, $c_A = 1.1966$ and 1.1467 x 10^{-3} e.s.u., also infer the paramagnetic character of the adduct, having one unpaired electron on its oxygen atom predicting that during the reaction H^+ of $[NP(OH)_2]_3$ has reacted in presence of conc. H_2SO_4 and reacted with OH^- of salicyclic acid with the elimination of H_2O molecule and forming hexahydroxycyclotriphosphazene salicylate. The peaks have divided into three parts repeating successively, suggesting that three molecule of salicylic acid have reacted with one molecule of $[NP(OH)_2]_3$ as follows:



^{1}HNMR spectrum (fig. 2) of the adduct possess four sets of signals, out of which four signals, a set in the range of chemical shift, δ 6.677 – δ 8.103 ppm are due to two parallel P-N bands linked with other P-N band of the P_3N_3 ring showing the two signals at the chemical shift, δ 8.636 and d 8.949 ppm. The three signals in the range of chemical shift, δ2.184 - δ 6.329 ppm are according to the H atoms of three C_6H_5 groups linked differently to P_3N_3 ring. Again a broad signal of low intensity at the chemical shift, δ10.856 to δ11.636 ppm is for the P-N ring. Thus from the ^{1}HNMR spectrum, it is clear that three salicylic molecules have linked to one P_3N_3 ring through oxygen atoms differently as shown by its structure (fig. 3).

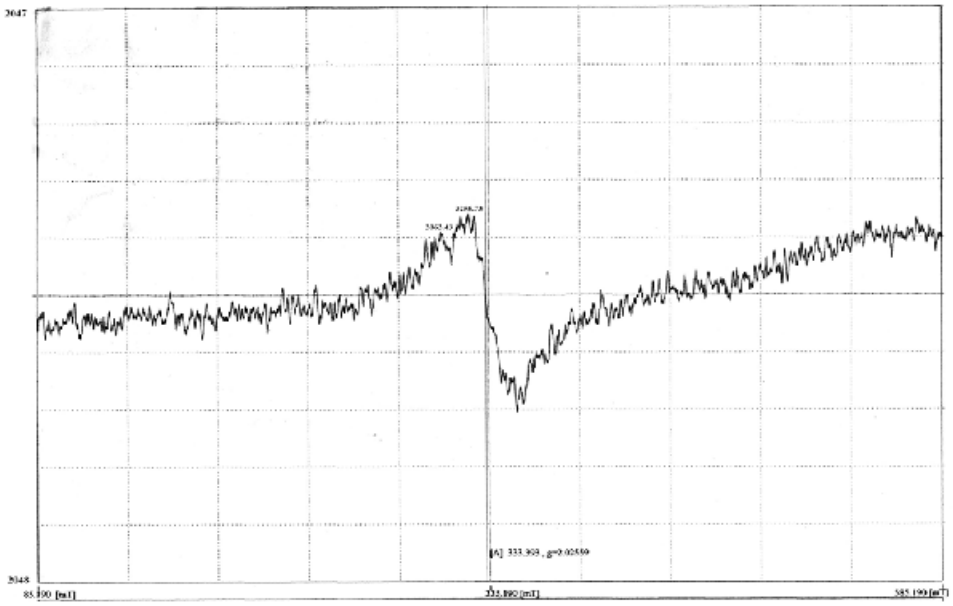


Fig. 1: E.P.R. Spectrum of the adduct

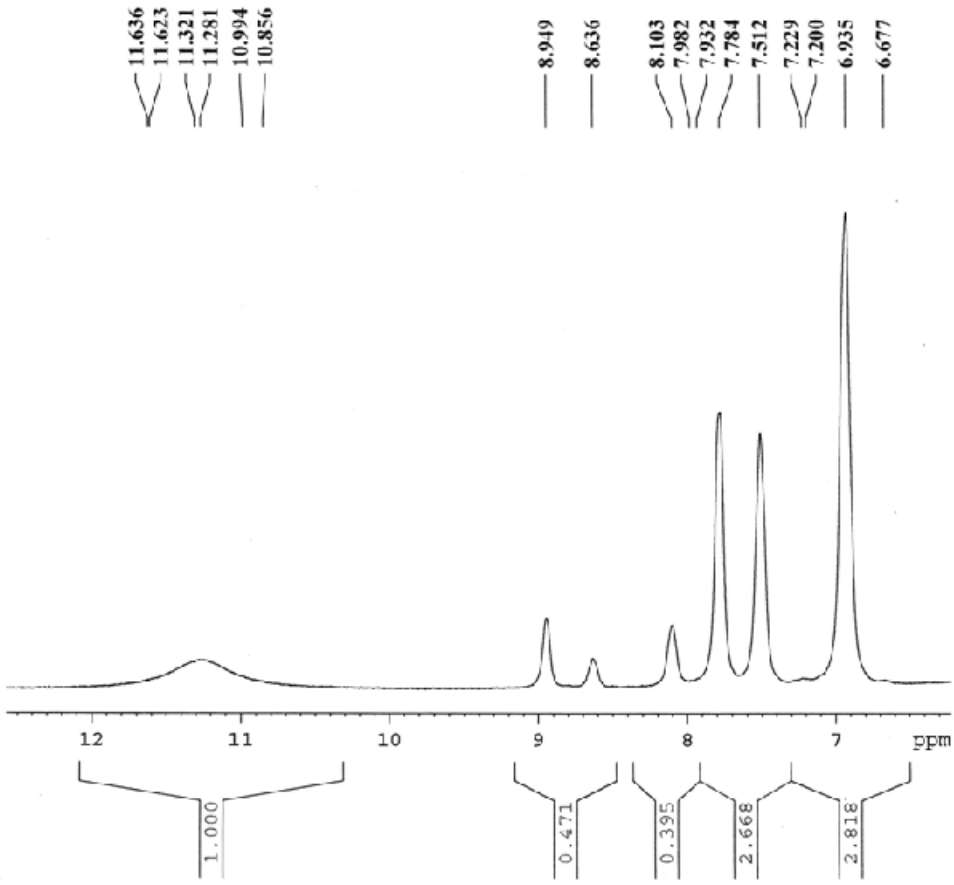


Fig. 2: ^{1}HNMR Spectrum of the adduct

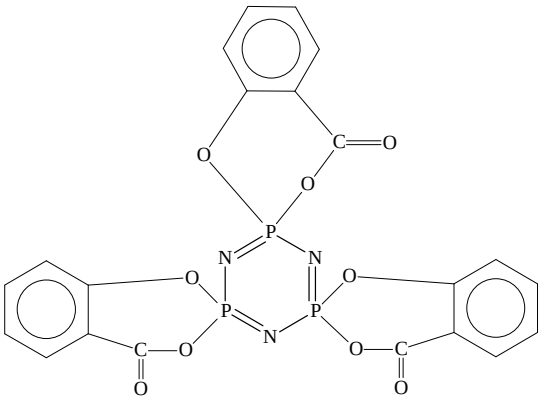


Fig. 3: Structure of the adduct

The values of interplaner distance d, calculated[11] (table -1) from its XRD are very much close to theoretical values. The values of $\sin^2$, and milar index, hkl alongwith the axial ratios and axial angles were calculated. The values of axial ratios, a_0 = 3.3128Å, b_0 = 1.5615Å, c_0 = 9.6938Å and axial angles a = 108.44°, b = 153.44° and g = 90.01° inferred the triclinic geometrical packing of the molecule in the adduct.

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