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EPR, NMR AND XRD SPECTRA OF ADDUCT OF $[NP(OH)_2]_3$ WITH HIPPURIC ACID

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ABSTRACT

The adduct is found paramagnetic having one unpaired electron with transition of electron, while the XRD reveals the presence of P-N ring, possessing 120°, Interior angle and 135°, Exterior angle along with the 90° inferring linkage of hippurate group to P-N ring as shown by its ^{1}H NMR spectrum.

Key words: Paramagnetism, Geometry, Transition, Adduct.

INTRODUCTION

The adduct of $[NP(OH)_2]_3$[1] prepared by known process, with hippuric acid as reported[2]. To establish its geometrical structure, U.V., E. P. R., ^{1}H NMR and XRD studies, done, are being presented.

EXPERIMENTAL

$[NP(OH)_2]_3$ was synthesized from $[NPCl_2]_3$[3] used as starting material, the adduct of $[NP(OH)_2]_3$ with hippuric acid, has been prepared as reported (loc. cite.), U.V., E. P. R., ^{1}H NMR and XRD spectra were recorded subsequently on Parkin-Elmer -15PC, (200-800 nm), Varian's X-E-4 band, Bruker DRX-300 spectrometres at RT and PW-1710 X-ray powder diffractometer using λ = 1.5418 Å and Cu Kα, as radiator in the 2θ range 0-80°.

RESULTS AND DISCUSSION

On the basis of mass and IR spectra as well as gravimetric[4] estimations, the adduct has been assigned as $[P_6N_6(CO)_2O_5(OH)_3CN(CH_2)_2CONH(C_6H_5)_4]$ having molecular weight

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860 $gmol^{-1}$ (loc. cite). In its U.V. spectrum three bands at 200, 225, and 775 nm were found. The former band at 200 nm equivalent to 6.2 ev is according to the charge transfer transitions[5] showing the ionic environment in the adduct, while the later band at 225 and 775 nm are $\pi \rightarrow \pi^*$ transition due to double bond in hippuric acid, suggesting that OH group of the hippuric acid reacted with OH group of $[NP(OH)_2]_3$ in presence of conc. H_2SO_4 with the elimination of water and forming C^+-O^- bond between hippuric acid and $[NP(OH)_2]_3$ to form the adduct as –

$$2\,[NP(OH)_2]_3 + C_6H_5\text{–}CONH\text{–}CH_2\text{–}COOH \xrightarrow{\text{Conc. } H_2SO_4} [P_6N_6(CO)_2O_5(OH)_3CN(CH_2)_2CONH(C_6H_5)_4] + H_2O + \text{Other product}$$

The ionic environment is also supported by a broad peak of high intensity in its E. P. R. spectrum (Fig. 1) inferring its paramagnetic character. The values of magnetic moment μ_{eff} = 1.8961 BM and magnetic susceptibility, χ_A = 1.4986 x 10^{-3} e.s.u., which are corresponding to one unpaired electron in the adduct.

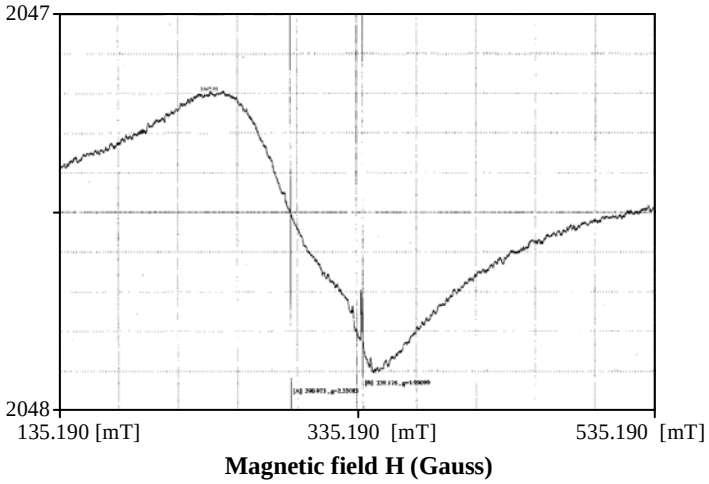

Fig. 1: E. P. R. Spectrum of the adduct

^{1}H NMR spectrum (Fig. 2) of the adduct consist a signal at chemical shift, δ 0.007 ppm for free OH group of $[NP(OH)_2]_3$. The other signals at δ 0.891 and 1.281 ppm, are due to two H atoms of CH_2 groups, which are linked to other signals in the range of δ 3.103 to δ 3.567 ppm for C_6H_5 group having a main peak with two doublet shoulder of both side of the central peak. The signals repeatedly blurred indicating the linkage of hippuric acid in

different positions to P-N ring through its oxygen atoms of OH group forming C-O-P bond as found in its I.R. spectrum (loc.cite) inferring its structure as reported (loc. cite).

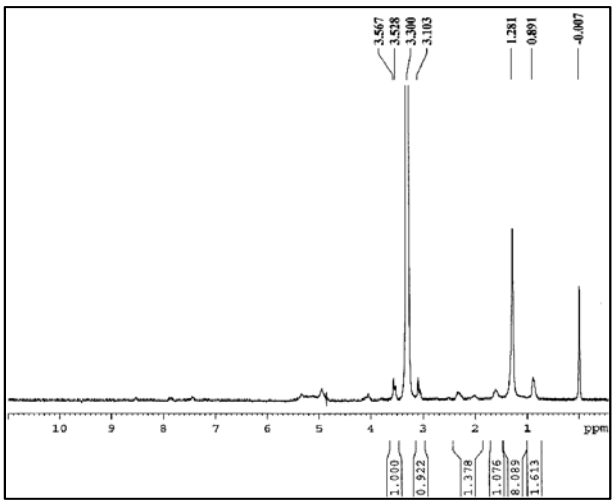

Fig. 2: ^{1}H NMR spectrum of the adduct

To know the exact geometrical structure[6] of the adduct, its X.R.D. spectrum recorded in 2θ range 0-80^o has a prominent peak at 33^o for the P-N ring. Form XRD Spectrum the values of $\sin^2\theta$, Millar index, hkl and interplanner distance, 'd' were calculated. The values of 'd' resembles to the theoretical ones (Table 1) for the distorted hexagonal geometry of the adduct. The axial angle 120.01^o for the interior angle of P-N ring, while the angle 135.02^o is for the exterior OH group of the P-N ring. This OH group reacted with hippuric acid perpendicularly 90^o as found confirming the reported structure as (Fig. 3).

Table 1: XRD pattern of the adduct

S. No.	2θ (degree)	$\sin^2\theta$	q ($h^2 + k^2 + l^2$)	hkl	d (Å)	
					Obs.	Theo.
1.	17.00	0.02184	0.02184 x (1)	100	5.2158	5.2111
2.	27.50	0.05649	0.02824 x (2)	110	6.4890	3.2406
3.	31.58	0.07404	0.02468 x (3)	111	2.8331	2.8306
4.	33.33	0.08224	0.02056 x (4)	200	2.6884	2.6859
5.	38.00	0.10599	0.02119 x (5)	210	2.3679	2.3659

Cont…

S. No.	2θ (degree)	$\sin^2\theta$	q ($h^2 + k^2 + l^2$)	hkl	d (Å)	
					Obs.	Theo.
6.	48.00	0.16543	0.02067 x (8)	220	1.8955	1.8937
7.	53.83	0.20490	0.02276 x (9)	300	1.7031	1.7016
8.	54.67	0.21085	0.02108 x (10)	310	1.6789	1.6774
9.	58.83	0.24121	0.02192 x (11)	311	1.5697	1.5683
10.	64.50	0.28474	0.021903 x (13)	320	1.4447	1.4435
11.	72.17	0.34690	0.021681 x (16)	400	1.3089	1.3077

q_{avg} = 0.246524

a_0 = 1.5526 Å, b_0 = 1.2676 Å, c_0 = 2.8350 Å, α = 120.01°, β = 135.02°, γ = 90°

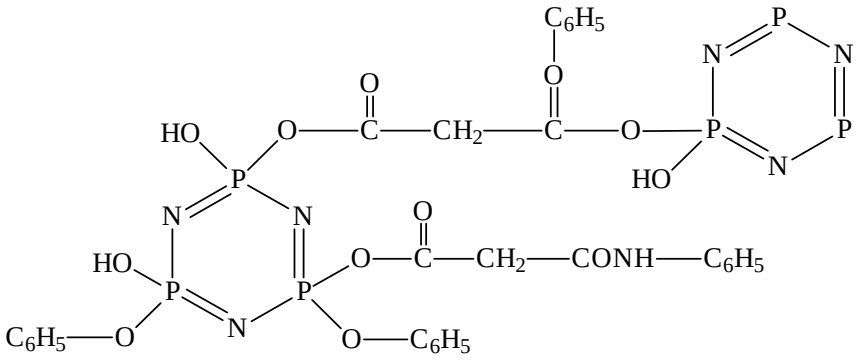

Fig. 3: Structure of the adduct

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REFERENCES

1. I. Rani and S. P. S. Jadon, Asian J. Chem., **20(7)**, 5711-5716 (2008).
2. A. Gupta and S. P. S. Jadon, Int. J. Chem. Sci., **7(4)**, 2867-2871 (2009).
3. S. P. S. Jadon, Asian J. Chem., **15**, 151 (2003); **17**, 1312 (2005).

4. A. I. Vogel, A Text Book of Quantitative Inorganic, Longman, London (1961).

5. B. N. Figgis, Introduction to Ligand Fields, Wiley Eastern Limited, New Delhi (1976).

6. M. M. Woolfson, An Introduction to X-ray Crystallography, Vikas Publishing House Pvt. Ltd., Cambridge University Press (1978).

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