



## **CHARACTERISATION OF Mn (II) DIHYDRO PHOSHAZENIDE**

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### **ABSTRACT**

Complex of Mn (II) with hexahydrocyclo-triphosphazene was synthesized. The complex was studied with the help of Mass, IR and EPR spectra, assigning its molecular formula as  $(N_3P_3H)_6-Mn_3-N_2P_3H_2$  with quadridentated coordination and hexagonal geometry of the complex.

**Key words :** Dihydro Phosphazenide, Manganese, Complex

### **INTRODUCTION**

On the N-atom of  $(NPCl_2)_3$ , a lone pair of electrons is present. Due to this lone pair of electrons, it was used as a ligand and its various metal complexes have been reported<sup>1-8</sup>. Its reduced product, hexahydrocyclo-triphosphazene, (HHCTP),  $(NPH_2)_3$  (synthesized), was also used as ligand to prepare its complexes<sup>10-15</sup>. The reaction product of (HHCTP), with Mn (II) chloride was synthesized and its investigations are being reported here.

### **EXPERIMENTAL**

By the reaction of Na/ $C_2H_5OH$  on  $(NPCl_2)_3$ , the reduced product,  $(NPH_2)_3$ , hexahydrocyclo-triphosphazene was obtained. The mass produced, was separated, washed with dry  $C_2H_5OH$  and ether, dried and stored in vacuo. The complex of  $(NPH_2)_3$  with  $MnCl_2$  was prepared by refluxing both in equimolar ratio in DMF for 6 to 8 h.

The pinkish product, obtained, was filtered, washed with  $C_6H_5Cl$ ,  $C_2H_5OH$  and ether. Dried product was stored in vacuum desiccator over fused  $CaCl_2$ .

The above complex was analysed quantitatively and qualitatively by well known

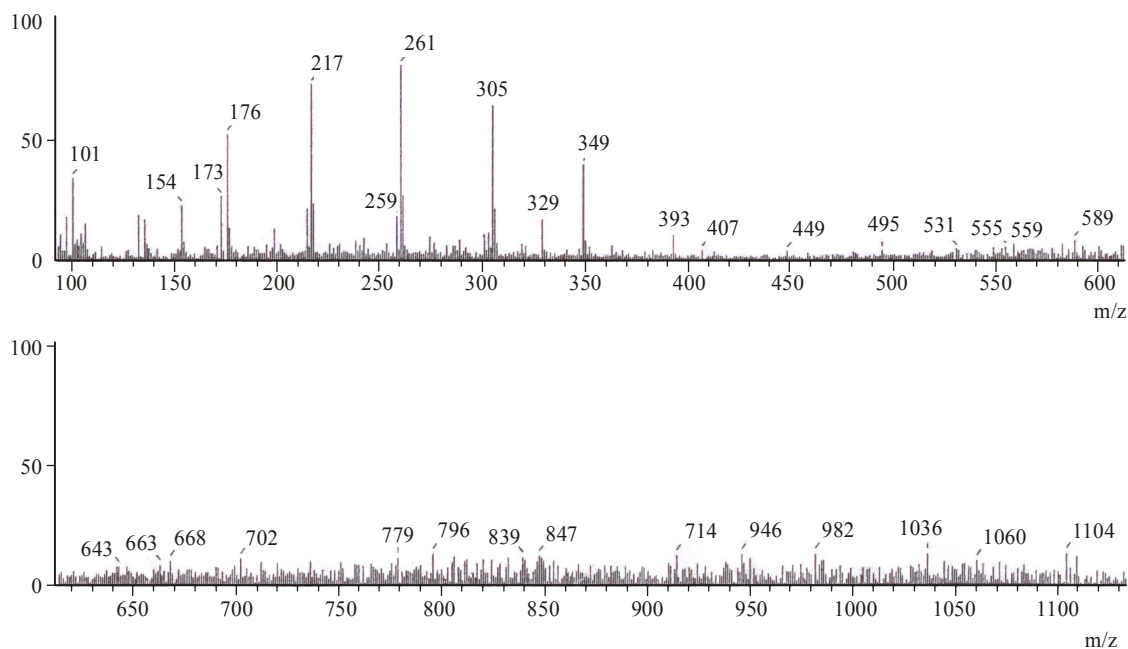
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methods<sup>16</sup>. XRD, Mass, IR and EPR spectra were recorded on PW 1710 diffractometer (Cu K $\alpha$ ,  $\lambda = 1.5405$ ) from RTM, Nagpur University, Mass Spectrometer Jeol SX-102 (FAB), FTIR spectrophotometer Shimadzu 8201 PC (4000-400  $\text{cm}^{-1}$ ) from CDRI, Lucknow and EPR Spectrometer VARIAN – E-112 from SAIF IIT Chennai, respectively.

## RESULTS AND DISCUSSION

On the basis of quantitative estimations, % found are N-25.36, P-58.96, H-007, Mn-14.94 and molecular weight 1104.3 g/mol. The complex is termed and formulated as Mn (II) dihydrophosphenide,  $(\text{N}_3\text{P}_3\text{H})_6\text{-Mn}_3\text{-N}_2\text{P}_3\text{H}_2$ , (Fig. 4) which is supported by the prominent mass line at  $m/z$ -1104 observed in its mass spectrum (Fig. 1).



**Fig. 1 : Mass spectrum of complex**

The mass pattern of the complex may be explained by FAB fragmentation process as follows-

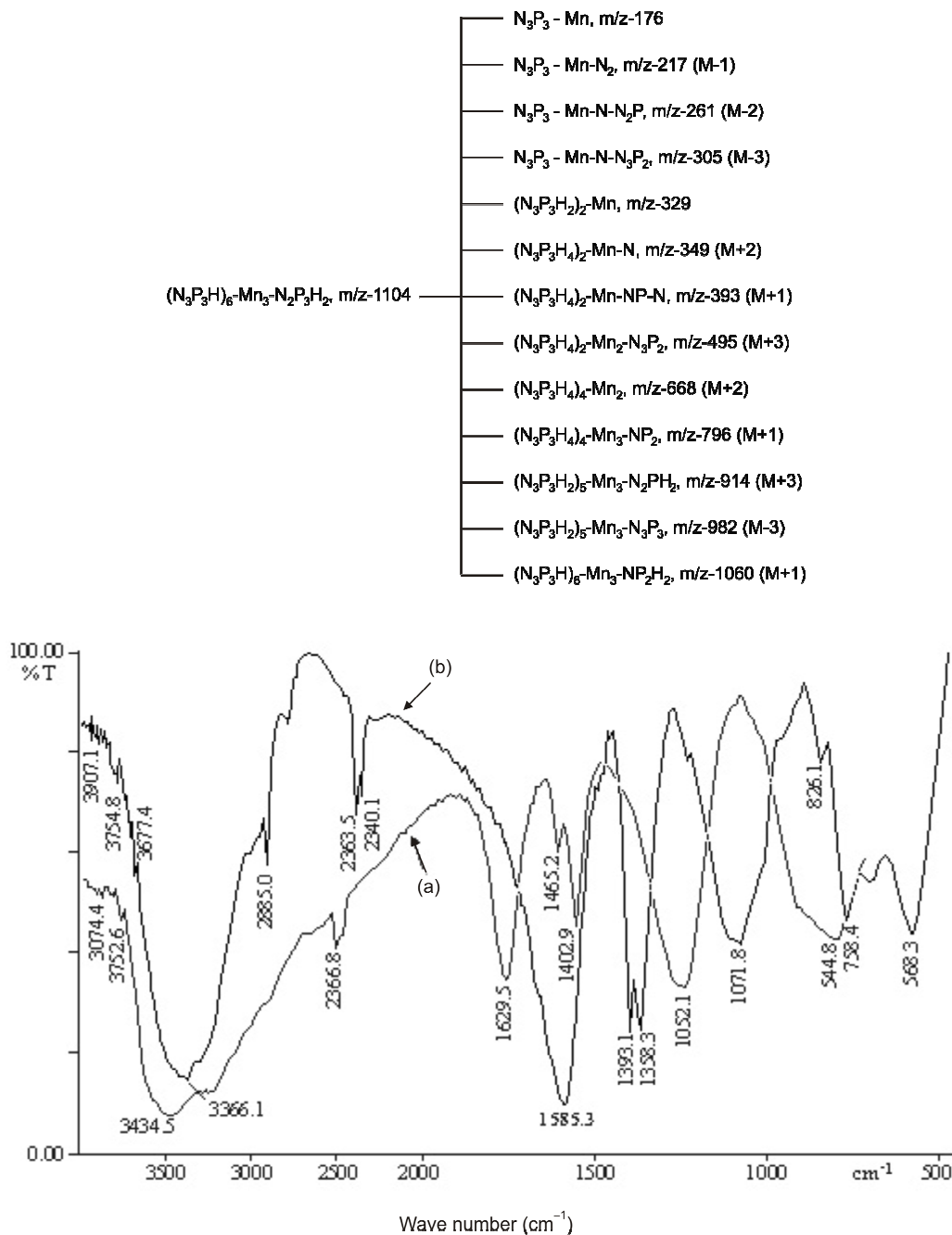


Fig. 2 : IR Spectra (a) ligand (b) complex

This complex formation is supported by frequencies observed in its IR spectrum, which is compared to that of ligand, having the frequencies at 568.3-758.4(b), 826.1 (w), 1071.8, 1358.3-1585.3 (b), 2340.1-2885.0 (s)  $\text{cm}^{-1}$  (Fig. 2), corresponding to four P-N $\rightarrow$ Mn, P-N, N-P-H and P = N bands, suggesting a quadridentated linkage of P-N ring to Mn (II).

**Table 1 : EPR spectra of complex**

Temp.	Magnetic field $H_0(\text{Gauss})$	$g_x = g_y$	$g_z$	$g_{av}$	$\mu_{eff}$ (B. M.)	$\chi \times 10^{-3}$ esu
RT	3281	1.6429	2.0109	1.7741	1.5363	0.9837
LNT	3207	1.6059	2.0573	1.7692	1.5321	1.4974

EPR spectra of the complex were recorded, at room temperature (RT) and liquid nitrogen temperature (LNT). A single peak (Fig 3) indicates paramagnetic character of this complex, which is also sustained by the values of  $\mu_{eff} = 1.5363$  B. M. and magnetic susceptibility,  $\chi = 0.9837 \times 10^{-3}$  esu (Table 1). The value of  $g_z$  is greater than that for free electrons, 2.0109 indicating the sharing of electrons of P and N atoms present in the P-N ring along with its coordination through N atom of P-N rings to  $\text{Mn}^{2+}$  ions, because the value of  $g_x = g_y = 1.6429$  and  $g_{av} = 1.7741$  (at RT) and  $g_x = g_y = 1.6059$  and  $g_{av} = 1.7692$  (at LNT) (Table 1), are less than 2.0 corresponding to vacant 'd' energy shell of Mn atom to accept the electron pairs from N atom of the P-N ring. Thus in this complex, covalent bonding in P-N ring as well as coordinate linkage of Mn (II) with phosphazene ring persists. The values of  $\mu_{eff}$  are corresponding to the presence of one unpaired electron in  $\text{Mn}^{2+}$  for  $3d^5$  configuration.

From XRD spectrum for the complex, recorded in  $2\theta$  range, hkl and interplanar distance "d" were calculated. The values of interplanar distance "d" are in close agreement to theoretical once. The values of axial ratios  $a_0 = b_0 = 5.9966 \text{ \AA}$  and  $c_0 = 4.8968 \text{ \AA}$  and axial angles  $\alpha = \beta = 90^\circ$  and  $\gamma = 120^\circ$  (Table 2), suggests hexagonal geometry of the complex.

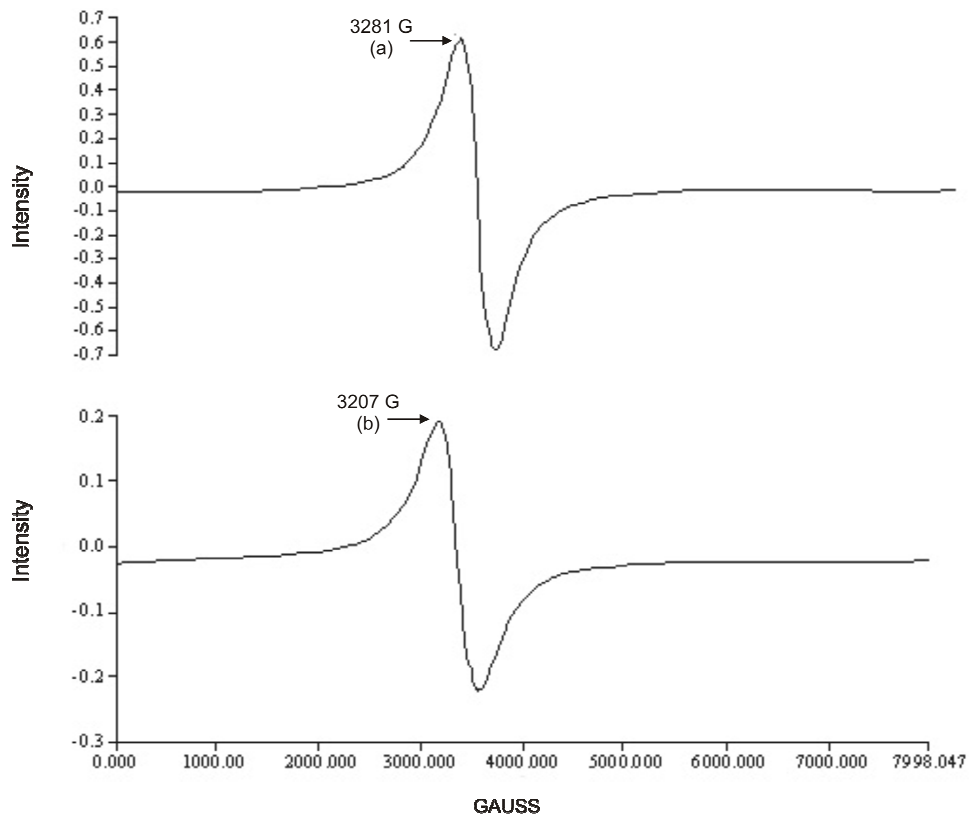


Fig. 3 : EPR spectra of complex at (a) RT (b) LNT

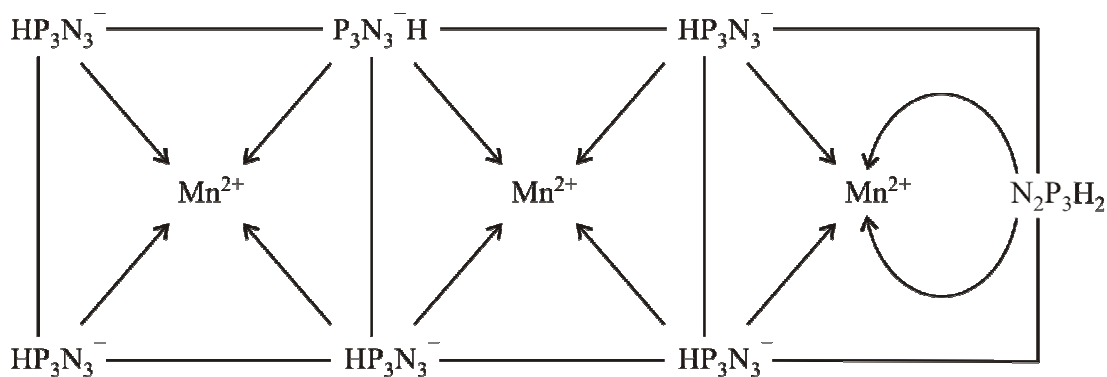


Fig. 4 : Proposed structure of the complex,  $(N_3P_3H)_6-Mn_3-N_2P_3H_2$

**Table 2 : X-ray diffraction pattern of complex**

$2\theta$ (°)	$\sin \theta$	$\sin^2 \theta$	$(h^2 + k^2 + l^2) Q$	hkl	D (Å) Obs.	D (Å) Theo.
14.49	0.1261	0.0159	1x. 0159	100	6.1079	6.1118
17.67	0.1535	0.0235	1x. 0235	100	5.0152	5.0178
19.03	0.1653	0.0273	2x. 0136	110	4.6597	4.6571
20.275	0.176	0.0309	2x0154	110	4.3763	4.3751
24.31	0.2105	0.0443	3x. 0147	111	3.6583	3.6567
29.23	0.2523	0.0636	4x. 0159	200	3.0528	3.0537
31.66	0.2727	0.0744	5x. 0148	210	2.8238	2.8237
44.575	0.3792	0.1438	9x. 0159	221	2.031	2.0325
45.425	0.3861	0.149	9x. 0165	221	1.995	1.9951
56.45	0.4729	0.2236	14x. 0159	321	1.6287	1.6289
66.19	0.546	0.2981	19x. 0156	331	1.4107	1.4108
75.285	0.6107	0.3729	24x. 0155	422	1.2612	1.2613
84	0.6691	0.4477	29x. 0154	432	1.1512	1.1511
84.245	0.6707	0.4498	29x. 0155	432	1.1484	1.1487

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