

NOTE**Synthesis and Characterization of Al(III) Complex of
1,3,5-Hexahydrocyclophosphazene**

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The reaction product of $(\text{NPCl}_2)_3$ with Al(III) chloride was synthesized and its characterization, are being reported herewith with the help of mass, IR and EPR spectra, assigning its dimeric nature of the complex as $\text{Al}(\text{N}_3\text{P}_3\text{H}_2)_3$.

Key Words: Al(III) complex, 1,3,5-Hexahydrocyclophosphazene.

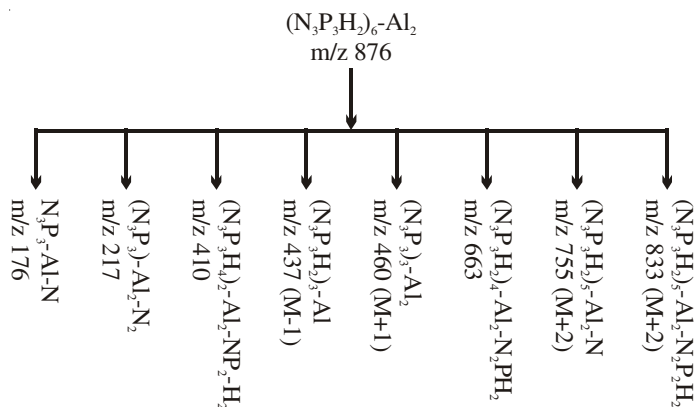
Due to lone pair of electrons present on N atom of $(\text{NPCl}_2)_3$, different complexes and adducts of $(\text{NPCl}_2)_3$ with metals have been reported¹⁻⁴. Its reduced product, hexahydrocyclophosphazene $(\text{NPH}_2)_3$ synthesized⁵ was also used as ligand to prepare its complexes⁶⁻⁸. The reaction product of $(\text{NPH}_2)_3$ with Al(III) chloride was synthesized and characterized.

1,3,5-Hexahydrocyclophosphazene $(\text{NPH}_2)_3$ was prepared by the reduction of $(\text{NPCl}_2)_3$ with sodium ethoxide. The white mass, produced, was separated, washed with dry ethyl alcohol and ether, dried and stored in vacuum. The complex of $(\text{NPH}_2)_3$ with AlCl_3 was prepared by refluxing both in equimolar ratio in DMF for 6 to 8 h.

The white coloured product, obtained, was filtered, washed with chlorobenzene, ethenol and ether. Dried product was stored in vacuum desiccator over fused CaCl_2 . The complex was analyzed qualitatively and quantitatively by well known methods⁹. XRD and IR Spectra were recorded on PW1710 diffractometer ($\text{CuK}\alpha$, $\lambda = 1.5405$) and FTIR spectrophotometer Shimadzu 8201 PC ($4000-400 \text{ cm}^{-1}$).

On the basis of analytical data of complex; % found Al-6.16, N-28.76, P-63.69, H-1.36 and m.w. is 875.5 g/mol, the complex is termed and assigned as Dihydro Al(III) phosphazene, $\text{Al}_2(\text{N}_3\text{P}_3\text{H}_2)_6$, which is supported by the prominent mass line at $m/z-876$ observed in its mass spectrum. The formation of complex is also supported by the prominent mass line at $m/z-437$ for fragment $(\text{N}_3\text{P}_3\text{H}_2)_3-\text{Al}(M-1)$. The mass pattern of the complex may be explained on the basis of FAB Fragmentation process (**Scheme-I**).

The formation of this complex is upheld by vibrations observed in its IR spectrum which is compared to that of ligand, having the frequencies at 609.9 (b,S), 1104.6 (b,S), 1637.1 (d), 2340.4-2363.9 (d), 3454.8 (b) cm^{-1} shifted to higher region as subsequently for P-N \rightarrow M, P-N, H-P-N and P = N bands, suggesting that ligand has co-ordinated, through its N atom to Al(III) and some H atoms have reacted to AlCl_3 forming and eliminating HCl molecules.



EPR spectra of the complex showed the signals corresponding its paramagnetic character, which is also sustained by the values of μ_{eff} and magnetic susceptibility, χ (Table-1). The value of g_z , and g_{av} is greater than the free electrons 2.003 indicating the sharing of electrons of Al atom *i.e.* aluminium atom has linked with covalent bond to P-N ring alongwith its coordination through N atom of P-N rings, because the values of $g_x = g_y = 1.523, 1.6838$ and 0.8287 are less than 2.0 corresponding to vacant energy cell of Al atom to accept the electron pairs from N-atom of the P-N ring. Thus in the complex the covalent bonding as well as coordinate linkage with phosphazene ring persist, suggesting the complex as structure shown in Fig. 1 in dimeric form of $Al_2(N_3P_3H_2)_6$.

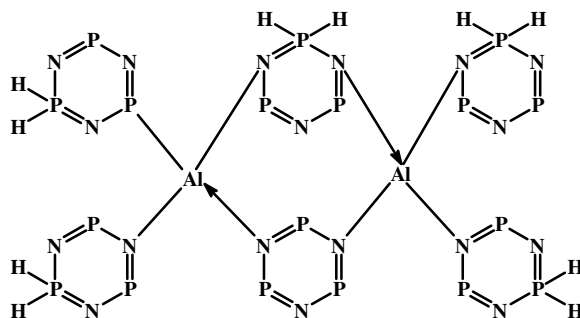


Fig. 1. Dimeric structure of $Al_2(N_3P_3H_2)_6$ complex

TABLE-1
EPR SPECTRA OF COMPLEX

Temp.	Magnetic field No. (Gauss)	$g_x = g_y$	g_z	g_{av}	μ_{eff} (BM)	$\chi \times 10^{-3}$ esu
RT	2325	1.5523	2.8378	2.7140	1.7938	1.3411
	2522	1.6838	2.6161	2.0424	1.7687	1.3038
LNT	1655	0.8287	3.9867	2.3991	2.0776	2.7536

From XRD spectrum for the complex, recorded in 2θ range from 170 to 840 the values of $\sin^2\theta$, hkl and interplanar distance "d" were calculated (Table-2). The values of "d" are in close agreement to theoretical once. The values of axial ratios $a_0 = b_0 = 4.7506 \text{ \AA}$ and $c_0 = 3.8793 \text{ \AA}$ and axial angles $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$, expounds hexagonal geometry of the complex.

TABLE-2
X-RAY DIFFRACTION PATTERN OF COMPLEX

2θ ($^\circ$)	$\sin \theta$	$\sin^2 \theta$	$(h^2 + k^2 + l^2) Q$	Hkl	d (\AA) obs.	d (\AA) theo.
17.685	0.1537	0.0236	1X0.0236	100	5.0110	5.0112
19.030	0.1653	0.0273	1X0.0273	100	4.6597	4.6571
22.850	0.1980	0.0392	1X0.0392	100	3.8886	3.8868
25.540	0.2210	0.0488	2X0.0244	110	3.4848	3.4847
28.025	0.2421	0.0586	2X0.0293	110	3.1812	3.1816
29.960	0.2584	0.0668	3X0.0224	111	2.9800	2.9799
31.680	0.2729	0.0745	3X0.0245	111	2.8220	2.8219
32.140	0.2768	0.0766	3X0.0255	111	2.7827	2.7826
33.845	0.2910	0.0847	4X0.0212	200	2.6463	2.6466
38.620	0.3306	0.1093	5X0.0218	210	2.3294	2.3293
45.450	0.3863	0.1492	6X0.0248	211	1.9940	1.9943
48.775	0.4129	0.1705	8X0.0213	220	1.8655	1.8660
58.750	0.4905	0.2406	10X0.0240	310	1.5703	1.5705
75.310	0.6109	0.3732	16X0.0233	400	1.2609	1.2607
84.010	0.6691	0.4478	18X0.0248	411	1.1511	1.1511

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