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NOTE

Synthesis and Spectral Characterization of Ni(II) Complex of Hexahydrocyclotriphosphazene

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The Ni(II) complex of hexahydrocyclotriphosphazene $[(NPH_2)_3]_2$ has been synthesized and investigated spectrometrically. Quantitative analysis and mass spectrum of the product assigned its molecular formula $[(NPH_2)_3]_2 \cdot NiSO_4 \cdot 6H_2O$. Its IR, UV and ^{1}H NMR spectra have confirmed quadridentate N-coordinated complex formation.

Key Words: Synthesis, Spectral analysis, Ni(II) complex, Hexahydrocyclotriphosphazene.

The complexes of 1,3,5-hexachlorotriphosphazene $(NPCl_2)_3$ as a six-membered cyclic ring having electron pair in spare at its N-atom have been reported[1-9]. On reduction in non-aqueous solution, it gives hexahydrocyclotriphosphazene $[(NPH_2)_3]_2$. Its complex with Ni(II) compound haS been synthesiZed and spectrometric investigations are being reported here.

1,3,5-Hexachlorotriphosphazene was prepared by refluxing PCl_5 and NH_4Cl in a non-polar solvent such as tetrachloroethane or tetrabromoethane at about 140°C. The unreacted NH_4Cl was removed by filtration and $(NPCl_2)_3$ was separated from other polymers by column chromatography using $C_2H_4Cl_2$ as eluent. After that, $(NPH_2)_3$ was synthesized by reduction of $(NPCl_2)_3$ with Na/C_2H_5OH in non-aqueous solvent. The complex of Ni(II) compounds was prepared by refluxing their equimolar ratio in chlorobenzene. A parrot green mass was separated, washed with DMF followed by successive washing with C_2H_5OH and ether, dried and stored in vaccum over fused $CaCl_2$.

The FTIR, UV, ^{1}H NMR and mass spectra were recorded on Parkin-Elmer Spectrum RXI (4000–450 cm^{-1}), Perkin-Elmer Lambda-15, Bruker DRX-300 (300 MHz FTNMR) with temperature 298 K, JEOL SX 102 (DA-6000) mass spectrometer/data system using argon/xenon (6 kV, 10 mA) as the FAB gas using matrix.

The complex is a parrot green coloured solid which decomposes on heating at 360°C. Elemental analysis (%), Found (Calcd.): N 15.40 (15.41), P 34.10 (34.12), H 4.40 (4.40), S 5.80 (5.87), Ni 10.80 (10.82) and m.w. wt 544 (545) inferred formulated the complex as $[(NPH_2)_3]_2 \cdot NiSO_4 \cdot 6H_2O$, which is also supported by its mass lines at m/z at 199, 391, 544, 787, 846, subsequently for the $(NPH_2)_3 \rightarrow Ni(M - I)$, $(NPH_2)_3$—Ni—(NPH_2)—Ni$(M - 2)$, $[(NPH_2)_3]_2 NiSO_4 \cdot 6H_2O$, $(P_3N_3)_4 \cdot NiSO_4 \cdot 5H_2O$ (M + 2) and $(P_3N_3)_5 \cdot NiSO_4 \cdot H_2O$ (M – 2) fragments occurred in its mass spectra.

The vibrations appeared in its IR spectrum (Table-1) at 627.6 for H—P—N → M, 1103.7 for SO_4^{2-}, 1402.8 for P—N ring, 1467.2 for P—N ring, 1649.5 for H—P—N→M, 2367.6 for H—O—N and 3409.1 for O—H indicate the quardi-dentative linkage of $(NPH_2)_3$ to Ni^{2+} forming the square-planar complex.

TABLE-1

IR SPECTRAL DATA OF COMPLEX

S.No.	Frequencies (cm^{-1})	Bond assigned	Force constant ($k \times 10^5$ dyne/cm^2)
1.	627.6	H—P—N→M	0.2077
2.	1103.7	SO_4^{2-}	6.943
3.	1402.8	P—N ring	11.217
4.	1467.2	P—N ring	12.270
5.	1649.5	H—P—N→M	1.434
6.	2367.6	H—P—N	3.001
7.	3409.1	O—H	—

The two peaks at 273.6 and 337.8 nm are found in its electronic spectrum, out of which the former band is due to charge transfer transition while the latter assignment is on account of pπ-pπ transition caused by P—N ring.

The value of oscillatory strength at ($f = 2.4 \times 10^{-5}$) is according to spin allowed Laport forbidden transition suggesting the spin orbital coupling of P—N ring of $(NPH_2)_3$ to Ni^{2+}. The energy of the former band is also according to ionic enviornment due to Ni^{2+} ion, the value of band gap energy ($\Delta E_g = 0.403$ eV) and the number of conducting electrons ($n_c = 1.4987 \times 10^2$) expounds the good conducting character of complex.

The signals in ^{1}H NMR spectrum (Table-2) have appeared in three sets; two sets of six signals happened to be at chemical shift from δ 0.7802–1.478 and δ 7.302–0.822 ppm are for $P\langle^{H}_{H}$ groups of two $(NPH_2)_3$ rings present in the complex while peaks at chemical shift from δ 2.016–4.864 ppm are on account of P—N bonds. From these results it is inferred that two $(NPH_2)_3$ ring have coordinated quadridentatively to Ni^{2+} ions having square-planar geometry as expressed by Fig. 1.

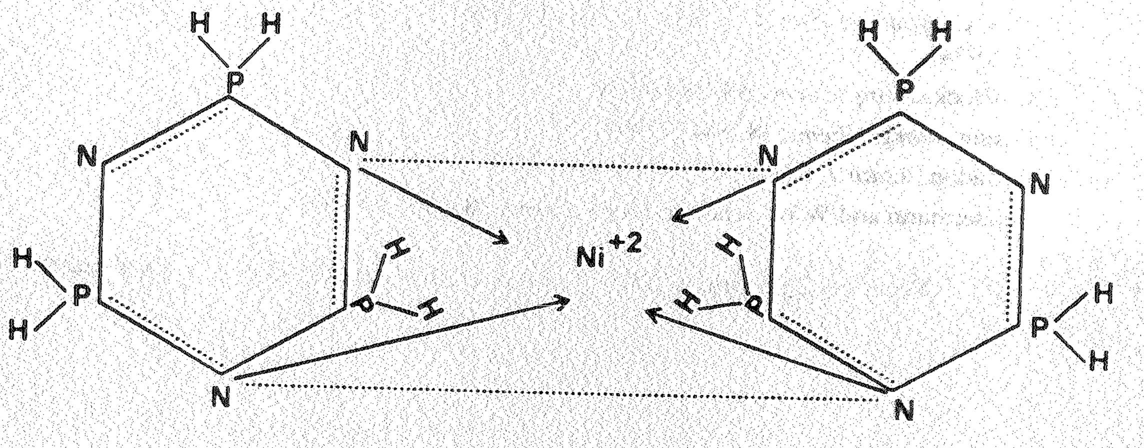

Fig. 1. Proposed structure of complex $[(NPH_2)_3]_2 \cdot NiSO_4 \cdot 6H_2O$

TABLE-2

^{1}H NMR SPECTRAL DATA OF COMPLEX

S. No.	Frequencies (Hz)	δ (PPM)	τ(10 – δ)	J (Hz)	Intensity ratio of peaks (%)
1.	257.79	0.780	9.22	6.61	13.34
2.	267.705	0.810	9.91	9.915	29.17
3.	344.711	1.043	8.957	77.006	27.5
4.	384.371	1.163	8.837	39.66	15.84
5.	416.099	1.359	8.741	31.728	15.84
6.	488.479	1.478	8.522	72.38	8.34
7.	666.288	2.016	7.984	177.80	17.5
8.	822.614	5.489	7.511	156.32	100
9.	1097.590	3.321	6.679	274.97	100
10.	1153.114	3.489	6.511	55.52	100
11.	1607.552	4.864	5.136	454.43	4.17
12.	2413.311	7.302	2.698	805.75	5.0
13.	2639.703	7.987	2.013	226.39	5.84
14.	2680.024	8.109	1.891	40.32	5.01
15.	2717.371	8.222	1.778	37.34	4.17

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