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Spectroscopic Investigations of The Reaction Products of $(NPH_2)_3$ With Si(IV)

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Hexahydrocyclotriphosphazene, $(NPH_2)_3$ was used as a ligand and on refluxing 150-200 ºC in presence of benzene with $SiCl_4$, the two reaction products, first mass aggregated, termed as Si(A) and on concentration of filtrate, product obtained, was termed as Si(B). On the basis of their ^1H, ^{31}P, NMR, UV and XRD spectral investigations, Si(A) and Si(B) have assigned the subsequently as $(P_3N_3H_4)_5Si_3Cl_5$ and $(P_3N_3H_4)_5(SiCl_2)_4$.

Key Words: Hexahydrocyclotriphosphazene, Si(IV).

INTRODUCTION

Due to presence of lone pair in spare on N atom of hexachlorocyclotriphosphazene, $(NPCl_2)_3$ was used as ligand and various complexes[1-4] and polymers[5] with metal have been reported. Its reduced adduct hexahydrocyclotriphosphazene, $(NPH_2)_3$ has also been synthesized[6]. It also behaves as a ligand and its various complexes with Mo, Fe, Ni, Cu(I) have been reported[7-9]. The studies of reaction product of $(NPH_2)_3$ with Si(IV) are being presented here with.

EXPERIMENTAL

Hexachlorocyclotriphosphazene, $(NPCl_2)_3$ was prepared as described[2]. For the preparation of hexahydrocyclotriphosphazene, $(NPH_2)_3$, the reduction of $(NPCl_2)_3$ by Na/C_2H_5OH was done. The complexes of $(NPH_2)_3$ with Si(IV) was prepared by mixing 300 mg $(NPH_2)_3$ with 50 mL of $SiCl_4$ in benzene and refluxing for 6 h. The mass deposited on the bottom of the flask was separated, washed with benzene and ether and termed as Si(A). The filtrate was also concentrated and product found was termed as Si(B). Qualitative estimations were carried out along with, ^1H, ^{31}P NMR, UV and XRD diffraction spectra recoded subsequently on, Bruker DR X 300 (300 MHz FT NMR) from CDRI Lucknow, DS X 300 MHz from IISc Bangalore, perkin Elmer Lambda-15 UV/Vis spectrometer (200-800 mm) from CDRI Lucknow and Philips model PW1710 diffractometer by using Cu-K_α (λ 1.5400 Å) from SAIF Punjab University, Chandigarh.

RESULTS AND DISCUSSION

The geometrical structure of reaction products Si(A) and Si(B) are supported by their ^{31}P NMR and ^{1}H NMR spectra. ^{31}P NMR spectrum of product Si(A) consists adjacent two signals, one strong signal of high intensity at 0.84 ppm and other one is blurred signal and shifted to lower region as compared to ligand suggesting that P_3N_3 rings have coordinated to Si(IV) atom. ^{31}P NMR spectrum of Si(B) consists single strong signal at chemical shift 0.832 ppm along with other blurred signals which expounds the linkage of single P-N ring having all three equivalent P atoms linked to Si(IV) atoms through its N-atom.

The ^{1}H NMR spectrum of Si(B) have 5 bunches of signals (Table-1b) corresponding to $N_3P_3H_4$ molecule bonded to Si-Cl in the complex. In ^{1}H NMR spectrum of complex Si(A), the number of signals for H atoms have shifted and reduced to lower regions 1.312 to 1.443 ppm compared to that of ligand, indicating that during the reaction of $(NPH_2)_3$ with $SiCl_4$, some H-atom of hexahydrocyclotriphosphazene have displaced.

TABLE-1a
^{1}H NMR SPECTRAL DATA OF THE COMPLEX Si(A)

S. No.	Frequencies (Hz)	Chemical shift (δ, ppm)	τ (10-d)	J (Hz)
1	393.76	1.312	8.688	7.20
2	400.96	1.336	8.664	7.50
3	408.46	1.361	8.639	7.21
4	415.67	1.385	8.615	17.40
5	433.07	1.443	8.557	422.27
6	855.34	2.835	7.165	331.33
7	1186.67	3.954	6.046	7.21
8	1193.88	3.978	6.022	7.20
9	1201.08	4.002	5.998	7.50
10	1208.58	4.027	5.973	7.21
11	1215.79	4.051	5.949	227.79
12	1443.58	4.810	5.190	–

Two bands at 231.20 and 332.80 nm (Table-2) have been observed in UV spectrum of Si(A) complex. First band (equivalent to 5.363 e.v. energy) indicate the ionic environment caused by charged transfer transition. It is also supported by oscillator strength and frequency ratio (ν_1/ν_2) ~1-2. Transfer of electron shows the reduction of some P-atom of P_3N_3 ring (removal of H-atom from some P-atom), from $P^{5+} \rightarrow P^{3+}$ state.

The assignment at 332.80 nm is due to pπ-dπ transition of P_3N_3 ring, which shows partial ionic bond formation in Si(A) complex. Electronic spectrum of Si(B) complex consist four bands, at 396, 485.6, 658.6 and 717.6 nm (Table-2) showing pπ-dπ transition. The disappearance of high absorbity band indicate the absence of ionic environment and divalent state of Si atom in Si(B) complex.

TABLE-1b

^{1}H NMR SPECTRAL DATA OF THE COMPLEX Si(B)

S. No.	Frequencies (Hz)	Chemical shift (δ, ppm)	τ (10-d)	J (Hz)
1	385.05	1.283	8.717	8.71
2	393.76	1.312	8.688	7.20
3	400.96	1.336	8.664	7.50
4	408.46	1.361	8.639	7.21
5	415.67	1.385	8.615	9.90
6	425.57	1.418	8.582	7.50
7	433.07	1.443	8.557	8.07
8	441.14	1.467	8.533	260.24
9	701.38	2.337	7.663	149.46
10	850.84	2.835	7.165	37.81
11	888.65	2.961	7.039	48.32
12	936.97	3.122	6.878	186.07
13	1123.04	3.742	6.258	7.21
14	1130.25	3.766	6.234	49.22
15	1179.47	3.930	6.070	7.20
16	1186.67	3.954	6.046	14.41
17	1193.88	3.978	6.022	7.20
18	1201.08	4.002	5.998	7.50
19	1208.58	4.027	5.973	9.00
20	1217.58	4.051	5.949	5.11
21	1222.69	4.074	5.926	55.22
22	1277.91	4.258	5.742	6.90
23	1284.81	4.281	5.719	7.50
24	1292.31	4.306	5.694	–

TABLE-2

UV SPECTRA OF LIGAND AND COMPLEXES

Ligand & complexes	Assigned band (nm (cm^{-1})	Molar absorbity (ε)	ν_1/ν_2	Dq (cm^{-1})	Oscillator strength 'f' × 10^{-5}	Band Gap energy Δ Eg ev (ergs × 10^{-12})	Number of conducting electrons (Nc)
Ligand	200.00 (50000.00)	0.400	1.6640	1995.19	0.36900	1.24 (1.98)	8.47 × 10^5
	332.80 (30048.08)	0.038	–	–	0.00348	–	–
Si(A)	231.20 (43252.59)	0.045	1.4394	1320.45	0.01220	0.82 (1.31)	1.28 × 10^6
	332.80 (30048.08)	0.024	–	–	0.00219		–
Si(B)	396.00 (25252.52)	0.320	1.2263	465.94	0.10790	0.578	1.82 × 10^5
	485.60 (20593.08)	0.128	1.3563	540.94	0.00770	0.670	1.57 × 10^5
	658.60 (15183.72)	0.214	1.0898	125.23	0.00402	0.156	6.40 × 10^6
	717.60 (13931.45)	0.214	–	–	0.00301	–	–

From XRD diffraction pattern, recorded, in 2θ rang from 10^o to 70^o (Table-3), the values of $\mathrm{Sin}^2\theta$, hkl and interplanar distance 'd' which resemble with theoretical values were calculated. The values of axial ratio $a_o=b_o \neq c_o$ and axial angle $\alpha = \beta = 90^o$, $\gamma = 120^o$ depict distorted hexagonal packing of Si(A) complex. The values of d for Si(B) complex are also in close agreement to that of theoretical once and the values of axial ratio $a_o=b_o \neq c_o$ and axial angle $\alpha = \beta = 90^o$, $\gamma = 120^o$, forced to assume that the molecules of Si(B) have also distorted hexagonal geometrical array.

TABLE-3
XRD PATTERN OF THE COMPLEXES Si(A) AND Si(B)

S. No.	Si(A) Complex				Si(B) Complex			
	$\mathrm{Sin}^2\theta$	hkl	d (Å)		$\mathrm{Sin}^2\theta$	hkl	d (Å)	
			Obs.	Theo.			Obs.	Theo.
1	0.0092	100	8.0020	8.0000	0.0106	100	7.4711	7.4655
2	0.0165	110	5.9897	5.9884	0.0137	110	6.5777	6.5726
3	0.1990	111	5.4513	5.4532	0.0241	111	4.9589	4.9593
4	0.0273	200	4.6598	4.6571	0.0388	200	3.9080	3.9070
5	0.0390	210	3.9001	3.9003	0.0459	210	3.5944	3.5927
6	0.0490	211	3.4807	3.4820	0.0667	220	2.9821	2.8080
7	0.0674	220	2.9671	2.9664	0.0803	221	2.7190	2.7192
8	0.0711	221	2.8892	2.8886	0.0860	310	2.6262	2.6255
9	0.0802	310	2.7189	2.7184	0.0960	311	2.4855	2.4854
10	0.0854	311	2.6361	2.6352	0.1037	222	2.4680	2.3913
11	0.0920	222	2.5396	2.5390	0.1146	320	2.2748	2.2744
12	0.1030	320	2.4003	2.4000	0.1205	321	2.2185	2.2181
13	0.1245	400	2.1827	2.1826	0.1533	322	1.9670	1.9673
14	0.1323	322	2.1178	2.1176	0.1669	331	1.8851	1.8849
15	0.1410	411	2.0513	2.0508	0.1721	420	1.8565	1.8563
16	0.1517	331	1.9776	1.9774	0.1837	421	1.7972	1.7967
17	0.1609	420	1.9199	1.9197	0.1993	332	1.7255	1.7250
18	0.1669	421	1.8851	1.8849	0.2095	422	1.6829	1.6825
19	0.1784	332	1.8240	1.8235	0.2307	431	1.6037	1.6034
20	0.1921	423	1.7578	1.7574	0.2396	511	1.5736	1.5734
21	0.2013	430	1.7170	1.7166	0.2556	520	1.5237	1.5237
22	0.2087	431	1.6858	1.6857	0.2627	521	1.5029	1.5027
23	0.2155	511	1.6593	1.6592	0.2834	440	1.4470	1.4469
24	0.2338	521	1.5931	1.5928	0.3045	531	1.3959	1.3957
25	0.2570	440	1.5192	1.5192	0.3142	442	1.3742	1.3740
26	0.2601	441	1.5103	1.5102				
27	0.2713	530	1.4798	1.4786				
28	0.2849	442	1.4438	1.4431				
29	0.2912	610	1.4277	1.4273				
30	0.3028	532	1.4005	1.3998				
31	0.3156	620	1.3718	1.3708				
32	0.3276	540	13.466	1.3456				

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