



Spectroscopic investigation of the reaction product of cyclodichlorophosphazene trimer (PNCl₂)₃ with Ni (II) Chloride

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ABSTRACT

A complex of (PNCl₂)₃ with NiCl₂ has been prepared by refluxing (PNCl₂)₃ and NiCl₂ in ethanol. The complex has composition (P₃N₃Cl₄NiCl₄²⁺), from quantitative estimation, IR and UV spectral studies it is concluded that low spin six-coordinated Ni complex is formed via coordination through three nitrogen, two opposite chlorine and delocalized π electrons of phosphazene ring.

1. Introduction

Synthesis of cyclodichlorophosphazene trimer (PNCl₂)₃ and its characterization by IR and UV spectral studies has been described^[1-4]. Only few complexes of (PNCl₂)₃ with SbCl₅, TaCl₅, AlBr₃, FeSO₄, CuCl₂ have been prepared and investigated^[5-7]. The reaction of (NPMe₂)₄ with CuCl₂ in methyl ketone has been reported^[8] and the compound has structure with one ring nitrogen atom coordinated to CuCl₂ group and opposite protonated. The preparation and studies of the complex of (PNCl₂)₃ with NiCl₂ is being presented here. Recently electrical conduction on solution grown thin film of (PNCl₂)₃ with Zr(IV) under different illuminating conditions has been studied^[9-10].

2. Experimental

Cyclodichlorophosphazene trimer (PNCl₂)₃ was prepared^[11-12] by refluxing 0.5 mol each of PCl₅ and NH₄Cl in 80 ml tetrachloroethane solvent for 72 h. colourless mass formed was separated followed by successively washing with distilled water and tetrachloroethane to remove unreacted NH₄Cl and PCl₅. The colourless mass was extracted with petroleum ether and trimer being soluble in petroleum ether was recovered. The formation of trimer was confirmed by its m.pt. and IR spectral data^[13]. The complex of (PNCl₂)₃ with NiCl₂ was prepared by refluxing an equimolar solution of (PNCl₂)₃ and NiCl₂ in alcohol for about 24h. Light green coloured precipitate formed was separated and washed with alcohol for removal of unreacted reactants if, there any. The complex was dried at room temperature and stored in vacuo. The complex was analyzed qualitatively and quantitatively using gravimetric and atomic absorption spectral techniques^[14]. Molecular weight of the complex was determined

ebulliometrically in refluxing benzene^[15]. IR spectra of the complex and the ligand were recorded in the KBr pellets (4000-400cm⁻¹) on Bruker IFS-66, VFT-IR spectrophotometer. Electronic spectrum (200-800 nm) was recorded on UV-VIS spectrometer.

3. Results and discussion

Analytical of the data complex (found P, 19.46; N, 8.79; Cl, 59.46; Ni, 12.29%) and molecular weight 477.7 lead to proposed the molecular formula of the complex [P₃N₃Cl₈Ni]. The complex is soluble in ether and benzene. It does not melt but decomposes above 400°C. The formation of ligand is confirmed by its m.pt. found as 114°C and its IR spectrum. The assignments of characteristic infrared frequencies for the ligand and the complex are listed Table 1.

On the available literature IR spectrum of the complex is interpreted and compared to that of (PNCl₂)₃. The strong absorption band at 756.9cm⁻¹ due to free P-N-Cl vibration and two other frequencies at 799.7cm⁻¹ and 938cm⁻¹ indicate presence of two P-N-Cl bands having co-ordinate chlorine. The bands at 1115.7cm⁻¹, 1384.6cm⁻¹ and 1409.2cm⁻¹ correspond to coordinated nitrogen of P=N groups. The band at 3420.3cm⁻¹ is due to of P₃N₃ ring. The peaks 413.1 and 497cm⁻¹ correspond to ν(Ni-N) and ν(Ni-P₃N₃) bond. The band at 2903.9cm⁻¹ is due to P-Cl group. The two bands of P-Cl group found in the ligand are absent in the IR spectrum of the complex, but two bands at 1608.9 and 1631cm⁻¹ are found indicating the presence of two Cl⁻ ions. The presence of two Cl⁻ ions bands suggest that during complex formation P-Cl bond is cleaved and two Cl⁻ ions of phosphazene ring shifted to Ni atom. It is inferred that three N,

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two opposite Cl atoms and delocalized π electrons of the ring are coordinated to Ni atom via transfer of two chlorine of ligand to Ni atom, has a coordination number six in this complex. Electronic spectrum of the complex shows a single band at 262 nm due to charge transfer transition of Cl⁻ ion of P-Cl group of phosphazene ring to Ni atom. Absence of d-d transition may be due to charge transfer of Cl⁻ ion to Ni atom and absence of d-d transition also rules out the presence of unpaired electron in the Ni²⁺ and corresponds to electronic configuration (n-1) d¹⁰ ns⁰.

Table-1. IR spectral data of the ligand and its complex

Ligand, (PNCI ₂) ₃ cm ⁻¹	Ni(II) complex cm ⁻¹	Vibrations
----	413.1	v (Ni-N)
----	497	v (Ni-P ₃ N ₃)
521	756.9	v (N-P-Cl)
801.9	799.7	v (N-P-Cl)
1070	938	v (N-P-Cl)
1169.7	1115.7	v (P=N)
1400.9	1384.6	v (P=N)
1643.4	1409.2	v (P=N)
----	1608.9	v (Cl ⁻)
----	1631.3	v (Cl ⁻)
2853.3	2903.9	v (P-Cl)
2924.1	----	v (P-Cl)
2961.1	----	v (P-Cl)
3187.8	3420.3	v (P ₃ N ₃)

4. Conclusion

From IR and UV spectral studies it is concluded that two Cl atoms of P-Cl bond of the phosphazene ring is transferred to Ni atom and three N, two opposite Cl, delocalized electrons of P₃N₃ ring is coordinated to Ni atom lead to proposed the composition of the complex [P₃N₃Cl₄NiCl₄]²⁻.

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