

**NOTE****Synthesis and Characterization of Polymeric Complex of Cu(II) with Cyclodichloro Phosphazene**

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( $\text{PNCl}_2$ )<sub>3</sub> is used as ligand to prepare its complex with  $\text{CuCl}_2$ . To know the nature and composition of the complex its IR, UV and EPR spectra are analyzed along with quantitative estimation and molecular weight determination. The various parameters energy gap ( $\Delta E$ ),  $\mu_{\text{eff}}$ ,  $g_{\text{II}}$ ,  $g_{\perp}$ ,  $\chi_A$ , A/B and oscillation strength (f) have also been computed. It is concluded from IR, UV and EPR spectra that the complex is a semiconductor polymer having the composition  $[(\text{P}_3\text{N}_3\text{Cl}_5)^+(\text{CuCl}_3^-)]_3$ .

**Key Words:** Synthesis, Characterization, Cu(II)-Polymeric complex, Cyclodichlorophosphazene.

Synthesis and investigations of cyclodichlorophosphazene trimer ( $\text{PNCl}_2$ )<sub>3</sub> and its complexes with  $\text{AlCl}_3$ ,  $\text{SbCl}_5$ ,  $\text{TaCl}_5$  have been reported<sup>1-5</sup>. The preparation and studies of the complex of  $\text{CuCl}_2$  with ( $\text{PNCl}_2$ )<sub>3</sub> are being presented here.

Cyclodichlorophosphazene trimer ( $\text{PNCl}_2$ )<sub>3</sub> was prepared<sup>6,7</sup> by refluxing 0.5 mol each of  $\text{PCl}_5$  and  $\text{NH}_4\text{Cl}$  in 80 mL tetrachloroethane solvent for 72 h. To prepare the complex, ethanolic solution of  $\text{CuCl}_2$  and ( $\text{PNCl}_2$ )<sub>3</sub> were mixed together in equimolar ratio and refluxed for about 24 h. The dark green product formed was separated and washed with ethanol to remove unreacted reactants. It was dried and stored *in vacuo*. For estimations, the complex was analysed qualitatively and quantitatively by atomic absorption spectroscopy and gravimetrically<sup>8</sup>. Molecular weight was determined by viscosity method using benzene as standard solvent. IR (KBr pellet) (4000-400  $\text{cm}^{-1}$ ) and UV (800-200 nm) were recorded on Bruker IFS-66VFT-IR and UV-Vis-NIR spectrometer, respectively. The EPR spectrum was recorded on EPR X/Q band spectrometer at 300 K.

The complex is amorphous, m.p. at 126°C. It is soluble in benzene, acetone and ether. Chemical analysis: % found N, 8.71; P, 19.27; Cu, 13.16; Cl, 58.86. Thus the molecular formula of the complex is assumed to be  $(\text{P}_3\text{N}_3\text{Cl}_8\text{Cu})_3$  (m.w. 1447.5).

The IR spectrum of the complex shows bands at 954 and 562  $\text{cm}^{-1}$  for two NPCl bands possessing a coordinated Cl atom. The vibrations 1098 and 1052  $\text{cm}^{-1}$  correspond to two (P=N) bonds with coordinated N atom. The vibrations 1927 and 1402  $\text{cm}^{-1}$  indicate the presence of free (P=N) bond and  $\delta_d(\text{P-Cl})$  mode, respectively. The assignment at 3310.8  $\text{cm}^{-1}$  is due to  $\text{P}_3\text{N}_3$  ring containing delocalized  $\pi$  electrons. Two bands of P-Cl groups present in the ligand (Table-1) are found absent in the IR spectrum of the complex but two bands at 1626 and 1598  $\text{cm}^{-1}$  due to two  $\text{Cl}^-$  ions suggest that during complex formation P-Cl bond of each  $(\text{PNCl}_2)_3$  unit is cleaved and antipodal  $\text{Cl}^-$  ion of each  $(\text{PNCl}_2)_3$  unit are shifted to Cu ion. Thus  $(\text{PNCl}_2)_3$  is linked to  $\text{CuCl}_2$  by quadridentate bridging of Cu ion through coordination by N and Cl terminals and transfer of antipodal  $\text{Cl}^-$  ions of  $(\text{PNCl}_2)_3$  ring, forming a coordinated trimer.

TABLE-1  
IR SPECTRA ( $\text{cm}^{-1}$ ) OF THE LIGAND AND ITS Cu(II) COMPLEX

Ligand $(\text{PNCl}_2)_3$	Cu(II) complex	Vibrational assignments
521	562	$\nu(\text{NPCl})$
801	954	$\nu(\text{NPCl})$
1070	1052	$\nu(\text{P=N})$
1169	1098	$\nu(\text{P=N})$
1400	1402	$\nu(\text{P=N})$
1643	–	$\nu(\text{NPCl})$
–	1598	$\nu\text{Cl}^-$
–	1626	$\nu\text{Cl}^-$
–	1927	$\delta_d(\text{P-Cl})$
2853	–	$\nu(\text{P-Cl})$
2924	–	$\nu(\text{P-Cl})$
2961	–	$\nu(\text{P-Cl})$
3187	3310	$\nu(\text{P}_3\text{N}_3)$

The electronic spectrum shows two peaks at 243 and 274 nm. The peak at 243 nm which is below 250 nm indicates that the polymer belong to cyclic phosphazene series<sup>9</sup>. The peak at 274 nm is due to charge transfer in  $\text{CuCl}_2$  caused by its electrovalent character. The computed value for oscillator strength ( $f = 5.75 \times 10^{-4}$ ), energy gap ( $\Delta E = 0.57 \text{ eV}$ ) suggest the spin allowed laporte forbidden transition and semiconductive nature of the polymer. Absence of  $d-d$  transition band in the UV spectrum may be due to an overlap between the end of the charge transfer band and a  $d-d$  absorption band.

The EPR spectrum of the complex shows a symmetric broad peak of high intensity, indicating the presence of unpaired electron. The broadness

of peak also suggest transfer of electrons from Cl and N atoms of  $(\text{PNCl}_2)_3$  to Cu atom of  $\text{CuCl}_3$ . This implies a coordinate bond and polymerization of  $(\text{P}_3\text{N}_3\text{Cl}_5)^+ (\text{CuCl}_3^-)$  unit to trimer with quadridentate bridging of each unit through the Cu atom. The values of magnetic moment,  $\mu_{\text{eff}}$  1.74 BM and magnetic susceptibility,  $\chi_A$   $2.04 \times 10^{-3}$  confirm the presence of unpaired electron, indicating semiconductivity and paramagnetism in the complex.

The values of  $g_{\parallel}$  (1.9668),  $g_{\perp}$  (2.0895) and A (85 gauss), which indicate empty shell and electron transfer, also support coordination. The ratio of low field to high field amplitude A/B, 1.3, greater resonance line width  $\Delta H$ , 40 gauss and  $g_{\perp}$  (2.0895) suggest the conducting nature of polymer as these characteristics were found in superconductor<sup>10-12</sup>.

Since the cyclic structure of  $(\text{PNCl}_2)_3$  has been reported<sup>13,14</sup>, the composition of tetradentate cyclic trimer may be proposed as  $[\text{P}_3\text{N}_3\text{Cl}_5]^+ (\text{CuCl}_3^-)_3$ .

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