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Spectroscopic Investigation of The Reaction Product of Co (II) Chloride with 1,3,5-Hexachlorocyclotriphosphazene and its application as Photoactive material

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ABSTRACT

In an organic medium, 1,3,5-hexachlorocyclotriphosphazene (HCTP) and CoCl2 were reacted. IR, UV, and EPR spectrum studies, as well as quantitative estimations, were used to characterize the product. The composition of the reaction product has been determined to be (P3N3Cl5) $(CoCl3)^-$. A bidentate coordinated complex with Oh geometry and paramagnetic properties is the reaction product. Under both normal and varying lighting circumstances, the current transport mechanisms in the reaction product's thin films have been investigated. It is discovered that the film displays an Ohmic behavior at low fields and that the Pool Frenkel (PF) mechanism dominates the high field area. It infers that the reaction product may be used as photoactive material.

Keywords: 1,3,5-hexachlorocyclotriphosphazene (HCTP), Paramagnetic, Charge transfer, Pool Frenkel (PF), Photoactive

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INTRODUCTION

Polymers incorporating transition metal complexes have attracted considerable attention[1][2][3] due to their diverse applications in sensors[4][5][6][7], biomedical applications[8][9], and catalysis[10][11]. Complexes of 1,3,5-hexachlorocyclotriphosphazene (HCTP) with a few metals, including PCl_5[12], PF_5[13], $TiCl_4$, $ZrCl_4$[14], $SbCl_3$[15], and Me_3Sn[16][17], as well as Palladium complexes of phosphine-linked cyclophosphazenes[18], have been found because of the electrons that are spare on N atoms. Crystallography and photophysical characteristics of cyclic phosphazenes containing Pd (II), Pt (II), Ru (II), and Re(I) bipyridine complexes have been investigated by spectroscopic analysis and synthesis[19].

Recent studies have examined the reaction product of $(PNCl_2)_3$ with ethylamine and its use in acidic soil reclamation[20], as well as the electrical conduction of complexes of $(PNCl_2)_3$ with Fe (II) and Zr (IV) under various lighting conditions[21][22].

In view of this, synthesis, spectral characterization, and application as photoactive material of the reaction product of $CoCl_2$ with HCTP are being presented here.

EXPERIMENTAL

Aldrich make, Anal. R. grade, doubly distilled chemicals were used throughout the present work.

Synthesis

Synthesis of 1,3,5-hexachlorocyclotriphosphazene (HCTP)

The reported process was used to manufacture 1,3,5-hexachlorotriphosphazene [HCTP][23]. In short, 0.5 mol of PCl_5 and NH_4Cl each were refluxed for 72 hours in 80 mL of s-Tertrachloroethane. Following a series of washings with distilled water and s-Tetrachloroethane to eliminate any remaining unreacted PCl_5 and NH4Cl, a colorless material was isolated.

The cyclic trimer (Fig. 1) was formed, as confirmed by reported M.P. and FT-IR spectral studies[24]. The colorless mass was extracted using concentrated H_2SO_4, which primarily removed the trimer, which was then recovered by diluting the acid with water and then back-extracted with petroleum ether[25].

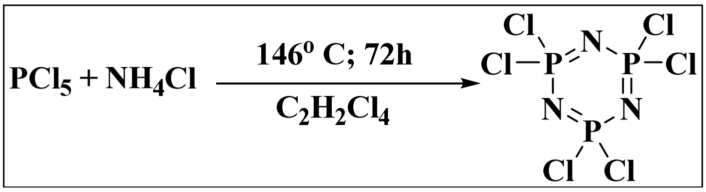


Figure 1: Reaction of phosphorous pentachloride (1 M) with ammonium chloride (1 M) for the synthesis of 1,3,5 Hexachlorocyclotriphosphazene (HCTP)

Synthesis of the complex of Co (II) Chloride with $(PNCl_2)_3$

Equimolar ethanolic solutions of $CoCl_2$ and $(PNCl_2)_3$ were combined to create the complex, which was then refluxed for 24 hours until the color changed. To get rid of any unreacted reactants, the pink mass that had formed was separated and then washed with petroleum ether and ethanol, respectively. After drying, the complex was kept in a vacuum over fused calcium chloride.

Estimations and recording of spectra

The complex was examined both qualitatively and quantitatively using established techniques for estimations. Benzene was used as a solvent in the viscosity method to calculate molecular weight. The complex's I.R. (400–4000 cm-1), electronic (200–800 nm), and E.P.R. spectra were then captured at room 300 K using IFS-66 VFT-IR, UV-VIS-NIR, and Varians E-X band spectrometers.

Measurement of I-V Characteristics

Using the isothermal immersion approach, the complex's film was applied on a glass slide that had been ultrasonically cleaned and kept at 300 K in a benzene solution[26]. To get rid of any remaining solvent, the film was vacuum-dried for roughly twenty-four hours. A mechanical stylus setup was used to measure the film's thickness. Before the copper electrode was vacuum-deposited onto the glass slide, a bare copper wire was positioned over the complex's layer. Following deposition, the copper wire was taken out, resulting in a 0.15 cm gap between the two electrodes.

The film was illuminated for ten minutes using sunshine, an 80W mercury lamp, and a 60W regular lamp. The light intensity of a typical lamp is 73.62 W/cm2, while that of a mercury lamp is 58.89 W/cm2. Measurements of the film's I-V properties under various lighting situations have been reported elsewhere[27]. Fig. 2 shows the schematic diagram of the experimental setup for the I versus V measurement.

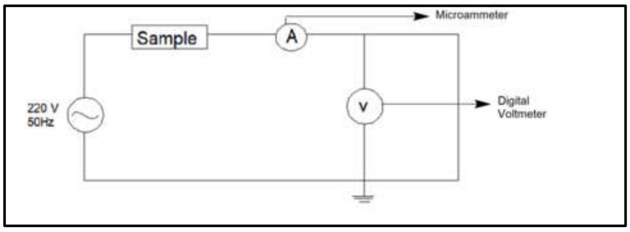


Figure 2: Experimental setup for I vs V measurement

RESULTS AND DISCUSSION:

Characterization of HCTP.CoCl₂

The intricate HCTP. CoCl2 is a pink amorphous solid that dissolves in ether, acetone, and benzene. When heated above 212°C, it decomposes rather than melts. The percentage of P 19.46, N 8.19, Cl 59.43, Co 12.32, and m.w.478.40 g mol-1 that were obtained in the analytical data for the molecular composition (P3N3Cl3) and (CoCl3) resembles their theoretical values.

IR has been used to confirm that the complex contains the various functional groups. When the vibrations seen in the complex's infrared spectrum are compared to those of HCTP (Table I), it is discovered that the frequencies 617.9 and 769.0 cm-1 correspond to two P=N Co bands, while the complex's IR spectrum's assignments at 982.9 and 1087.3 cm-1 are caused by free P=N groups in the ring.

The N-P-Cl bands are represented by the other vibrations in the upper area. It can be deduced from the IR data that HCTP has bidentatedly coupled with CoCl2 via its N atoms. Figures 3 and 4 show the infrared spectra of (PNCl2)3 and its combination with CoCl2, respectively.

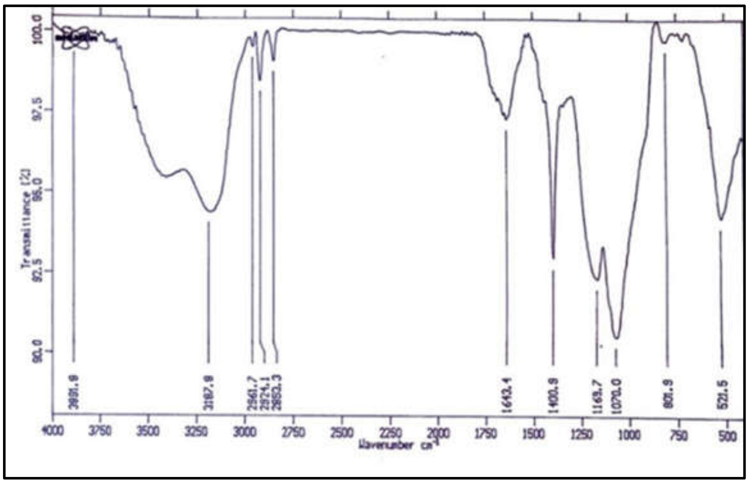


Figure 3: I.R Spectrum of 1,3,5-hexachlorocyclotriphosphazene (HCTP)

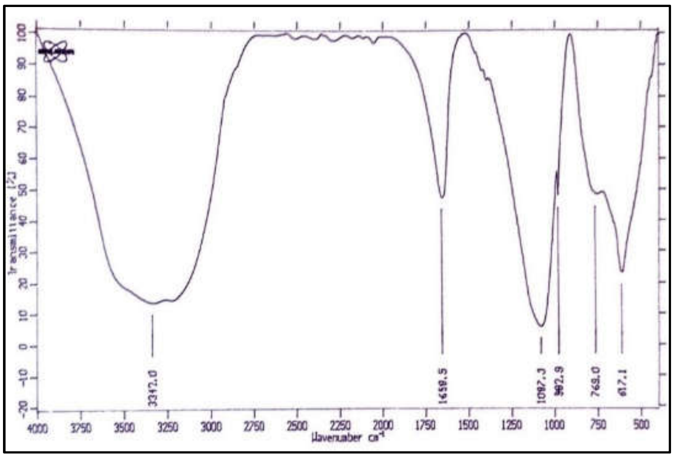


Figure 4: I.R Spectrum of the reaction product of 1,3,5-hexachlorocyclotriphosphazene (HCTP) with Co (II) chloride

Table 1: Comparison of IR spectra of HCTP and its complex HCTP.$CoCl_2$

Vibrations ν cm^{-1}		*Assignment*
HCTP$(PNCl_2)_3$	*HCTP.$CoCl_2$*	
521.5		PCl_2
	617.9	P-N → M
	769.0	P-N → M
801.9		P=N
	982.9	P=N ring
1070.0	1087.3	P=N
1169.7		N-P-Cl
1400.9		N-P-Cl
1643.4	1658.5	N-P-Cl
2853.3		P-Cl
2924.1		P-Cl
2961.7		P-Cl
3187.8	3342.0	Cyclic P_3N_3 ring

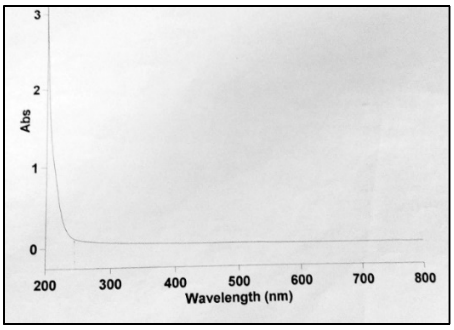


Figure 5: Electronic spectrum of the reaction product of 1,3,5-hexachlorocyclotriphosphazene (HCTP) with Co (II) chloride

A single peak at 248 nm in the complex's electronic spectrum (Fig. 5) represents the charge transfer transition. The spectrum's greater absorbance value (3.18) suggests that the molecule might be employed as a photoactive material and could have applications in this field. The complex's strong absorbance and charge transfer further imply that it is very conducting.

The other bands pΠ - dΠ for P-N ring of HCTP and $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ for Oh Co^{2+} are absent suggesting the linkage of HCTP to $CoCl_2$ forming N coordinated complex.

EPR spectrum (Fig 6) of the complex shows 16 peaks $(2\times\frac{7}{2}+1)(2\times\frac{1}{2}+1)$ which arises due to hyperfine interaction between Co and P atom inferring the presence of free electron on P atom. The complex's paramagnetic nature is shown by the magnetic moment, μeff 1.75 BM, and magnetic susceptibility, χa, 3.61X10-3, which were computed from the complex's EPR spectrum. The coordination is further supported by the empty shell and electron transfer values of $g_{\parallel}$ 1.996 and $g_{\perp}$ 2.0578, respectively. The complex's free-electron, $g_{\perp}$ 2.0578, explains that the P-Cl bond has broken, transferring the Cl atom to the Co2+ ion and oxidizing it to the Co3+ ion. This is supported by the value of μeff 1.75 BM based on single or unpaired electrons, which results in the complex's Co3+ ion.

The reaction maybe

$$P_3N_3Cl_6 + CoCl_2 \longrightarrow (P_3N_3Cl_5)(CoCl_3)$$

The presence of a free-electron on the P atom also supports the highly conducting nature of the complex as evidenced by the electronic spectrum of the complex.

Scan range 20X100 G	Field set 3300G	Temperature RT
Microwave frequency 9.39 GH	Microwave power 5 mW	Modulation amplitude 0.5 X 10 G
Modulation frequency 100 kHz		

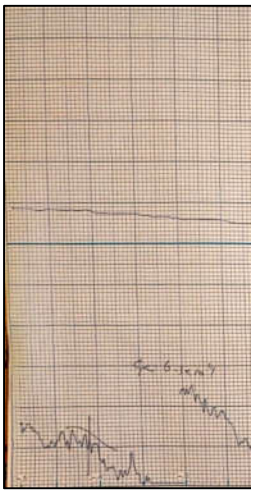


Figure 6: EPR spectra of the reaction product of 1,3,5-hexachlorocyclotriphosphazene (HCTP) with Co (II) chloride

From the results, it is concluded that HCTP has acted as an oxidizing agent during refluxion with the formation of a bidentatedly coordinated complex as shown by its structure (Fig. 7)

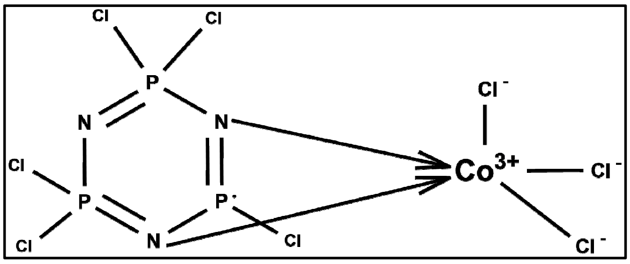


Figure 7: Proposed structure of the reaction product of HCTP with Co (II)chloride

APPLICATION AS PHOTOACTIVE MATERIAL

I-V CHARACTERISTICS:

The I-V characteristics of the (P3N3Cl5) (CoCl3) film under various lighting circumstances and normal illumination are displayed in Fig. 8. Both regular and mercury light, with intensities of 73.62 W/cm2 and 58.89 W/cm2, respectively, were used to illuminate the films. For ten minutes, sunlight was likewise shone on the other film. These charts demonstrate how the type of illumination affects the current's magnitude. For all four films, the log I against log V plots are primarily linear in low fields. Two forms of conduction can be seen in films that are normal, ordinary, lighted by sunlight, or by mercury light.

For all four curves, the computed slope value in the low field zone is ≈ 1 (Fig. 10). This shows that ohm's law holds good in the low field region. The high field area slopes of thin films under normal, ordinary, mercury, and sunlight are 1.080, 1.106, 1.064, and 1.233, respectively. While curvature is seen in the high field region, indicating a non-ohmic zone, the linearity for all lighting circumstances in the lower voltage region is caused by the charge carrier velocity's independence from the applied field. Slope increased significantly in the high field zone, rising from 1.055 to 1.080, 0.998 to 1.106, 1.014 to 1.064, and 1.032 to 1.233 in sunlight, normal, ordinary, and mercury, respectively.

There is a 19% rise in slope in film that is exposed to sunshine, compared to 11% in a 100 W conventional bulb, 5% in mercury light, and 2% in normal light in the high field zone. This suggests that sunlight has reduced the surface barrier, which in turn has increased the emission current. However, the slope of the thin-film irradiated by sunlight changes from 1.233 to 0.797 in the high field zone, indicating that the space charge limiting region has caused charge carrier saturation. Figure 9 shows a replot of the data from Figure 8 as log I vs V1/2 for each of the four films.

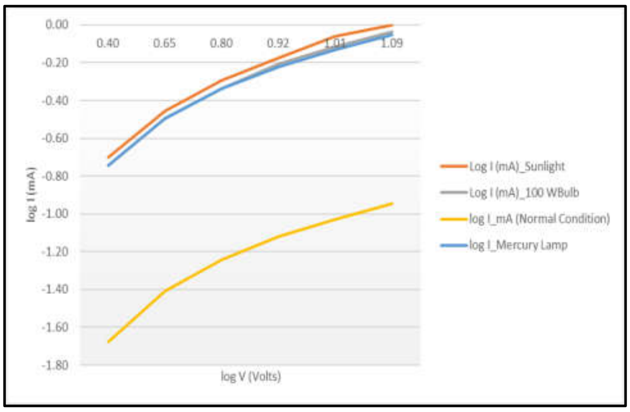


Figure 8: log I vs log V under different illuminating conditions

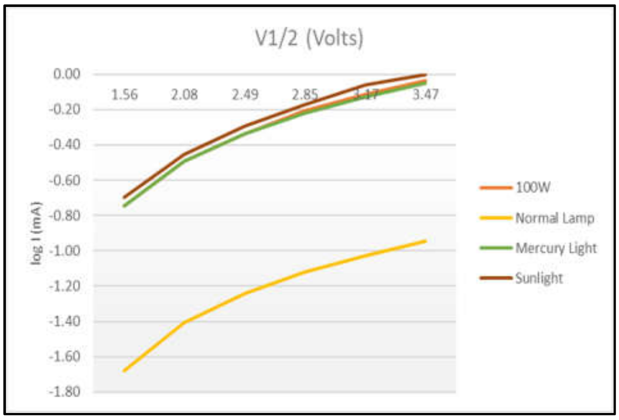
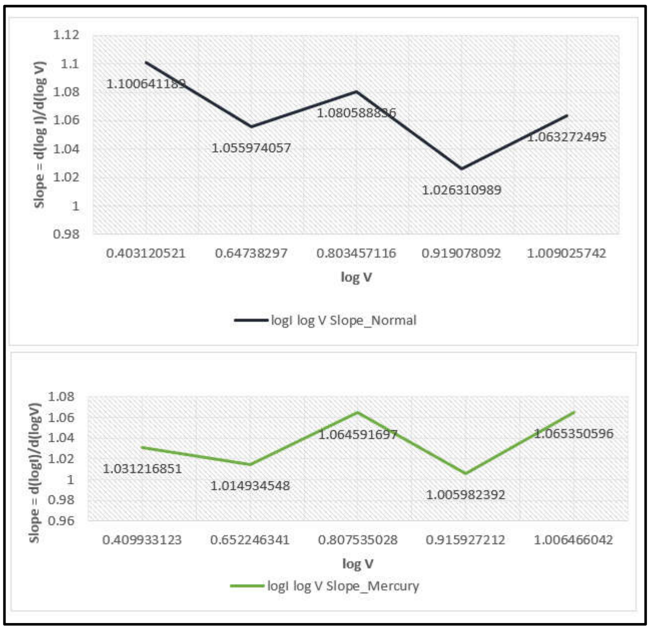


Figure 9: log I vs V1/2 under different illuminating conditions

All four curves in the log I versus V1/2 plots exhibit linearity in the high field region and curvature in the lower field. This discovery indicates that, when β is a constant, current in the high field zone obeys I α exp (β V1/2). Only when high field conduction is controlled by the Richardson Schottky (RS) or Pool Frenkel (PF) effects can such a current dependence be seen (Lamb 1967).

The only point of distinction between the two being the values of β i.e., $\beta_{PF} = 2\ \beta_{RS}$. The experimental value of β has been calculated by using the relation β_{PF} = kT X slope.

Where k = Boltzmann constant. The values of β_{PF} and slope are shown in table 2.



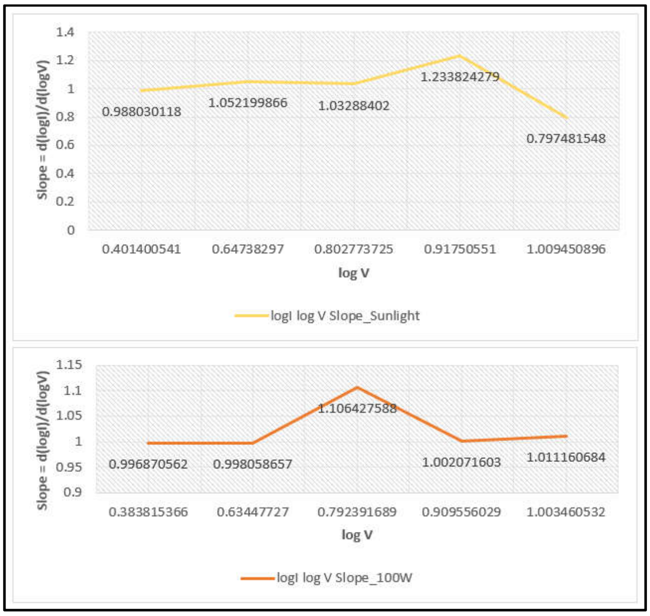


Figure 10: Slope versus log V under different illuminating conditions

Table 2: Values for βPF calculated from the slope of log I versus V1/2 plots.

Temperature in K	*The film under normal condition*		*Film illuminated with an ordinary lamp*		*Film illuminated with mercury light*		*Film illuminated with sunlight*	
	Slope	β_{PF}	*Slope*	β_{PF}	*Slope*	β_{PF}	*Slope*	β_{PF}
298	0.34	$13.9X10^{-24}$	0.36	$14.8X\ 10^{-24}$	0.34	$13.9X10^{-24}$	0.33	$13.5X10^{-24}$

The theoretical values of β_{RS} are calculated by using the Schottky relation

$$\beta_{RS} = \left(\frac{e^3}{4\pi\varepsilon_o\varepsilon_r}\right)^{1/2},$$

where e is the electronic charge, ε_r is the dielectric constant of the complex and ε_o is the permittivity of free space. We have used e= $1.6 X 10^{-19}$ C, ε_o = $8.85 X 10^{12}$ F/m. 3.62 X 10-24 is the computed value of βRS. The conduction process follows the Pool Frenkel (PF) mechanism if βPF > βRS, and the Schottky type conduction mechanism when βPF = βRS. For the films under various illuminations, the experimental value of βPF >βRS (Table II) indicates that the PF mechanism is the most dominant mechanism of conduction at high fields. Additionally, it is shown that conduction is more common in the film that is exposed to sunlight (Fig. 9 log I vs V1/2).

CONCLUSION

Based on the data, it can be inferred that thin films exposed by sunlight exhibit superior conduction when compared to films illuminated by regular lamps and mercury light. Conduction is nearly the same in films that are lit by mercury light and regular lamp light. In the high field area, however, the Pool Frenkel (PF) mechanism dominates all four films.

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