Asian Journal of Chemistry Vol. 15, No. 1 (2003) 151–154

X-Ray Powder Diffraction Pattern of Fe(II) Complex of 1,3,5-Hexachlorotriphosphazene

S.P.S. JADON
Department of Chemistry, S.V. College, Aligarh, India

The complex of 1,3,5-hexachlorotriphosphazene (HCTP), $(PNCl_2)_3$ with iron(II) acetate has been synthesised and investigated spectrometrically. The frequencies for P—N→M, P—Cl_2, P—N ring along with CH_3COO^- ion have been observed in its IR and laser Raman spectra. The electronic spectrum of the complex has shown bands according to charge transfer, $^4T_{1g} \leftarrow {}^4A_{1g}$ and $p\pi$-$p\pi$ transitions inferring the hexadentated coordination of two $(PNCl_2)_3$ rings to Fe(II)-acetate. X-ray diffractometric studies explain the coordination of two $(PNCl_2)_3$ deformed rings through Fe^{2+} ion bridging having sandwich structure in a triclinic geometrical packing

Key Words: XRD, Fe(II) Complex, 1,3,5-Hexachlorotriphosphazene

INTRODUCTION

1,3,5-Hexachlorotriphosphazine (HCTP), $P_3N_3Cl_6$ or $(PNCl_2)_3$, which has six-membered cyclic ring, has electron pairs in spare at its N atoms due to which some of its complexes with PCl_5, PF_5, $TiCl_4$, $ZrCl_4$, $AlBr_3$ and Me_3Sn have been reported[1–8]. The synthesis of the complex of HCTP with Fe(II) compound and its spectrometric investigation are being reported here.

EXPERIMENTS

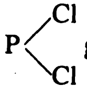
HCTP was prepared by passing dry NH_3 gas into PCl_5 solution, dissolved in tetrachloroethane, kept at 100–150°C on a hot plate. The heating was done for 6 h. NH_4Cl formed was separated by filtration and trimer $(PNCl_2)_3$ along with other halides was obtained by distilling filtrate under reduced pressure. Further $(PNCl_2)_3$ was refined by column chromotography, using $C_2H_2Cl_4$ as fluent. The complex of HTCP, $(PNCl_3)_2$ with Fe(II) was synthesised by refluxing equal ratio, 0.5 g $(PNCl_2)_3$ and $Fe(CH_3COO)_2$ each in DMF for 24 h. The light yellow mass formed was separated, washed with DMF followed by successive washing with ethanol and ether, dried and stored *in vacuo*.

The elemental analysis of the complex was done by recording its atomic absorption spectrum on ESCA 750 in the range of 100–900 nm. IR and laser

Raman spectra were graphed on Perkin-Elmer 785 (4000–200 cm^{-1}) and NR-1000 Jasco (1800–400 cm^{-1}) using $Ar_{10}N$ laser beam ($\lambda = 4.880$ Å) spectrometers respectively. Electronic and X-ray powder diffraction spectra of the complex were taken, subsequently, on UV 260 Shimadzu (800–2000 nm) and XRD model PW-1130100 using CuK_α ($\lambda = 1.540$ Å) and 1–55°, 2θ range at room temperature.

RESULTS AND DISCUSSION

The complex of HCTP, $(PNCl_2)_3$ with iron(II) acetate is yellowish solid and it does not melt up to 400°C. Analytical data: % found (calcd.): P 21.23 (21.38), N 9.78 (9.65), Cl 48.40 (48.96), H 0.70 (0.69), Fe 6.24 (6.44) and m.w. 868.66 (870.00) formulate the complex as $Fe(CH_3COO)_2{\cdot}(PNCl_2)_6$ explaining that two rings have linked to $Fe(CH_3COO)_2$ molecule.

This view is supported by the vibration observed at 260(s), 270(s), 290(s) cm^{-1} for three P—N→M bands, 300, 320(s), 350(s) and 660(s) due to  $P{<}^{Cl}_{Cl}$ groups in its IR spectrum. The frequencies at 400(b) and 420(s) on account of P—N rings are found along with the peaks at 1456 to 1370 and 1650–1620 cm^{-1} for CH_3COO^- ion in higher region, suggesting that all three N atoms of each $(PNCl_2)_3$ ring have coordinated to Fe^{2+} ion, forming Fe^{2+} bridged and hexadentated coordinate complex of $Fe(CH_3COO)_2$ with HCTP, which is also inferred by assignments at 375 cm^{-1} for P—N→M, 400(b) and 430(s,w) due to two P – N rings, and frequencies at 480(s) and 500(b) cm^{-1} for groups seen in laser Raman spectrum of the complex.

In the electronic spectrum of the complex the four bands at 810 nm for charge transfer transition caused by $Fe(CH_3COO)_2$, 1440 nm due to $^4T_{1g} \leftarrow {}^4A_{1g}$ transition showing complexation of Fe^{2+} ion with HCTP, while 1560 and 1910 nm consequently are according to p_π-p_π transitions indicated by P—Cl and P—N groups of $(PNCl_2)_3$ ring. The happening of coordination is expouded by the frequency ratios $\nu_1/\nu_2 < 1$ and values of oscillator strength 'f' found of the order of 10^{-7} for spin forbidden laporte forbidden transition expressing the spin orbital coupling, *i.e.*, coordination of ligand→metal with confirmation of hexadentated coordination of two $(PNCl_2)_3$ rings to $Fe(CH_3COO)_2$ expressing sandwich type structure as shown by Fig. 1. The value of Dq 909.1 cm^{-1}, which is too much higher than the value for free Fe^{2+} ion, also infers the complexation. From the X-ray diffraction pattern of the complex, the values of sin θ hkl, d (Å), average axial angles and axial ratios have been calculated inferring the triclinic geometrical array of the complex. The values determined for atomic angle (Table-1) and atomic distance (Table-2) expound that each $(PNCl_2)_3$ ring which has deformed during complexation, has linked to each other through Fe^{2+} ion bridging, forming hexadentated coordinated sandwich type structure of $Fe(CH_3COO)_2(HCTP)_2$ as expressed by Fig. 1.

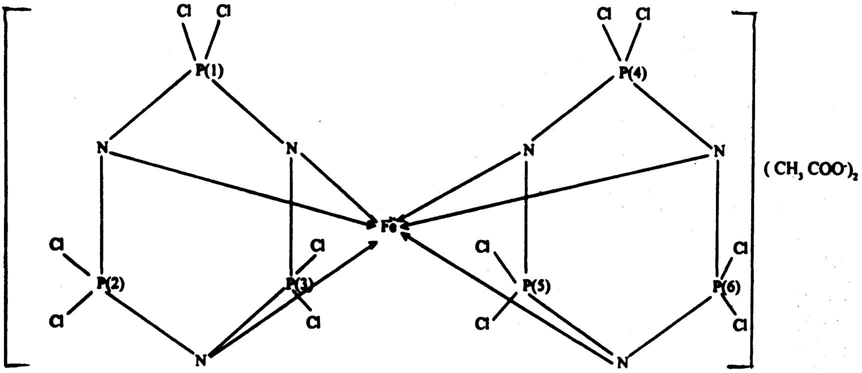


Fig. 1. Structure of $(HCTP)_2 \cdot Fe(II)OAc$

TABLE-1
AXIAL ANGLES OF $Fe(CH_3COO)_2(HCTP)_2$

S.No.	Atoms		Angles (deg)
1.	N(3)-P(1)-N(1)	=	135.00
2.	P(1)-N(1)-P(2)	=	125.26
3.	N(1)-P(2)-N(2)	=	135.00
4.	P(2)-N(2)-P(3)	=	125.26
5.	N(2)-P(3)-N(3)	=	135.00
6.	P(3)-N(3)-P(1)	=	125.26
7.	Cl-P(1)-Cl	=	116.00
8.	Cl-P(2)-Cl	=	108.00
9.	Cl-P(3)-Cl	=	116.00
10.	P(4)-N(4)-P(5)	=	125.26
11.	N(4)-P(5)-N(5)	=	135.00
12.	P(5)-N(5)-P(6)	=	125.26
13.	N(5)-P(6)-N(6)	=	135.00
14.	P(6)-N(4)-P(4)	=	125.26
15.	N(6)-P(4)-N(4)	=	135.00
16.	Cl-P(4)-Cl	=	116.00
17.	Cl-P(5)-Cl	=	116.00
18.	Cl-P(6)-Cl	=	108.00

TABLE-2
AXIAL DISTANCE OF $Fe(CH_3COO)_2(HCTP)_2$

S.No.	Atom	ao (Å)	bo (Å)	co (Å)
1.	P(1)	2.48	2.87	2.03
2.	P(2)	4.97	5.28	4.54
3.	P(3)	7.46	6.42	5.56
4.	P(4)	9.95	10.01	10.00
5.	P(5)	12.44	12.45	12.20
6.	P(6)	14.57	14.62	14.24

ACKNOWLEDGEMENT

The author wishes to express his thanks to the Director, USIC, Delhi University, Delhi for providing instrumental facilities.

REFERENCES

1. J. Ensley and P.B. Udy., *J. Chem. Soc. (A)*; 3005 (1970).
2. H. Binder, *Z. Anorg. Allg. Chem., (Ger.)*, **383**, 130 (1971).
3. Ya. Busleav, B.V. Levin, M.Z.G. Ry, S.P. Petrosynnts and B.V. Micronova, *Zh. Neorg. Khim. (Russ.)*, **14**, 3245 (1969).
4. D. Millington and B.B. Sower, *J. Chem. Soc. (Dalton Trans.)*, **23** (1973).
5. H.W. Roesky and H. Weizer; *Chem. Ber. (Ger)*, **106**, 280 (1973).
6. ———, *Chem. Ber (Ger.)*, **107**, 1153 (1974).
7. H.R. Allock, *Inorg. Chem.*, **38**, 280 (1999).
8. O.S. Jung, *Inorg. Chem.*, **38**, 5447 (1999).

(*Received*: 20 May 2002; *Accepted:* 5 August 2002) AJC-2810