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NOTE

X-Ray Diffraction Pattern of the Complex of 1,3,5-Hexachlorocyclotriphosphazene with Cobalt(II) Acetate

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X-ray powder diffraction spectrum of the complex of 1,3,5-hexachlorocyclotriphosphazene with $CoAc_2$, assigned as $(PNCl_2)_2{\cdot}CoAc_2$ quantitatively, suggested its Co^{2+} bridged hexadentated sandwich structure.

Key Words: X-ray diffraction, Co(II) acetate.

A few N-coordinated complexes of 1,3,5-hexachlorocyclotriphosphazene with some metal compounds have been reported[1–9]. X-ray powder diffraction studies of the complex of HCTP with $CoAc_2$ are being presented.

HCTP was synthesized as reported[10], using Aldrich make AnalaR grade chemicals. To prepare the complex ethanolic solutions of both HCTP and $CoAc_2$ were mixed together and refluxed for 24 h till violet coloured mass was formed. The obtained product was washed with ethanol and diethyl ether sucessively, dried and stored *in vacuo*.

Quantitative analysis of the complex was done gravimetrically[11] and from its atomic absorption spectrum, recorded on ESCA-750 (100–900 nm). IR, electronic and XRD spectra were carried out, subsequently, on the Perkin-Elmer 785 (4000–200 cm^{-1}), UV-260, Shimadzu (800–2000 nm) and PW-1130100 diffractometer using CuK_α ($\lambda = 1.540$ Å) in 1–55°C, 2θ range at room temperature.

Analytical data of the complex of HCTP with $CoAc_2$ for the molecular composition $(PNCl_2)_2{\cdot}CoAc_2$ % found (calcd.), P 21.20 (21.30), N 9.67 (9.60), Cl 48.60 (48.75), C 5.70 (5.50), H 0.60 (0.69), Co 6.60 (6.75) and m.w. 876.74 (873.0) g mol^{-1} are in close agreement the values obtained from atomic absorption spectrum of the complex.

The vibrations at 260 (d) cm^{-1} for $P—N{\rightarrow}Co$: 295–300 (bd) cm^{-1} for two $P—N{\rightarrow}Co$, 385 and 520 cm^{-1} due to P—Cl, 660 (s), 690–746 (b) and 825 cm^{-1} for P═N ring, 1060–1160 cm^{-1} for N—P—Cl and 1360–1700 cm^{-1} due to CH_3COO^- ions are observed in the IR spectrum of the complex, indicating hexadentated coordination of two $PNCl_2$ molecules with one $CoAc_2$ mol.

UV spectrum of the complex consists five bands, one at 810 nm (12345.70 cm^{-1}) for the charge transfer transition, while peaks at 1000 and 1460 nm are due to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions inferring O_h geometry of Co^{2+} complexes. The remaining bands at 1680 and 1900 nm are on account of σ and π bonds at P—N ring of 1,3,5-hexachlorocyclotriphosphazene. The O_h geometry is also confirmed by low value of magnetic moment $\mu_{eff} = 1.498$ BM, which is too much lower than 2–3.5 for O_h cobalt complexes. The values of frequency ratio $v_1/v_2 < 1$, oscillator strength 'f' of the order 10^{-7} for spin-forbidden-Laporte-forbidden transition and spin-orbital coupling constant, ($\lambda_s = 140.7$ cm^{-1} low from free Co^{2+} ion), determined by the equation as:

$$\mu_{eff} = 3.89 - \frac{15.59\lambda_s}{\Delta_0}$$

express coordinated linkage compounding the sandwich structure as Fig. 1 of $[(PNCl_2)_3]_2 \cdot CoAc_2$, complex formed.

XRD spectrum of the complex possesses 18 prominent peaks, for which atomic angles (Table-1) and atomic distance (Table-2) were calculated from the values of $\sin^2 \theta$, hkl and 'd' found from its XRD pattern. The results confirm Co^{2+} ion bridged, hexadentated, P—N→Co sandwich array of the complex $[(PNCl_2)_3]_3 \cdot CoAc_2$.

TABLE-1

ATOMIC DISTANCE OF THE COMPLEX, $[(PNCl_2)_3]_3 \cdot CoAc_2$

S. No.	Atoms	Angles (°)
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(6)—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 DISTANCES OF $[(PNCl_2)_3]_2 \cdot CoAc_2$

S. No.	Atom	a_0 (Å)	b_0 (Å)	e_0 (Å)
1.	P(1)	2.53	1.79	2.19
2.	P(2)	5.07	5.37	4.62
3.	P(3)	7.60	7.64	7.24
4.	P(4)	10.13	11.05	9.89
5.	P(5)	12.66	12.67	12.43
6.	P(6)	15.20	14.67	14.59

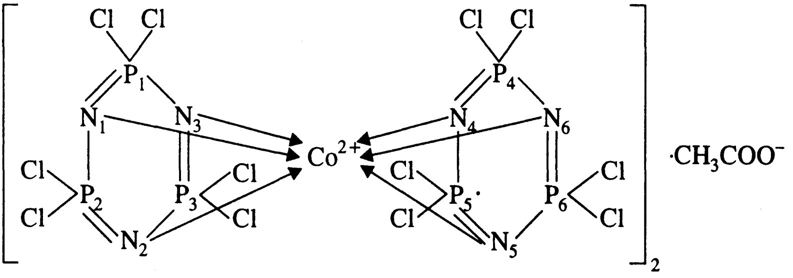

Fig. 1. Proposed structure of the complex, $[(PNCl_2)_3]_2 \cdot CoAc_2$

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