



MASS, IR AND EPR SPECTRAL CHARACTERISATION OF Cd (II) PHOSPHAZENIDE

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ABSTRACT

Complex of Cd (II) with hexahydro-cyclotriphosphazene (HHCTP) was synthesized, and studied with the help of Mass, IR and EPR spectra, assigning its molecular formula as $(N_3P_3H_4)_5\text{-Cd}$ having pentadentated coordinated linkage and trigonal-bipyramidal geometry.

Key words: Cadmium (II), Phosphazenide, Mass, IR, EPR.

INTRODUCTION

Various complexes and adducts of $(N\text{P}Cl_2)_3$ with metals have been reported¹⁻⁸, but a few complexes of $(N\text{P}H_2)_3$ with metals have been synthesized⁹⁻¹². The investigations of reaction product of (HHCTP) with Cd (II) chloride are being reported herewith.

EXPERIMENTAL

$(N\text{P}Cl_2)_3$ was prepared by refluxing NH_4Cl and PCl_5 in chlorobenzene at the 150°C for 6 to 12 h by using AnalaR grade chemicals. $(N\text{P}H_2)_3$ was prepared by the reduction of $(N\text{P}Cl_2)_3$ with $\text{Na}/\text{C}_2\text{H}_5\text{OH}$ as reported¹³. The complex of $(N\text{P}H_2)_3$ with CdCl_2 was prepared by refluxing both in equimolar ratio (1 : 1) in DMF for 6 to 8 h. White coloured mass obtained was separated, washed with DMF, ethanol and ether, dried and stored in vacuum desiccator over fused CaCl_2 .

The complex was analysed qualitatively and quantitatively by well known methods¹⁴. EPR and Mass spectra were recorded subsequently on varians X-E-4 band (4-8K Gauss) and Jeol Sx-102 (FAB) spectrometers. IR spectrum was recorded on Shimadzu 8201, PC ($4000\text{-}400\text{ cm}^{-1}$) FTIR spectrophotometer.

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RESULT AND DISCUSSION

In the complex, N and P were tested as NH_4^+ and PO_4^{3-} ion and found positive while test for Cl^- ion was found negative. The analytical data, % found, N-26.02, P-57.62, H-2.47, Cd-13.87 and molecular weight 807.46 gm/mol formulated the complex as $(\text{N}_3\text{P}_3\text{H}_4)_5\text{-Cd}$, which is supported by the prominent mass at m/z 807.5, 767, 782 and 789 appearing in its mass spectrum (Fig. 1) according to the $(\text{N}_3\text{P}_3\text{H}_4)_5\text{-Cd}$, $(\text{N}_3\text{P}_3\text{H}_2)_4\text{-Cd-N}_3\text{P}_2\text{H}_2$ (M+1), $(\text{N}_3\text{P}_3\text{H}_2)_4\text{-Cd-N}_2\text{P}_3\text{H}_2$ (M - 1) and $(\text{N}_3\text{P}_3\text{H}_4)_4\text{-Cd-N}_2\text{P}_3\text{H}_2$ (M - 2), fragments, respectively.

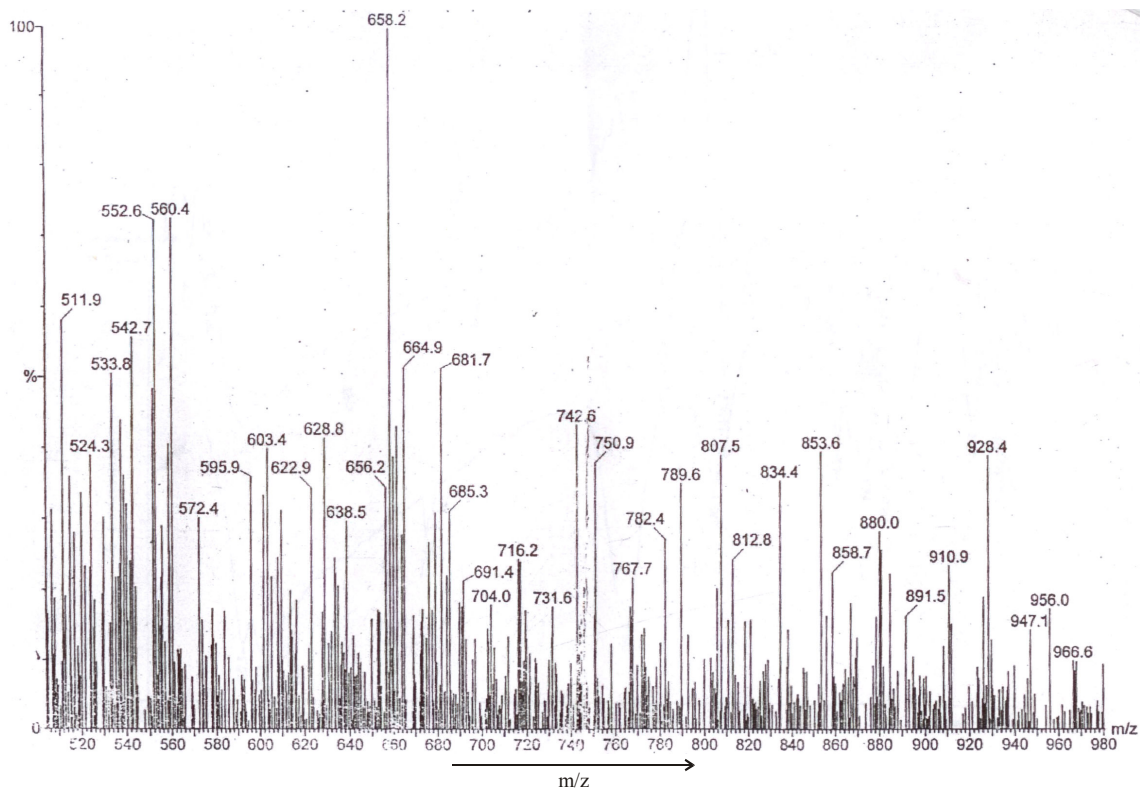


Fig. 1: Mass spectrum of $\text{Hg}(\text{N}_3\text{P}_3\text{H}_4)_5\text{-Cd}$

The other mass lines in its mass pattern may be explained by FAB fragmentation process as –

The formation of this complex is supported by its IR spectrum (Fig. 2) having the vibrations at 555-1380, 1442-1853 and 2340-3778 cm^{-1} . Subsequently for the H-P-N \rightarrow M, H-P-N, H-P=N bands, suggesting pentadentate coordinated linkage of P_3N_3 ring to Cd^{2+} ion.

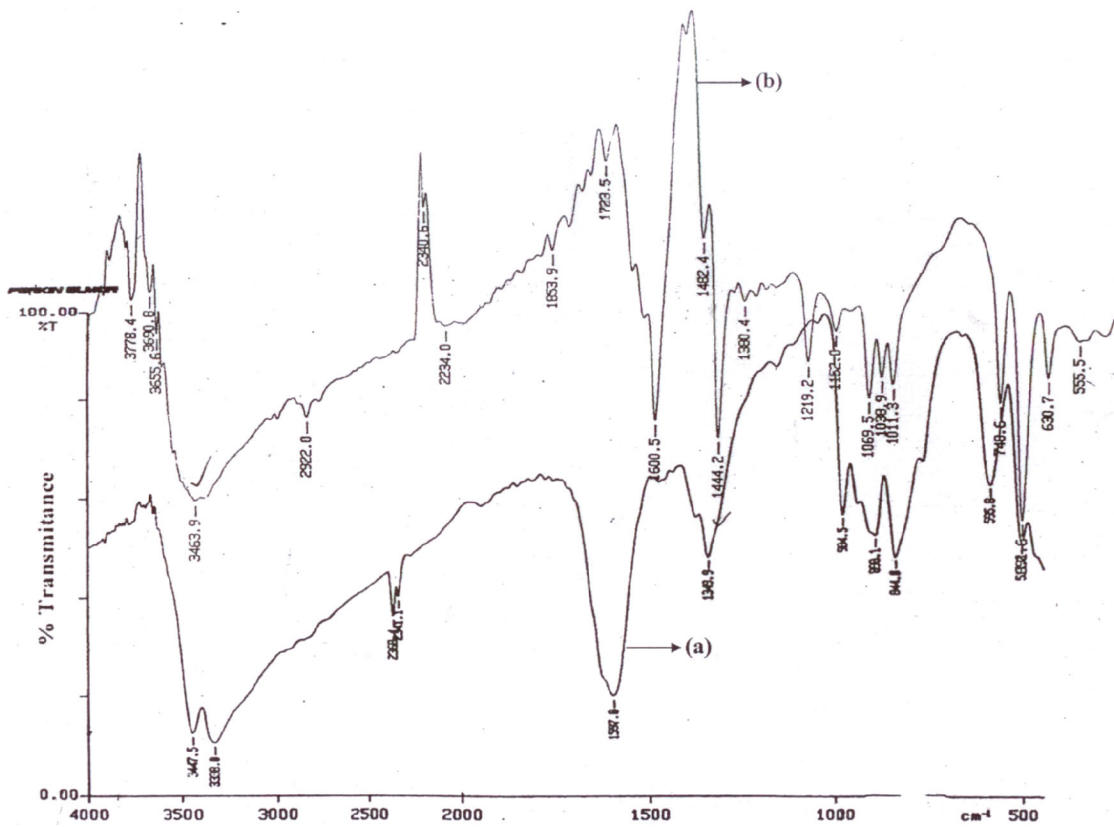
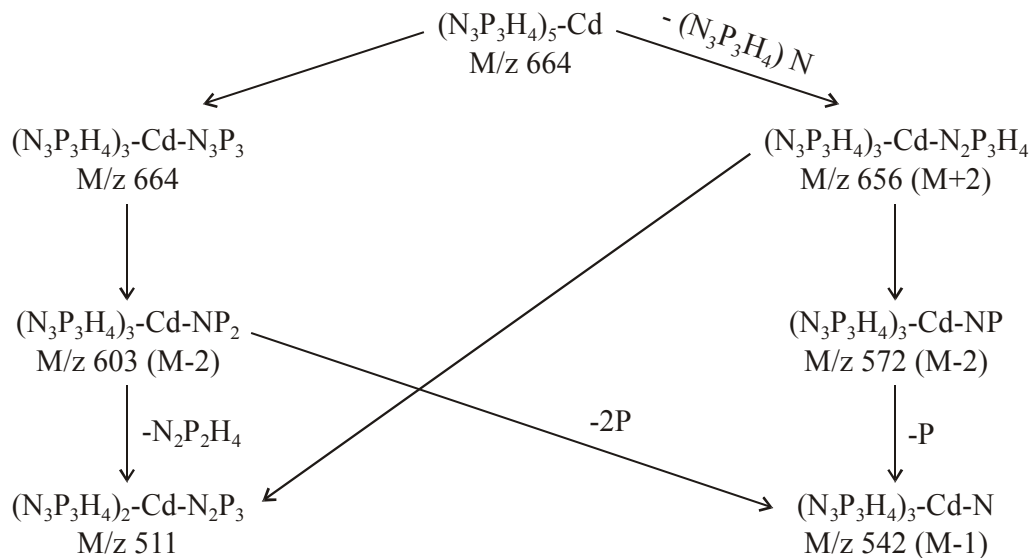
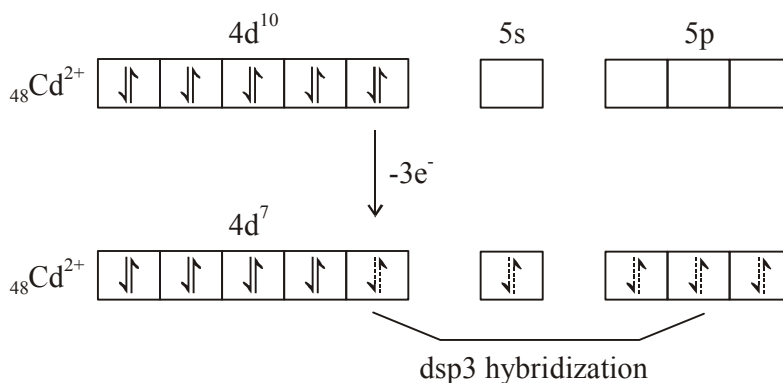


Fig. 2: IR Spectrum of ligand (a) and complex (b)

This view is also supported by the appearance of signals in its EPR spectra at both; RT and LNT (Fig. 3); thus, showing the paramagnetic character of the complex, while the complexes of Cd (II) generally exhibit diamagnetic nature. The paramagnetic character is confirmed by the magnetic momentum μ_{eff} 1.1461 B. M. (R. T.), 1.370 B. M. (L. N.T.) and magnetic susceptibility χ_A 5.844×10^{-4} esu at R. T. and 1.1973×10^{-3} esu at L. N. T. according to one unpaired electron in Cd^{2+} ion. The value of $g = 1.3515 < 2$ indicates the presence of vacant shell in Cd atom to form the coordinate linkage with P_3N_3 ring.

The presence of unpaired electron on Cd^{2+} ion may be due to loss of three electrons to reduce phosphorus atoms $\text{P}(\text{V}) \rightarrow \text{P}(\text{III})$ state of N_3P_3 ring as -



Trigonal bipyramidal geometrical complex is formed through dsp^3 hybridization. The presence of one unpaired electron on Cd^{2+} ion expound mono-nuclear complex ruling out any other geometry except trigonal bipyramid¹⁵. The structure of the complex may be represented as Fig. 4.

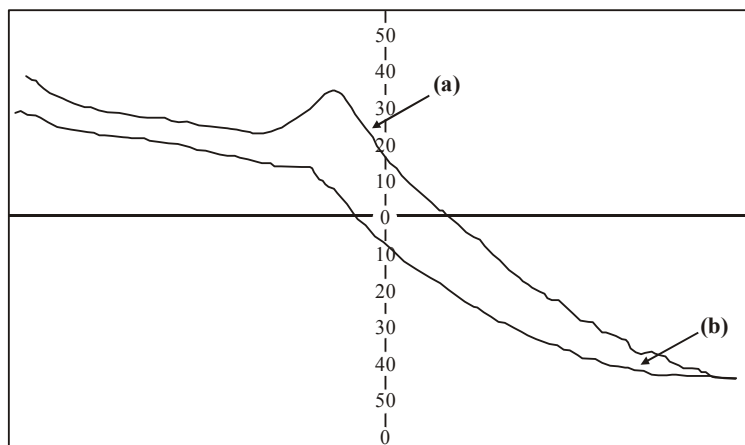


Fig. 3: EPR Spectra of complex at (a) RT and (b) LNT

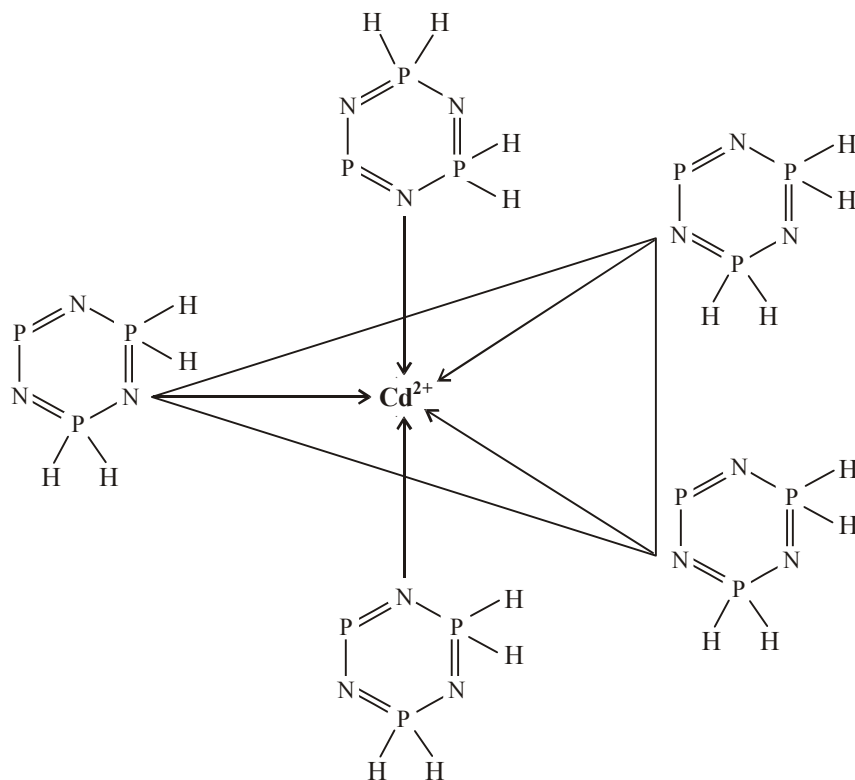


Fig. 4: Structure of $(N_3P_3H_4)_5-Cd$

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