

NOTE**Mass and EPR Spectra of Zinc(II) Cyclotriphosphazene**

NEETU SINGH and S.P.S. JADON*

*Department of Chemistry, S.V. College, Aligarh -202 001, India**E-mail: sps_jadon@yahoo.co.in*

Complex of Zn^{2+} with hexahydrocyclotriphosphazene was synthesized. The complex was characterized with the help of mass, IR and EPR spectra, assigning its molecular formula as $Zn(N_3P_3H_4)_3$ as tridentated coordinated complex.

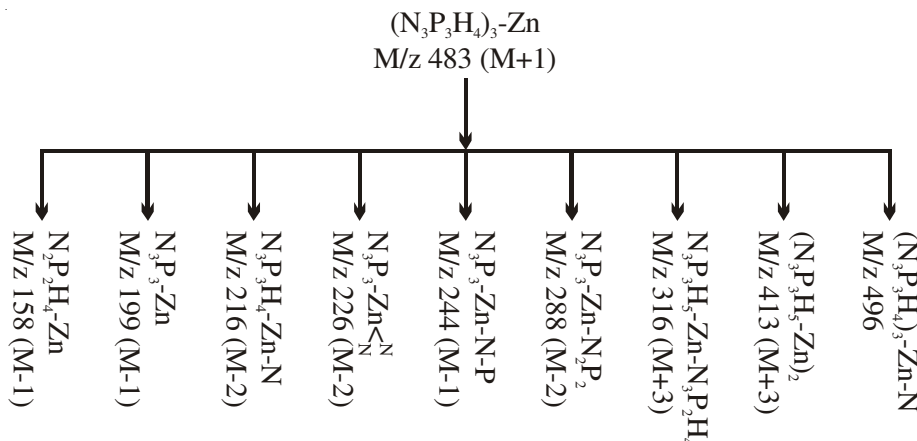
Key Words: Zinc(II) cyclotriphosphazene, Mass, EPR spectra.

Various complexes and adducts of $(N_3P_3H_4)_3$ with metals have been reported¹⁻⁴ but a few complexes of $(N_3P_3H_4)_3$ with metals are reported⁵⁻⁷. The investigations of reaction products of cyclotriphosphazene (H_2CTP) with Zn(II) chloride are reported here.

$(N_3P_3H_4)_3$ was prepared by refluxing NH_4Cl and PCl_5 in chlorobenzene at the 150 °C for 6 to 12 h. $(N_3P_3H_4)_3$ was prepared by the reduction of $(N_3P_3H_4)_3$ with sodium ethoxide. The white mass of $(N_3P_3H_4)_3$, produced, was separated, washed with dry ethyl alcohol and ether, dried and stored in vacuum. The complex of $(N_3P_3H_4)_3$ with $ZnCl_2$ 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 C_6H_5Cl , ethanol and ether, dried and stored in vacuum desiccator over fused $CaCl_2$.

The complex was analyzed qualitatively and quantitatively by well known methods⁸. EPR and mass spectra were recorded on varians X-E-4 band (4-8 k Gauss) and Jeol SX-102 (FAB), spectrometers, respectively. IR spectrum was graphed on Shimadzu 8201 PC (4000-400 cm^{-1}) FTIR spectrometer.

The quantitative estimations, % found N 26.47, P 58.61, H 1.26, Zn 13.65 and molecular weight 482.82 g/mol formulated the complex as $Zn(N_3P_3H_4)_3$ which is supported by the prominent mass lines at m/z 473 and 483 for the subsequent fragments $(N_3P_3H_4)_3-Zn$ (M+3) and $(N_3P_3H_4)_3-Zn$ (M+1) observed in its mass spectrum. The mass lines at the m/z 437, 457, appeared, according to $(N_3P_3H_4Zn)_2-P$ (M-2) and $(N_3P_3H_4Zn)_2-N_3P_3H_4$ (M-2) fragments, respectively. The other mass lines in its mass pattern may be explained by FAB fragmentation process, as follow:



The mass lines at M/z 226 for $N_3P_3-Zn ^N$ ($M-2$) for fragment, explains the co-ordination linkage of three N-atoms of three phosphazene ring to Zn atom.

The formation of this complex is supported by its IR spectrum, having the vibration at 470 (triplet), 1115 (broad, singlet), 1443 (multiplet), 1635 (doublet), 3405 (broad) cm^{-1} subsequently for three $P-N \rightarrow M$, $P-N$, one $H-P-N$ and $P=N$ bands suggesting that $(NPH_2)_3$ has co-ordinated through its N atom to Zn(II) and some H-atoms of two PH_2 groups have reacted to $ZnCl_2$ forming 2HCl molecule and tridentated co-ordinated complex.

The peak at 231 nm for the charge transfer transition along with other peak at 312 nm for the $p\pi-p\pi$ transition of the P-N ring have occurred in its electronic spectrum, indicating that $(NPH_2)_3$ has reacted with the $ZnCl_2$ with elimination of HCl forming ionic tridentated Zn(II) phosphazene.



Both EPR spectra recorded, at RT and LNT have a single peak, indicating paramagnetic character of the complex. This is confirmed by the value of the magnetic moment μ_{eff} 1.0875 BM and magnetic susceptibility χ_A 5.0875×10^{-4} esu and number of unpaired electrons two inferring the previous view as supported by the IR and UV spectra. Its structure may be proposed as Fig. 1.

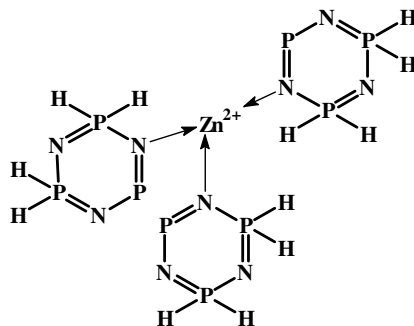


Fig. 1. Proposed structure of $Zn(N_3P_3H_4)_3$

ACKNOWLEDGEMENTS

The authors express their thanks to the Director , SAIF, CDRI, Lucknow and I.I.T., Chennai for providing instrumental facilities.

REFERENCES

1. H.R. Allcock, C.A. Crane, C.T. Morrissey, J.M. Nelson, S.D. Reeves, C.D. Honeyman and J. Manners, *Macromolecule*, **29**, 7740 (1996).
2. W.E. Krause, M. Parvez, K. B. Vischer and H.R. Allcock, *Inorg. Chem.*, **35**, 6337 (1996).
3. R.P. Singh, A. Vij, R.L. Kirchmeier and J.M. Shreeve, *Inorg. Chem.*, **39**, 375 (2000),
4. F. Palacios, C. Alonso and G. Rubiales, *J. Org. Chem.*, **62**, 1146 (1997).
5. A. Sundermann, W.W. Scholler and M. Reiher, *Inorg. Chem.*, **38**, 29 (1999).
6. S.P.S. Jadon, *Asian J. Chem.*, **15**, 151 (2003); **17**, 1312 (2005).
7. R.P. Singh, A. Vij, R.L. Kirchmeier and J.M. Shreeve, *Inorg. Chem.*, **39**, 375 (2000).
8. A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, L.B.S. Publisher New Delhi, India (1968).

(Received: 29 December 2008;

Accepted: 25 August 2009)

AJC-7793