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Novel Dinuclear d^{10}-Metallophosphazenes with Unusual Solution Fluxionalities. Synthesis and Structures of $[ICu(\mu,\eta^3,\eta^3\text{-}L)CuI]$ and $[Cl_2Zn(\mu,\eta^2,\eta^3\text{-}L)ZnCl_2]$ (L=Hexakis (3,5-dimethylpyrazolyl)cyclotriphosphazene)

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Reaction of hexakis(3,5-dimethylpyrazolyl)cyclotriphosphazene(L) with three fold excess amount of MX_n in CH_2Cl_2 gave unprecedented dinuclear metallophosphazenes $[X_nM(\mu\text{-}L)MX_n]$ (MX_n=CuI, $ZnCl_2$) which show not only novel coordination behaviour of L but also unusual solution fluxionalities involving two metal centers.

Phosphazenes, cyclic or polymeric forms, are unique carriers for transition metals owing to their ability to serve as versatile multifuntional ligands and templates.[1-3] The introduction of transition metals to phosphazenes has been achieved by use of exocyclic groups attached to ring phosphorus or by forming direct phosphorus-metal bonds and/or ring nitrogen-metal bonds. Particularly, the use of cyclotriphosphazenes with cyclopentadienyl exocyclic groups provided a new class of small molecule mononuclear metallophosphazenes as well as a novel route to polymeric metallophosphazenes.[4] Recent revisit[5,6] to the use of relatively venerable phosphazene compound, hexakis(3,5-dimethylpyrazolyl)cyclotriphosphazene (L),[7] resulted in the first adventitious observation[6] of structurally characterized unusual dicopper(II) complex of a pyrazolylcyclophosphazene oxide. In an effort to synthesize polynuclear metallocyclic phosphazenes, prompted by the paucity of such class, unprecedented dizinc(II) and dicopper(I) complexes of L were prepared and characterized. Herein, brief accounts of the synthesis, X-ray structures and fluxionalities of $[ICu(\mu,\eta^3,\eta^3\text{-}L)CuI]$ (**1**) and $[Cl_2Zn(\mu,\eta^2,\eta^3\text{-}L)ZnCl_2]$ (**2**) are reported.

The compounds **1** and **2** were prepared as analytically pure colourless crystalline solids in yields of 67 and 42%, respectively,[8] by allowing a 3: 1 molar slurry of MX_n (MX_n = CuI, $ZnCl_2$) and L (0.2 mmol) in 30 ml CH_2Cl_2 to react anaerobically at room temperature for 12h, followed by further workup. For **1**, the resulting reaction mixture was filtered and the concentrated filtrate was treated with excess Et_2O, affording the colourless crystalline product. In case of **2**, the resulting white precipitate was collected, washed and recrystallized from $CH_3CN\text{-}Et_2O$.

Single crystal X-ray analyses[9] revealed that the potentially multidentate ligand L bridges two metal centers *via* uniquely different binding modes in the compounds **1** and **2** whose molecular structures are displayed in Fig. 1 and 2, respectively. Both compounds constitute the first examples of structurally characterized dinuclear complex of L although the preparation of $L\cdot 2MCl_2$ (M= Pt, Pd;[7] Cu[5]) has been reported previously. In **1**, the ability of L to provide double tridentate N_3 cores involving phosphazene ring nitrogens affords two severely distorted tetrahedral Cu centers disposed on opposite sides of a rather planar

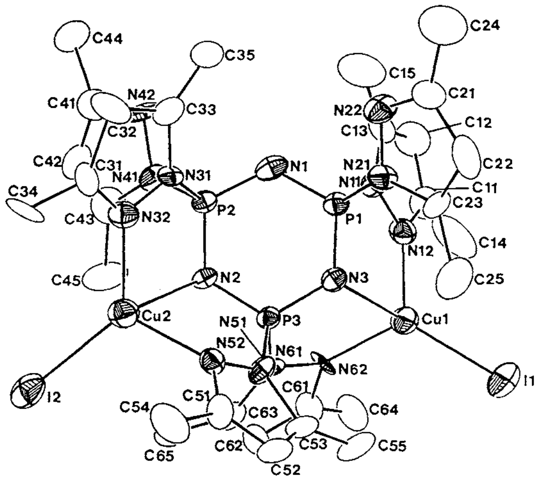

Fig. 1. Molecular structure of [ICu(μ,η^3, η^3-L)CuI] (**1**). Selected average dimensions: Cu-I 2.479(1), Cu-N (phosphazene ring) 2.477(2), Cu-N (non-geminal pyrazolyl ring) 1.978(4), Cu-N (geminal pyrazolyl ring) 2.056(26), P-N (phosphazene ring) 1.572(16), P-N (pyrazolyl ring) 1.676(10) Å; I-Cu-N 122.8(55), N (phosphazene ring)-Cu-N (pyrazolyl ring) 78.6(28), N (pyrazolyl ring)-Cu-N (pyrazolyl ring) 115.1(36), P-N-P 122.4(9), N (phosphazene ring)-P-N (phosphazene ring) 117.1(8)°.

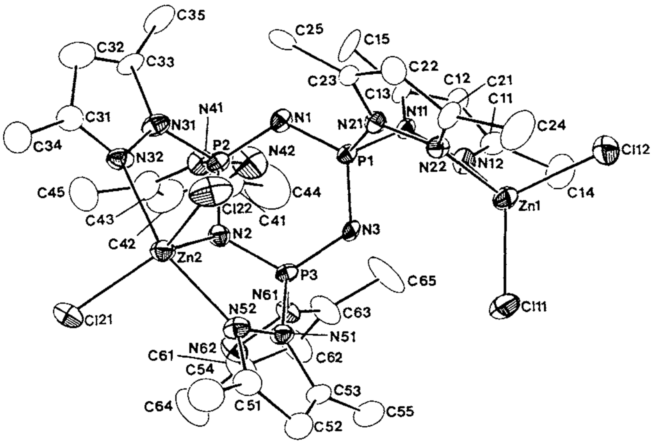

Fig. 2. ORTEP diagram of [$Cl_2Zn(\mu,\eta^2,\eta^3$-L)$ZnCl_2$] (**2**). Selected average parameters: Zn(1)-Cl 2.213(25), Zn(1)-N 2.079(11), Zn(2)-Cl 2.251(16), Zn(2)-N(2) 2.298(5), Zn(2)-N(pyrazolyl ring) 2.150(14), P-N (phosphazene ring) 1.584(9), P-N (pyrazolyl ring) 1.680(17) Å; Cl-Zn(1)-Cl 116.0(1), Cl(11)-Zn(1)-N 115.5(4), Cl(12)-Zn1-N 106.7(5), N-Zn(1)-N 94.2(2), Cl-Zn(2)-Cl 124.2(1), Cl-Zn(2)-N(2) 117.9(71), N(2)-Zn(2)-N(pyrazolyl ring) 76.5(5), N(32)-Zn(2)-N(52) 152.5(2), P-N-P 118.5(16), N (phosphazene ring)-P-N (phosphazene ring) 117.3(25)°.

phosphazene ring plane with a separation of 6.790(2) Å. The overall coordination behaviour of L in **1** including the participation of two geminal pyrazolyl nitrogens in bonding two different metal sites is similar to that observed in $[(CuCl_2)_2\{N_3P_3O(dmpz)_5\}]^-$ (dmpz= 3,5-dimethylpyrazolyl).(6) On the other hand, in **2**, L coordinates two $ZnCl_2$ units *via* geminal pyrazolyl η^2-N_2 core and *via* an η^3-N_3 bite similar to that in **1**, giving distorted tetrahedral(Td) and trigonal bipyramidal(TBP) geometries around zinc atoms, respectively. Metric analysis indicates that the distortion in the coordination spheres of both compounds is presumably due to the steric constraints imposed by the coordination nature of L and the extent of distortion is particulary large where the η^3-N_3 chelate core is involved. Relatively invariable N(phosphazene ring)-M-N(pyrazolyl ring) angles of 78.6° (M=Cu) and 76.5° (M=Zn) for Td and TBP geometries, respectively support the foregoing characteristics of L.

Some structural features of the cyclotriphosphazene rings in **1** and **2** are worthy of noting. Ring puckering toward the TBP zinc site is evident in **2** while the P_3N_3 ring remains rather planar in **1**. The dihedral angle of 35.9° between the P2-N2-P3 plane and the remaining P1-N1-P2-P3-N3 plane in **2** reflects the degree of ring deformation. The average P-N bond distance of 1.572 Å in **1** is shorter than that in **2** by 0.012 Å and the variation of P-N distances is random in **1** ranging from 1.546 to 1.591 Å but is rather uniform in **2**. The appearance of double ν_{PN} peaks for **1** and **2**,(8) a likely consequence of the involvement of phosphazene ring nitrogen in metal coordination, can be informatively compared with the single ν_{PN} peak of L at 1226 cm^{-1} regarding the effect of metallation on the phosphazene ring structure.

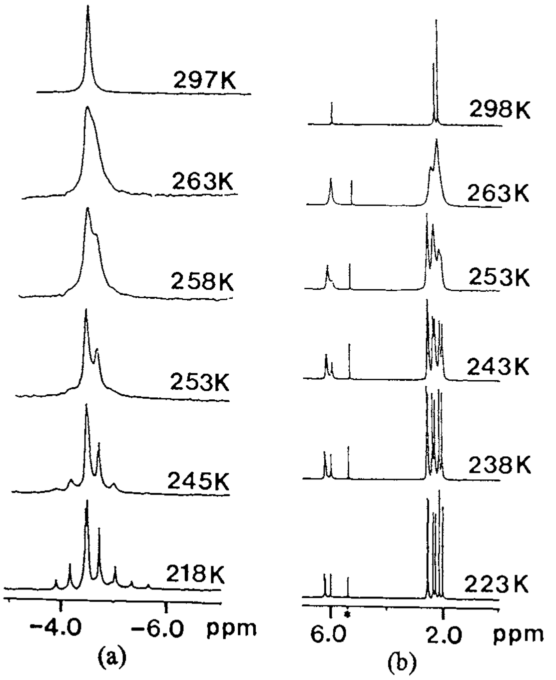

Fig. 3. Variable-temperature (a) 121.496MHz ^{31}P and (b) 300.13MHz ^{1}H FT NMR spectra of 1 in CD_2Cl_2.

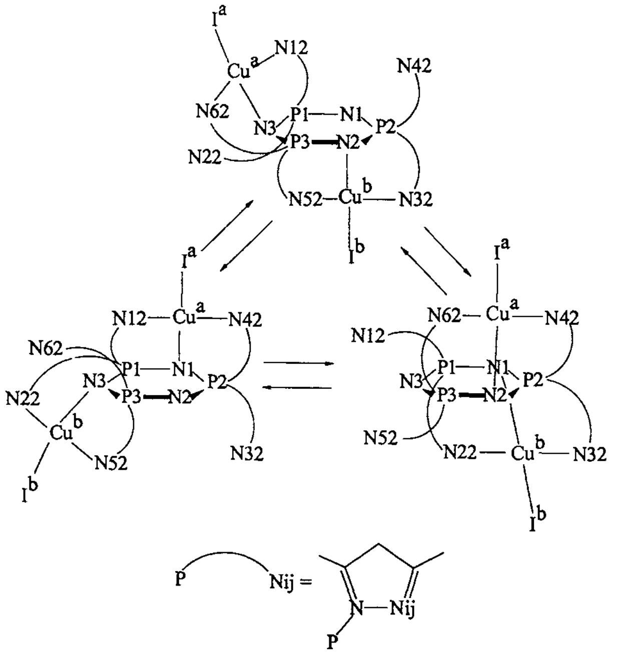

Fig. 4. Solution fluxional motion of 1 showing simultaneous merry-go-round type hopping of two copper centers.

In solution at ambient temperature, the compounds **1** and **2** lose their solid state symmetry of C_2 and C_1, respectively and undergo unique fluxional motions as observed by variable-temperature NMR spectroscopy. At low temperature limit, the solution symmetry of **1** in CD_2Cl_2 approaches to that of solid state, giving rise to A_2B phosphorus coupling pattern[10)] with δ_A, δ_B and J_{AB}(Hz) values of -4.52, -5.31 and 60.3, respectively and differenciation of three pairs of pyrazolyl rings (three 4-H and six CH_3 signals) in ^{1}H NMR spectra as shown in Fig. 3. The evidence at hand does not unequivocally reveal the nature of the fluxional motions of **1** but leads to possible dynamic processes involving a simultaneous merry-go-round type hopping of two copper centers arround a P_3N_3 phosphazene ring, as illustrated in Fig. 4, in addition to rotations of two non-geminal spectator pyrazolyl groups with respect to P-N bond.[11)] The compound **2**, on the other hand, shows unusual solvent dependency of fluxionality and in acetone, A_2B phosphorus coupling pattern is seen at 188 K while in dichloromethane at 203 K, a very complicated spectral pattern which can be explained in terms of A_2B and ABX phosphorus coupling patterns results. Efforts to establish the nature of the solution fluxionality of **2** and the reactivity of **1** and **2** toward poymerization are in progress.

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8) Satisfactory elemental analyses on C, H and N were obtained for both compounds. Data for **1**: IR(KBr) phosphazene ring ν_{PN}/cm^{-1} 1230 and 1201; ^{31}P NMR (CD_2Cl_2/CH_2Cl_2, referenced to external 85% aq H_3PO_4) δ -3.91(s); ^1H NMR (CD_2Cl_2) δ 6,08(s), 2.38(s) and 2.25(s). Data for **2**: IR(KBr) phosphazene ring ν_{PN}/cm^{-1} 1220 and 1200; ^{31}P NMR (CD_3CN) δ -0.15(s); ^1H NMR (CD_3CN) δ 6,14(s), 2.24(s) and 2.15(s).

9) *Crystallographic data* for **1**: $C_{30}H_{42}Cu_2I_2N_{15}P_3$, M= 1086.6, monoclinic, space group $P2_1/c$, a= 8.268(5), b= 22.365(6), c=23.325(17)Å, β= 93.06(3)°, V= 4307.0Å^3, Z=4, D_c= 1.675gcm^{-3}, R(Rw)= 0.079(0.093) for 5719 observed data [$F > 6\sigma(F)$], 470 refined parameters, ω/2θ scan mode with maximum 2θ value of 48°. For **2**: $C_{30}H_{42}Cl_4N_{15}P_3Zn_2$, M= 978.3, monoclinic, space group $P2_1/c$, a= 17.021(4), b= 12.161(3), c=23.608(12) Å, β= 107.72(2)°, V= 4654.8 Å^3, Z=4, D_c= 1.396gcm^{-3}, R(Rw)= 0.071(0.073) for 5718 observed data [$F > 6\sigma(F)$], 490 refined parameters, ω/2θ scan mode with maximum 2θ value of 45°. For both compounds, the diffraction data were collected at 293 K for **1** or at 296 K for **2** on an Enraf-Nonius CAD4 diffractometer. The structures were solved with use of Patterson method (SHELXS 86) and block matrix least-squares procedures (SHELX 76) on the CRAY-2S/4-128 computer.

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11) Considering the lability of copper compounds and the availability of two-coordinated copper(I) species, the observed variable temperature spectral change of **1** can be also explained by the merry-go-round type hopping of the two coordinated I-Cu-N(pz) units.

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