

METAL COMPLEXES OF A MULTIDENTATE CYCLOPHOSPHAZENE WITH IMIDAZOLE-CONTAINING SIDE CHAINS FOR HYDROLYSES OF PHOSPHOESTERS: A BIMOLECULAR DINUCLEAR PATHWAY.

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An imidazole-containing cyclophosphazene (ImCpz) multidentate ligand and its metal complexes (M_x -ImCpz; $x = 1, 2$, or 3 ; $M = Zn^{2+}$, Cu^{2+} , or Co^{2+}) have been prepared and used as artificial nuclease/phosphoesterase models. The catalytic activity of these complexes was examined toward hydrolysis of mono-, di-, and tri-phosphoester substrates (*p*-nitrophenylphosphate NPP, bis(*p*-nitrophenyl)phosphate BNPP, and tri(*p*-nitrophenyl)phosphate TNPP) in 75% DMSO buffer solution at pH = 7–11 and 37 °C under pseudo-first-order reaction conditions. All the complexes exhibit enzyme-like saturation kinetics toward the phosphoester substrates under the experimental conditions, with the copper complex exhibiting the highest catalytic proficiencies ($k_{cat} = 7.3 \times 10^{-4}$ to $3.1 \times 10^{-2} s^{-1}$ and $k_{cat}/K' = 0.0027$ to $99 s^{-1} M^{-1}$). The mechanism of the hydrolytic catalysis toward the faster substrate NPP was in further investigated at various conditions, which revealed a unique bimolecular dinuclear pathway, despite the multidentate nature of the ligand.