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Full Paper

新型大环多胺铜配合物金属胶束催化吡啶甲酸对硝基苯酚酯水解研究

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摘要 为模拟水解金属酶的疏水微环境及其催化过程中亲核剂的作用，合成了一种新的带羟乙基侧臂的大环四胺铜配合物。在Brij35胶束溶液中，详细研究了其催化2－吡啶甲酸对硝基苯酚酯（PNPP）水解的动力学和机理，并与相应的非取代大环多胺铜配合物进行了对比。结果表明，
该新型大环多胺铜配合物能有效地催化PNPP的水解；侧臂羟乙基和去质子化后的侧臂羟乙基可能作为反应过程中的催化活性物种；催化过程可能涉及由金属离子、配体及底物形成的三元复合物。

关键词 大环多胺, 铜（II）配合物, 羧酸酯, 金属胶束, 水解

分类号

Accelerated Hydrolysis of *p*-Nitrophenyl Picolinate Catalyzed by Metallomicelle Made from a Novel Macrocyclic Polyamine Copper(II) Complex

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Abstract A copper(II) complex **1** of a novel macrocyclic polyamine ligand with hydroxylethyl pendant groups, 4,11-bis(hydroxylethyl)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (**L**) has been synthesized and characterized. Rate enhancement for hydrolysis of *p*-nitrophenyl picolinate (PNPP) catalyzed by **1** was studied kinetically under Brij35 micellar condition. For comparision, the catalytic activity of corresponding copper(II) complex **2** of non-substituted macrocyclic polyamine ligand, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-cyclote- tradecane (**L'**) toward the hydrolysis of PNPP was also investigated. The results indicate that the macrocyclic polyamine copper(II) complex **1** effectively catalyzed the hydrolysis of PNPP, and the pendant ligand hydroxyl group or deprotonated pendant ligand hydroxyl group can act as catalytically active species in the reaction. A ternary complex kinetic model involving metal ion, ligand and substrate has been proposed, and the results confirmed the reasonability of such kinetic model.

Key words macrocyclic polyamine copper(II) complex carboxylic ester metallomicelle hydrolysis

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