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链酚胺型配体锌(Ⅱ)配合物模拟碳酸酐酶研究

解永树,寇福平,王平山,林瑞森,宗汉兴

浙江大学化学系.杭州(310027);中国科学技术大学化学系.合肥(230026)

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摘要 合成了酚胺型链状配体,N,N'-二(2-羟基苄基)丙二胺(H~2L)及其Zn(Ⅱ)配合物(ZnL),通过元素分析、IR和^1HNRM等手段进行了表征。采用pH电位滴定法,在25℃±0.1℃,I=0.1mol·dm^-^3(KNO~3)条件下,测定了配体的质子化常数以及配体与金属离子Zn(Ⅱ)配位反应平衡常数。讨论了配体与金属离子Zn(Ⅱ)的配位情况,得到了配位酚羟基的解离常数。运用分光光度法,在25℃±0.1℃,I=0.1mol·dm^-^3(KNO~3)条件下,在pH=5.5～9.0(50mmol·dm^-^3缓冲溶液)范围内,研究了配合物作为碳酸酐酶模拟物催化对-硝基苯酚乙酸酯(NA)水解动力学,
得到了NA酯水解的配合物催化速率常数k~N~P。实验结果表明,ZnHL^+的配位酚羟基的解离常数pK~a为6.83;催化速率常数k~N~P与pH之间不存在Sigmoidal型曲线关系,
而是在pH值中性附近有最大值,ZnHL^+对NA酯水解有很好的催化效果,并且采取双重催化机理,
是碳酸酐酶很好的模拟物。

关键词 碳酸酐酶 丙二胺P 羟基化合物 锌络合物 模拟酶 酶模拟 催化 反应动力学 平衡常数 硝基苯酚P 乙酸酯P 水解 国家教委高等学校博士学科点专项科研基金

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Research on Zn(Ⅱ) complexes with diaminodiphenol ligand as carbonic anhydrase model

Xie Yongshu,Kou Fuping,Wang Pingshan,Lin Ruisen,Zong Hanxing

Zhejiang Univ, Dept Chem.Hangzhou(310027);Univ Sci & Technol China, Dept Chem.Hefei(230026)

Abstract Chain ligand N,N'-bis(2-hydroxylbenzyl)-propylenediamine (H~2L) and its Zn(Ⅱ) complex (ZnL) were synthesized and characterized by elemental analysis, IR and ^1H NMR. By pH titration at 25℃±0.1℃ and I=0.1mol·dm^-^3(KNO~3), protonation constants of the ligand and equilibria constants of Zn(Ⅱ) complexation with the ligand have been determined. Modes of the ligand coordination to Zn(Ⅱ) were discussed, and the dissociation constant for the phenoxyl in complex ZnHL^+ was obtained. The kinetics of p-nitrophenyl acetate (NA) hydrolysis catalyzed by the complexes as carbonic anhydrase models was determined spectrophotometrically at 25℃±0.1℃ and I=0.1mol·dm^-^3 (KNO~3) in 10% (v/v) CH~3CN at pH 5.5～9.0 (50mmol·dm^-^3 buffers), and the second-rate constants for NA hydrolysis were obtained. The experimental results indicate that the dissociation constant pKa value for the phenoxyl in complex ZnHL^+ is 6.83. The pH-k~N~P profile does not exhibit a Sigmoidal curve and the k~N~P reaches a maximum point around neutral pH. The complex ZnHL^+ has very strong catalytic ability around neutral pH following the double-catalysis mechanism, and therefore is a good carbonic anhydrase model.

Key words CARBONIC ANHYDRASE PROPANEDIAMINE P HYDROXYL COMPOUNDS ZINC COMPLEX MODELS OF ENZYME ENZYME SIMULATION CATALYSIS REACTION KINETICS EQUILIBRIUM CONSTANT NITROPHENOL P ACETIC ACID ESTER P HYDROLYSIS

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