

配位化学中的直线自由能关系XXI: 铜(II)-13-取代苄基-1, 4, 8, 11-四氮杂环十四烷-12, 14-二酮配合物的生成及酸分解行为研究

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摘要 采用pH法,在25.0±0.1℃,I=0.1 mol.dm<sup>-3</sup> (KNO<sub>3</sub>)条件下,测定了13-取代苄基-1, 4, 8, 11-四氮杂环十四烷-12,14-二酮的质子化常数及其与Cu(II)配位的平衡常数。讨论了配体与金属离子的配位方式。在25.0±0.1℃,离子强度为0.1mol.dm<sup>-3</sup> (KNO<sub>3</sub>)下,采用分光光度法,研究了这些配体铜(II)配合物的酸分解动力学行为。探讨了配合物酸分解机理,得到了速控步的速率常数。发现配位反应平衡常数与配体的质子化常数及配合物酸分解反应速率常数之间存在较好的Hammett型和Bronsted型直线自由能关系。同时探讨了取代基对配合物生成及酸分解的影响情况。

关键词 [分光光度法](#) [反应机理](#) [氮杂环化合物](#) [铜络合物](#) [反应速度常数](#)

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**Linear free energy relationships in coordination chemistry XXI. Studies on the formation and acid-induced decomposition of copper (II)-13-(2'-hydroxyl)-substituted benzyl-1, 4, 8, 11-tetraazacyclotetradecane-12, 14-dione complexes**

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**Abstract** Complexation study on the Cu(II) complexes of ligands 13-(2'-hydroxyl)-substituted benzyl-1, 4, 8, 11-tetraazacyclotetradecane-12, 14-dione has been carried out by pH potentiometric titration at 25℃, I=0.10mol.cm<sup>-3</sup> (KNO<sub>3</sub>). The protonation constants of ligands and the formation constants of complexes were obtained. The coordination form of ligands with copper(II) and the stability of complexes were discussed. A kinetic study of acid-induced decomposition for these ligands' Cu(II) ocmplexes has also been investigated, in which reaction mechanism was postulated, and the rate constants were calculated. The results show there exists LFER between equilibrium constants of complexes and protonation constants of ligands. Good Bronsted-type LFER between rate constants and equilibrium constants of complexes has also been found. The effects of macrocyclic substituents on the formation and the decomposition of complexes were also discussed.

**Key words** [SPECTROPHOTOMETRY](#) [REACTION MECHANISM](#) [NITROGEN HETEROCYCLICS](#) [COPPER COMPLEX](#) [REACTION RATE CONSTANT](#)

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