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[Co(2,3-tri)(amp)Cl]^2^+几何经式异构体取代与重排规律、构效关系的研究

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摘要 对[Co(2,3-tri)(amp)Cl]^2^+四个几何经式异构体在不同条件下的取代及重排反应进行了详细的考察。因二元胺中吡啶环造成的空间拥塞，使cis异构体碱水解速度比trans异构体约快100倍，控制碱水解实验结果表明，每一异构体的水解产物均含四个经式异构体，且具有相同分布。实验过程中未观察到面式异构体。在二甲亚砜中加热的重排反应中，异构体m1表现出最高的反应性，cis异构体均首先转化为trans异构体m3，而后可观察到trans异构体m3与m4的平衡。利用时间分辨核磁共振仪测定了氘代水里各异构体中各活性氢的氘代化速度。反应活性最低的异构体m4具有氘代速度最快的活性氢，当这些活性氢完全氘代化时仍未见其水解或重排产物；而相同实验条件下异构体m1或m2中相应活性氢的氘代化速度则要缓慢得多，但同时可观察到水解和重排产物。这说明在碱催化水解过程中氘代速度快的活性氢与异构体的反应性并非正比关系，然而活性氢的氘代化是观察到异构体水解重排的必要条件。利用量子化学从头计算法在赝势基组RHF/LANL2DZ的水平上对该体系各异构体进行了结构优化计算，与对应异构体的晶体结构参数比较，一般相对误差不超过3%，从能量角度来看，cis异构体比trans异构体高出约4kJ/mol，而面式异构体则至少比经式异构体高约17kJ/mol;考虑溶剂化影响，一般约低5kJ/mol。考察结构参数结果显示，结构变形性参数能较好地解释异构体反应活性。

关键词 钴络合物 异构体 重排反应 取代反应 氘代化 从头计算法 吡啶 P 构效关系

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Study on the structure and reactivity of the geometric isomers of [Co(2, 3-tri)(amp)Cl]^2^+

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Abstract Kinetics of basic hydrolysis shows that the cis(N^*) mer-isomers (m1 or m2) are about 100-fold more reactive than the trans(N^*) forms (m3 or m4) due to steric strain caused by the pyridyl residue in the amp. No facial isomers have been found in the experiments. Detailed stereochemical studies using progressive NMR spectroscopy reveal that all mer reactants give a common product distribution in the basic hydrolysis reaction. Four substituted mer-isomers have been observed. Rearrangements of the isomers in DMSO at 100℃ show that the m1-Cl complex is the most reactive one, the cis(N^*) isomers (m1 and m2) yield m3-Cl complex first. A subsequent equilibrium between chloro species of m3 and m4 then takes place. Experiments of deuteration of the active protons in each isomer indicate that reactivity of an isomer is not proportional to the H-D exchange ratio which is observed before hydrolysis and rearrangement of the isomer. Ab initio computational results (RHF/LANL2DZ optimised structure) are well consistent with the crystal structural parameters of four geometric mer-isomers of [Co(2, 3-tri)(amp)Cl]ZnCl~4 with an maximum error of ±3%. The cis-mer isomers (m1 and m2) are calculated to be about 4 kJ/mol less stable than the trans-mer isomers (m3 and m4). However, the facial isomers are calculated to be at least 17 kJ/mol less stable than the mer isomers. Each isomer are calculated to be at least 5 kJ/mol more stable when the effect of solvent (water) is included using the Onsager model within the solvent continuum reaction field method. The distortions for the different isomers from the idealised octahedron are correlated with reactivity. The more severely distorted species is predicted to be more reactive.

Key words COBALT COMPLEX ISOMER REARRANGEMENT REACTION SUBSTITUTION REACTION AB INITIO CALCULATION P STRUCTURE ACTIVITY RELATIONSHIP

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