Studies on d¹⁰ Metal Complexes ofExpanded Hexamine Cage Ligands

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Background

We are investigating the solution and solid state structures of transition metal complexes of the expanded hexamine cage ligand Me₄tricosane. Of particular interest are complexes of Zn²⁺, Cd²⁺ and Hg²⁺. Their d⁰ configurations yields no net crystal field stabilization energy, allowing for the adoption of metal complexes with different geometries.

Further evidence for two interconverting forms of [Zn(Me₄tricosane)]²⁺ in solution was obtained by recording H and C NMR spectra at high and low temperatures.

The solid state structure of [Zn(Me₄tricosane)]²⁺ shows that the Zn²⁺ ion has a distorted octahedral coordination geometry, with the nitrogen atoms in either the S₆ or R₆ configuration.

However, the room temperature H and C NMR spectra of [Zn(Me₄tricosane)]²⁺ provide evidence for the existence of more than one conformation in solution. The H spectrum below shows sharp, high-intensity resonances from a C₄ symmetric form S, and broad low-intensity resonances for an asymmetric form A.

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The solid state structure of [Cd(Me₄tricosane)]²⁺ shows the Cd²⁺ adopts the rare trigonal prismatic geometry, with nitrogens in the configuration R₃S₃. Despite this high degree of symmetry the room temperature H and C NMR spectra show resonances consistent with the presence of two or more conformations, at least one of which is asymmetric. At high temperatures these resonances converge and simplify to give the spectrum expected for a complex with D₃ symmetry. The same behaviour (solid state and solution) is also observed for [Hg(Me₄tricosane)]²⁺.

Comparison of stereoisomers by DFT

Computational methods allow us to compare the conformations observed in crystal structures to those with a combination of R and S configurations for the nitrogens which result in an overall lower symmetry.