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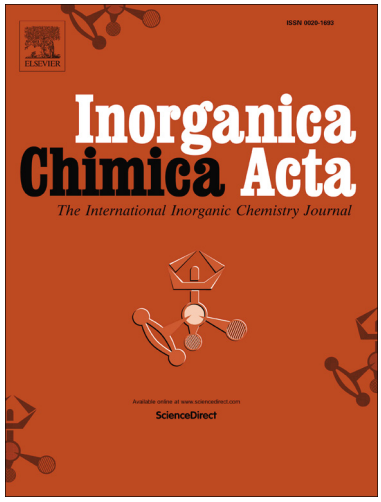

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Migration of 1,3-diazacyclohexane sub-rings in macrocyclic zinc(II) and cadmium(II) complexes

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Abstract

New Zn(II) complexes with 20-membered ring-contracted macrocyclic ligands ([Zn$\mathbf{L}^{\mathbf{trans}}$]$(ClO_4)_2$ (**1**) and [Zn$\mathbf{L}^{\mathbf{cis}}$]$(ClO_4)_2$ (**3**)) were synthesized and isolated, as well as a precursor Zn(II) complex ([Zn$\mathbf{L}^{\mathbf{prop}}$]$(ClO_4)_2 \cdot CH_3CN$ (**2**)) and a macrocyclic Cd(II) complex ([Cd$\mathbf{L}^{\mathbf{cis}}$]$(PF_6)_2$ (**5**)). X-ray structural analysis revealed that the coordinated macrocyclic ligand of **1** adopted a ring-contracted *trans*-form with two 1,3-diazacyclohexane sub-rings positioned in a *trans*-configuration with respect to the macrocyclic ring center, while in **3** and **5** the ligand adopted a ring-contracted *cis*-form. ^{1}H NMR and X-ray structural analysis revealed that the *trans*-form changed to the more stable *cis*-form in solution. This suggests that the 1,3-diazacyclohexane sub-ring is capable of migration in ring-contracted macrocyclic Zn(II) and Cd(II) complexes.

Key words: synthesis, zinc(II) complexes, cadmium(II) complexes, ring-contracted macrocycle, X-ray structure, ^{1}H NMR, 1,3-diazacyclohexane

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