Synthesis and Characterization of a Novel C₃-symmetric Ligand and its First Coordination Compound

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Introduction

C₃-symmetric triaminoguanidinium based ligands are able to coordinate soft metal ions like Zn(II)[1], Cd(II)[2] or Eu(III)[3] as well as hard metal ions like Ti(IV) or Zr(IV) in their tridentate chelating binding pockets. As the combination of ligands and metal ions provides flexible coordination environments, a variety of different discrete supramolecular coordination cages, such as tetrahedra[4], octahedra[4] and trigonal bipyramids[5], are accessible.

Background and Idea

This work is focused on the synthesis and characterization of positively charged coordination compounds and cages. This is achieved by the establishment of a new ligand type. The 2-pyridylene-N-oxide based ligand is able to chelate metal ions like the already literature known benzylidine-type ligands.[6] Additionally, three positive charges are introduced to the ligand which allow the coordination complex to achieve an overall positive charge.

Ligand Synthesis and Analysis

Simple five step synthetic routine: Z is produced by a standard routine with good yield (87%). The oxidation of Z is performed from the crude reaction product quantitatively. The 1,3-dioxolane (acetal) in 132.4(2) Å provides 2. The oxidation of 2 is performed by a standard routine with good yield (87%). The oxidation of 2 is split by acidic aqueous conditions. The triple Schiff-base reaction between 5 and various triaminoguanidinium salts (6) is carried out in aqueous ethanolic solutions and gives yields of 80-95 %. The anions of 6 can be exchanged by reaction with silver salts.

First Coordination Compound with Cadmium: Double-Decker

The reaction progress is easily monitored by 1H-NMR where a significant shifting of H4 is observed in every reaction step. The crystal structure of 4 is not described in literature yet.

Conclusion

A new C₃-symmetric ligand was prepared using standard procedures. The reaction sequence can be monitored by ¹H-NMR and ESI-MS easily.

The steric properties of the ligand could be changed easily, as the reaction between the pyridine based aldehyde and triaminoguanidinium salts are simple Schiff-base type reactions with nearly quantitative yields.

The coexistence of different coordination geometries of cadmium in one complex means a low energy barrier for the coordination transition.

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References


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