

Polycondensation versus metal template condensation of 2,2'-ethylenedithiodianiline with glyoxal

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SUMMARY:

A polymer with azomethine linkages is formed upon reaction of 2,2'-ethylenedithiodianiline (1) with glyoxal. The same reaction in the presence of Ni(II) and Cu(II) ions yields the corresponding metal complexes of the macrocyclic ligand. The driving force for the selectivity of this reaction may be attributed to the template effect of the metal ions. In the case of Co(II) ions, the polymer is formed as a by-product, together with the macrocyclic complex.

Introduction

Metal-oriented or so-called "metal template" condensations are of great importance because of their role in the preparation of macrocyclic ligands in high yields. There have been numerous examples¹⁾ of transition metal catalyzed macrocyclization involving 1,3-dienes or acetylenes alone or with appropriate olefins. In these cases macrocyclization occurs between metal π -complexed olefins. On the other hand, there are few reports on the macrocyclization arising from the reaction the coordinated ligands with another reagent. Perhaps the most significant efforts on the subject can be attributed to Bush²⁾, Curtis³⁾ and Tasker et al.⁴⁾. Certainly, the stereochemical relationship of the ligand to metal ion contributes to the stability and yield of the resulting macrocyclic complexes. We have previously observed⁵⁾ that in the reaction of acenaphthoquinone with two moles of *o*-aminophenol only one of the two carbonyl groups is converted to the azomethine group. Similar reaction in the presence of Co(II), Ni(II) and Cu(II) ions, which are capable of forming square-planar coordination complexes, produced the corresponding metal complexes of the compound possessing bisazomethine groups.

Metal template reactions are also widely used for the synthesis of crown ethers⁶⁾ and cyclams⁷⁾, which can selectively bind alkali and transition metal ions, respectively. On the other hand, macrocyclic ligating molecules receive attention not only for their metal binding capability but also for the stabilization of metal ions in unusual oxidation states⁸⁾ such as Cu(III).

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