Synthesis, Characterisation and Kinetic Studies of Acid-promoted Dissociation Reactions of the Nickel(II) Complex of a [Me_4(14)-tetraene-N_4] Macrocyclic Ligand

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The kinetics of acid-promoted dissociation reactions of Ni^{II} complex cations of an Me_4-tetraene macrocyclic ligand follow good first-order reactions with acids in various solvents with the rate of reaction proceeding faster in media of higher dielectric constant.

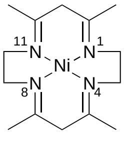
The chemistry of metal complexes of tetraaza macrocyclic ligands is of general interest because such compounds have been used as dyes and pigments[1] as well as having been advanced as models for more complex biological systems.[2] Much work has been carried out on 14-membered tetraaza macrocycles of transition metals (Ni, Cu, Cd)[3–5] but not many detailed kinetic studies on acid-promoted dissociations of these complexes have been reported.[6] A common feature of template reactions is the isolation of the macrocyclic ligand as a complex of the metal template ion, and such reactions are frequently the synthetic method of choice for the preparation of macrocyclic complexes. Here we report the synthesis, characterisation and acid-promoted dissociation of the Ni^{II} complex of a tetradentate tetraaza cyclotetradecane macrocyclic ligand.

Ethylenediamine and acetylacetone react in the presence of divalent nickel to form a 14-membered N_4-tetradentate macrocyclic complex. This complex, synthesised *via* a metal template method, is of the type [M[Me_4(14)-tetraene-N_4]] where the coordination takes place through the imine nitrogen atoms which are bridged by acetylacetone moieties. The complex was characterised by UV–VIS, IR, NMR and CHN analysis. The kinetics of acid-promoted dissociation reactions of complex cations of Ni^{II} were studied spectrophotometrically in HCl, HNO_3 and H_3PO_4 at 25.0 ± 0.1 °C in various organic solvents such as methanol, *N*,*N*-dimethylformamide, acetonitrile and 1,4-dioxane under pseudo-first-order conditions. Good first-order kinetics were observed in all cases. The rate-constant values show that the reaction proceeds faster in media of higher dielectric constant. The rate of reaction decreases with a decrease in the acid strength ($H_3PO_4 < HNO_3 < HCl$). The general mechanism proposed for the acid-promoted dissociation of polyamine complexes[6] may be adopted for this complex, as shown below:

$$[M(L)]^{2+} \longrightarrow [M(L)^*]^{2+}$$

$$[M(L)^*]^{2+} + H^+ \longrightarrow \text{products}$$

As shown above, a mechanism with the acid-dependent reaction of the 'activated' species $[M(L)^*]^{2+}$ has been proposed. Product analysis, done on the basis of a comparison of physical data such as boiling points, R_f values and spectral characteristics with those of the ligand, demonstrated that the product is the protonated ligand.



Techniques used: UV–VIS, IR, ^{1}H NMR, CHN analysis, TLC

References: 14

Figs. 1–3: First-order rate coefficients for acid-promoted dissociation reactions of [Me_4(14)-tetraene]Ni with HNO_3, HCl and H_3PO_4 at 25 °C in various solvents

Fig. 4: Arrhenius plots for the reactions of [Me_4(14)-tetraene]Ni complex with HNO_3 in 1,4-dioxane and DMF

Figs. 5 and 6: Proposed stepwise mechanisms for the acid-promoted dissociations of [Me_4(14)-tetraene]Ni with H_3PO_4, HCl and HNO_3

Fig. 7: UV–VIS scan of the complex, ligand and product

Tables 1–3: First- and second-order rate coefficients for acid-promoted dissociation reactions of [Me_4(14)-tetraene]Ni with HNO_3, HCl and H_3PO_4 at 25 °C in various solvents

Table 4: Solvent parameter values for the solvents employed

Table 5: Activation parameters for the reactions of [Me_4(14)-tetraene]Ni with HNO_3 in 1,4-dioxane and DMF

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