

Synthesis of Macrocyclic Complexes of Nickel(II)

An example of a metal ion templated cyclization reaction

Objectives: Synthesis of coordination complexes

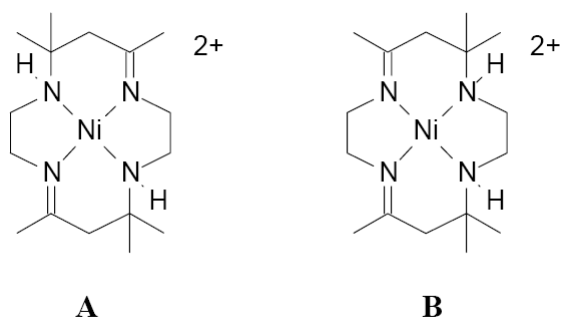
Use of metal ion as a template for a cyclization reaction

Use ^1H NMR, UV-visible and infrared spectra to characterize structural changes

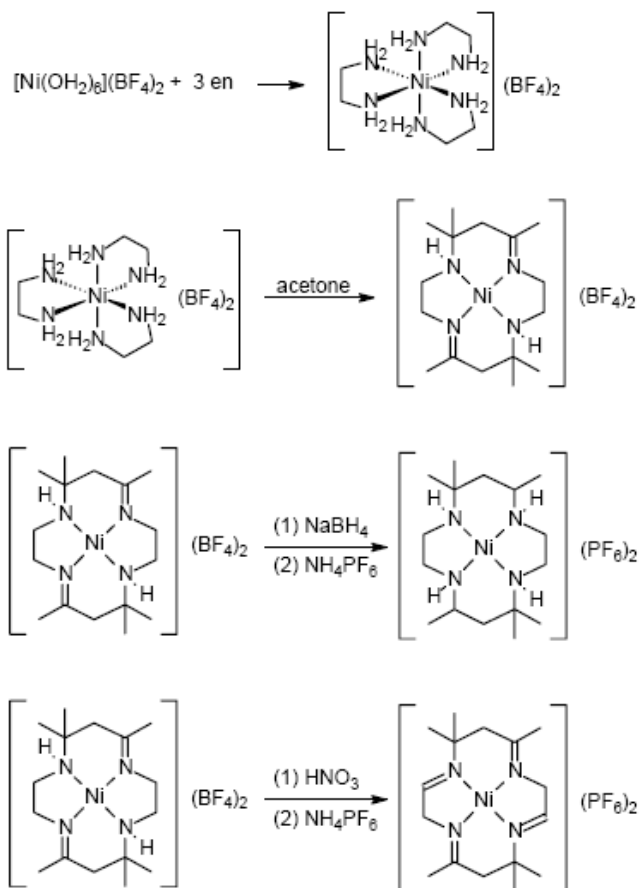
Determination of magnetic susceptibility

Introduction

A major portion of inorganic chemistry may be called coordination chemistry, that is the investigation of the properties, structure, and reactions of complexes formed by ligands coordinated to a transition metal center. Complexes with chelating ligands generally have increased stability relative to those of monodentate ligands, and even greater stability when the donor atoms are incorporated into a cyclic ligand that surrounds the metal ion, commonly referred to as a macrocyclic ligand. The fact that some macrocyclic ligands can be made only in poor yields, or not at all, in the absence of metal ions has led to the concept of the "template effect", i.e., that the metal coordinates and properly arranges the ligand precursor fragments in its coordination sphere, thereby assisting the linking process that produces the macrocyclic ligand. One of the earliest examples of a templated reaction involves the reaction of ethylenediamine (en), $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, with acetone in the presence of nickel(II) ion.¹ The products of this reaction **A** and **B** are remarkable in their stability under conditions that would destroy many other nickel(II) compounds, i.e., strongly acidic, oxidizing and reducing conditions.



In this sequence of experiments you will prepare $[\text{Ni}(\text{en})_3](\text{BF}_4)_2$ and complex **A**² by allowing a solution of the complex in acetone to stand from one lab period to the next. The very high kinetic stability of this complex will be illustrated by the oxidation and reduction of **A** without dissociation of the ligand (decomposition) from the metal. The sequence of reactions to be completed is:



In an six-coordinate environment a d^8 ion such as nickel(II) should have a $t_{2g}^6 e_g^2$ configuration and according to Hund's rule, two unpaired electrons. The usual way of determining the number of unpaired electrons is by the magnetic susceptibility and corresponding magnetic moment of a given compound.

Procedure

Synthesis of $[\text{Ni}(\text{en})_3](\text{BF}_4)_2$. Dissolve a 30 mmol portion of $[\text{Ni}(\text{OH}_2)_6](\text{BF}_4)_2$ in 40 mL of water and, with efficient stirring, add 100 mmol of ethylenediamine. After addition is complete, stir the solution for a few minutes and then gravity filter to remove any solid. Evaporate the solution until crystallization begins, then cool the solution in an ice-bath for 15 min to complete the crystallization. Separate the violet product by suction filtration, wash with 10 mL of ice-cold ethanol, then with 10 mL of ether and allow the material to air dry. Determine the quantity of dry product and obtain infrared (KBr pellet) and electronic (aqueous solution) spectra. Add ca. 0.2 g of the violet complex to 1-2 mL of conc. HNO_3 . Record your observation. Dissolve ca. 0.2 g of the violet complex in 1-2 mL of water and add 50 mg of

NaBH₄ and briefly heat the solution. Record your observation. Obtain the UV-vis (acetone) spectrum and determine the number of unpaired electrons via magnetic susceptibility.

Synthesis of Complex A. Dissolve [Ni(en)₃](BF₄)₂ in acetone (1 g complex per 2.5 mL acetone; use all but 1-2 g of your ethylenediamine complex) in an appropriate sized Erlenmeyer flask. Stopper the flask tightly with a rubber stopper and allow the solution to stand in the dark until the following week. To the dark orange solution that results, slowly add anhydrous ethanol while stirring the solution until a slight cloudiness persists (this will take ca. 10 mL per gram of complex). At this point scratch the bottom/wall of the flask with a glass stirring rod until crystallization begins. Slowly add another 5-10 mL of ethanol per gram of complex and then place the flask in an ice-bath for 30 min to complete crystallization.

Collect the yellow crystals by suction filtration and wash the product on the funnel with 5 mL portions of absolute ethanol until they are colorless. Then wash the product with 10 mL of ether and allow it to air dry. Determine the quantity of dry product and obtain infrared (KBr pellet), ¹H NMR (d₆-acetone) and UV-vis (acetone) spectra. Also determine the number of unpaired electrons via magnetic susceptibility.

Oxidation of complex A to complex C. Place approximately 200 mg (accurately weighed) of **A** contained in a large test tube, add 1 mL of concentrated HNO₃. Bring the mixture to a boil by carefully heating the tube in the flame of a Bunsen burner. Observe the evolution of NO, fumes and the formation of a dark orange solution. Cool the tube briefly, then add a solution of about 200 mg of NH₄PF₆ in 1 mL of water. Swirl to mix and cool the tube in an ice bath for 15 min. Collect the light yellow crystals by suction filtration and wash them with 5 mL portions of ice-water, ice-cold ethanol and ether. Allow the product to air dry. Determine the quantity of dry product and obtain infrared (KBr pellet), ¹H NMR (d₆-acetone) and UV-vis (acetone) spectra.

Reduction of complex A to complex D. Suspend about 200 mg (accurately weighed) of **A** in 5 mL of water in a small beaker and heat the mixture to about 80 °C. Add about 100 mg of NaBH₄ in small portions (keep the borohydride salt in a closed container except when transferring portions) over a period of 15-20 min with frequent stirring. After all of the reducing agent has been added, continue to heat the reaction mixture for 20-30 min until gas evolution has ceased and the solution has clarified. Filter off any insoluble material by suction filtration and adjust the pH of the solution to 2-3 with dilute HCl. Add a solution of about 200 mg of NH₄PF₆ in 1 mL of water to the filtrate (still contained in the suction flask) and mix well. Reduce the volume of the solution by about 1/3 by pulling air over it with the aspirator (through the fritted funnel). Cool the flask in an ice bath for 10-15 min, then suction filter the orange product and wash with a small amount of cold ethanol followed by a few

milliliters of ether. Allow the product to air dry. Determine the quantity of dry product and obtain infrared (KBr pellet), ^1H NMR (d_6 -acetone) and UV-vis (acetone) spectra.

UV-Visible Spectra

Transition metal complexes usually show three types of electronic bands: d-d (crystal-field) transitions (300 - 1,500 nm) with $10^{-2} < \epsilon < 10^3 \text{ M}^{-1} \text{ cm}^{-1}$; charge-transfer transitions (200 - 500 nm) with $10^3 < \epsilon < 10^5$ and transitions localized on the ligands. The last are $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$, with $10^3 < \epsilon < 10^5$ and usually occur in the ultraviolet region (unless the ligand itself is colored, of course). These are affected by coordination, the usual consequence being that the wavelengths shift slightly and the ϵ 's are altered somewhat.

As ever, the initial goal is to obtain absorption bands which are within a sensibly readable range on the spectrophotometer (say $0.3 < A < 2.0$). This suggests that for solutions in a 1.0 cm cell, the concentration should be of the order of 10^{-2} M for testing suitability in the d-d band region, and about 10^{-4} M for the CT/ $\pi \rightarrow \pi^*$ region. Submit the absorption spectra, together with the associated values of λ and ϵ .

To be included in the report:

- Yields of all complexes
- Magnetic data, including the number of unpaired electrons for $[\text{Ni}(\text{en})_3](\text{BF}_4)_2$ and complex **A**.
- Analysis of ^1H NMR and FT-IR for each complex. Include comparisons of the similarities and differences between complexes.
- Compare the similarities and differences in the UV-visible spectra for each complex. Be sure the spectra include molar absorptivities.

References

¹The early history of this and related chemistry is recorded in Curtis, N. F. *Coord. Chem. Rev.* **1968**,3, 3.

²Actually both **A** and **B** are formed; however, the amount of **B** is small and its greater solubility allows for the isolation of pure **A**.