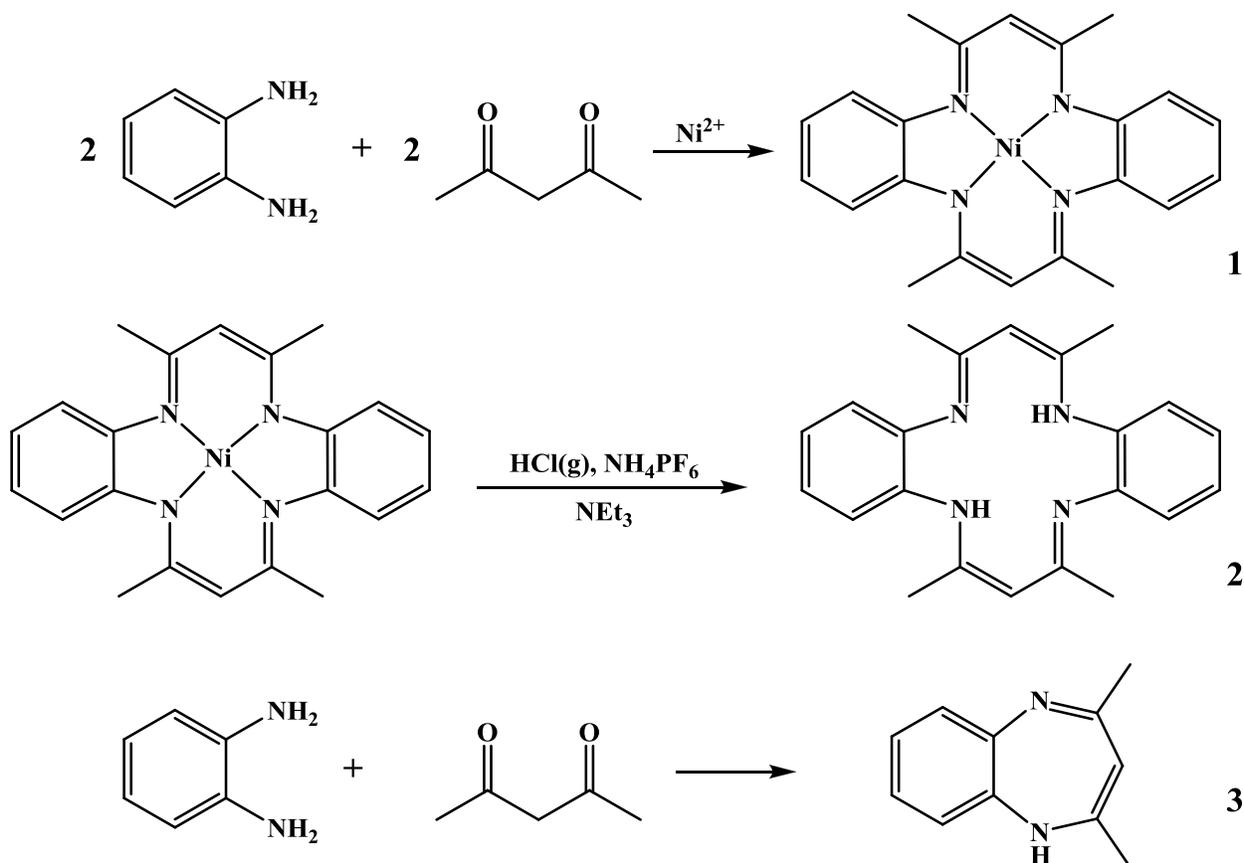


Preparation of Macrocyclic Complexes

The ability of certain transition metals, especially nickel, to act as a template in intermolecular Schiff-base reactions into macrocycle formation is well known^{3,4}. Of the many “macrocyclic template” reactions, the preparation of Geodken’s macrocycle **2** is particularly attractive⁶ for the good solubility/crystallinity of most of its complexes.



The original *Inorganic Synthesis* preparation⁶ calls for a 48-hour reflux in methanol for the nickel-templating reaction. However, changing the solvent to *n*-butanol reduces the reaction time to only three hours. Even shorter reaction times are possible, but they give somewhat lower yields of an inferior-quality product. Use of *n*-butanol reduces reaction time because its higher boiling point of (118 °C) compared to methanol (65 °C) causes both a faster rate and a shift of the equilibrium through evaporation of water from the reaction. The reaction can be followed visually because the mixture undergoes a number of color changes - the initial pale green color of the [Ni(*o*-(H₂N)C₆H₄)₃]²⁺ complex, the formation of the purple-colored organic **3** (also formed in the absence of a metal ion), and the final dark green macrocyclic complex **1** are readily seen. The nickel ion is readily removed after the macrocyclic complex is formed. Addition of HCl gas results in turquoise [H₄Mac][NiCl₄]. The nickelate anion can be replaced by PF₆⁻.³ The presence of a base yields the yellow free macrocycle [H₂Mac] **2**.

Preparation of the Nickel(II) Macrocyclic Complex

Place 2.00 g $\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$ (nickel(II) acetate tetrahydrate) (8.03 mmole), 1.73 g 1,2-phenylenediamine (1.60 mmole), 30 mL dry (molecular sieves) *n*-butanol, 1.7 mL (by syringe) 2,4-pentanedione (1.66 mmole), and a stir bar in a 100-mL round-bottom flask. Place a reflux condenser on the flask and set in an aluminum heating block on a hot plate/stirrer. Bring the mixture to a brisk reflux and stir for 2 hours, noting any color changes.

Remove the flask from the heat source and allow to cool until just warm to the touch. Add 30 mL methanol and cool the mixture in an ice-salt bath for at least 15 min to precipitate the purple, microcrystalline product. Vacuum filter and wash with methanol (about 2 x 10 mL; the washings should be colorless to pale green). A yield of 1.2-1.3 g (37-40%) is typical. Retain a small sample of product for IR analysis. Convert the rest of the product to free macrocycle as outlined below.

Preparation of $[\text{H}_4(\text{Macrocycle})][\text{NiCl}_4]$

Suspend 1.0 g of the nickel complex in 30 mL absolute ethanol in a 100-mL round-bottom flask. Bubble a moderate stream of HCl gas through the suspension, swirling occasionally. An apparatus to bubble HCl consists of a Pasteur pipette connected to a side arm test tube with a piece of rubber tubing. Place 1 mL of concentrated HCl in the test tube and secure it with a clamp. Insert the Pasteur pipette in the flask containing the macrocycle suspension. Using a second Pasteur pipet inserted into a one-hole stopper that fits the side arm test tube, carefully add drops of H_2SO_4 to the HCl solution with the stopper in the test tube. **Use caution as the mixture gets quite warm.** Once a large quantity of turquoise precipitate forms, filter and wash with ethanol and ether giving ~95% product.

Isolation of the Free Macrocyclic

Dissolve the turquoise $[\text{H}_4(\text{Mac})][\text{NiCl}_4]$ salt in 10 mL water. Occasionally white, water insoluble, impurities are present at this stage and can be removed by filtration. Add 1.0 g solid NH_4PF_6 to the filtrate and swirl until a large amount of white precipitate forms. Filter the $[\text{H}_4(\text{Mac})][\text{PF}_6]_2$ and wash with plenty of water until the product is pale green. (In this step the $(\text{NH}_4)_2\text{NiCl}_4$ by-product needs to be washed away to prevent nickel from re-inserting into the macrocycle upon basification; use of too much water results in product loss). Transfer the sticky product to a 25-mL Erlenmeyer flask, rinsing with methanol to maximize the mass of $[\text{H}_4(\text{Mac})][\text{PF}_6]_2$ transferred. Enough methanol should be present in the flask to cover the salt. Add triethylamine dropwise to the suspension and swirl. Filter the free yellow macrocycle, wash with methanol, and air dry. Yield ~59%. Record the IR spectrum.

Preparation of the Copper(II) Macrocyclic Complex

In a 10-mL round-bottom flask, add 0.1 g of $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ (copper(II) acetate monohydrate) (0.60 mmole), a stir bar, and 4 mL of acetonitrile. Attach a condenser and reflux until all of the copper(II) acetate dissolves. Add a suspension of 0.1 g of the macrocycle (0.56 mmole) in 1 mL of acetonitrile containing 0.20 mL of triethylamine down the reflux condenser and rinse residual

macrocycle into the reaction flask with an extra 1 mL of acetonitrile. Reflux the resulting dark-green solution for about 10 min, cool to room temperature, then in ice for 20 min. Filter the dark green microcrystalline product and wash with a small amount of acetonitrile and ether. Yield ~35%. Record the IR spectrum and compare with that of the nickel(II) macrocycle.

References

1. Ghadiri, M. R.; Soares, C.; Choi, C. *J. Am. Chem. Soc.* **1992**, 114, 825-831.
2. Marks, T. J. *Angew. Chem., Int. Ed. Engl.* **1990**, 29, 857-879.
3. Lindoy, L. F. *The Chemistry of Macrocyclic Ligand Complexes*; Cambridge University Press: Cambridge, 1989.
4. Sacconi, L.; Mani, F.; Bencini, A. In *Comprehensive Coordination Chemistry*; Wilkinson, G.; Gillard, R. D.; McCleverty, J. A., Eds.; Pergamon Press: Oxford, 1987; Vol. 5, Chapter 5, Sect. 50.5.9.
5. Merrell, P. H.; Urbach, F. L.; Arnold, M. *J. Chem. Educ.* **1977**, 54, 580-582.
6. Goedken, V. L.; Weiss, M. C.; Place, D.; Dabrowiak J. *Inorg. Synth.* **1980**, 20, 115-119.
7. Tait, A. M.; Busch, D. H.; Curtis, N. F. *Inorg. Synth.* **1978**, 18, 2-9.
8. Woodruff, W. H.; Pastor, R. W.; Dabrowiak, J. C. *J. Am. Chem. Soc.* **1976**, 98, 7999-8006.