# Novel Preparation of a Tetraaza Macrocycle

## An Advanced Inorganic Chemistry Laboratory

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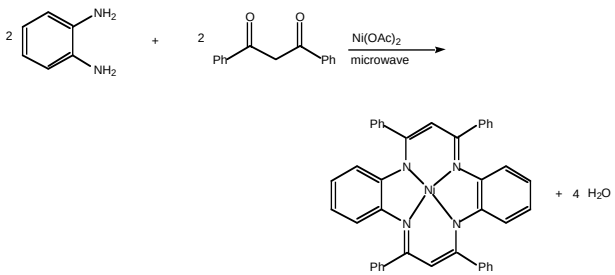
The synthesis and characterization of macrocyclic ligands and their transition metal complexes continues to be an active research area. These ligands are attractive as mimics of biological systems because they can incorporate a number of transition metal ions in a variety of oxidation states and some complexes have been shown to bind small molecules (e.g., $O_2$ or CO) (*1*). Recent investigations of these systems have also included catalysis, electropolymerization, and conductive materials studies (*2–4*).

A few undergraduate experiments described in the literature deal with this important class of compounds (*5, 6*). To augment these, we have developed a procedure for preparing a sterically crowded macrocycle that incorporates microwave heating.

### Results and Discussion

In the last few years, there has been a growing interest in the use of microwave heating in chemical synthesis (*7, 8*). The advantages of this heating method are an increase in reaction rates and the ability to facilitate some reactions that do not occur using more conventional energy sources. Our interest in synthesis via microwave heating developed because of difficulties encountered in attempts to prepare some dibenzotetraaza[14]annulene macrocycles.

The sterically congested macrocycle 6,8,15,17-tetraphenyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato nickel(II), abbreviated [Ni($Ph_4Bzo_2$[14]tetraene$N_4$)], had been an elusive molecule because of crowding in the proposed template intermediate. It is an attractive macrocycle for study because of its stability and solubility in organic solvents. Although the starting materials are commercially available, the published synthesis requires the reactants to be heated as a neat mixture under a constant flow of argon at high temperature (250–260 °C) for 90–120 minutes (*9*). These reaction conditions made [Ni($Ph_4Bzo_2$[14]tetraene$N_4$)] an ideal candidate for synthesis via microwave heating, and the resulting synthetic method is suitable for use in an undergraduate laboratory class. Although the yield is very low (0.7–1.5%), a typical experiment will produce 50–100 mg of macrocycle within the time-span of most laboratory classes—a sufficient amount for IR, NMR, UV-vis, or electrochemical studies. The reaction mixture is a complex collection of materials. Among the products identified by IR and $^1$H NMR were 2,4-diphenyl-3H-1,5-benzodiazepine, 2-phenyl-benzimidazole, nickel β-diketonate complexes (dihydrate and diamine adduct), and a significant amount of the template intermediate (*9*). The yield from the microwave synthesis is comparable to that from the published method, but the reaction is completed in about 20 minutes under less extreme conditions. Attempts to improve the yield by increasing reaction time resulted in the charring of all reaction materials and loss of the macrocyclic product.




[Ni($Ph_4Bzo_2$[14]tetraene$N_4$)]

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To absorb microwave energy, the reaction mixture must be in the liquid state. Thus it was found that the reaction materials liquefied faster when the lower-melting mixture of diamine and diketone was heated first. The size of the beaker is also an important factor. In larger beakers (250 and 400 mL), the reactants can spread over a greater surface area. Once the macrocyclic intermediate is produced, a glassy solid forms and the reaction stops. The beaker must be left open in order for all water vapor to escape, since the presence of *any* solvent (aqueous or nonaqueous) will preclude macrocycle formation. Since commercial microwave ovens cycle (i.e., turn off the microwave irradiation when the internal temperature reaches a certain level), it is recommended that the oven door be left open and the interior be allowed to cool after each macrocycle preparation.

In [Ni($Ph_4Bzo_2$[14]tetraene$N_4$)], the Ni(II) ion is in a square-planar environment, thus allowing for the use of NMR spectroscopy as a diagnostic tool. The $^1H$ and $^{13}C$ NMR spectra ($CDCl_3$) illustrate the high symmetry of this compound and the signals are easily assigned by students. Unfortunately, the presence of paramagnetic by-products in the crude reaction mixture prevents NMR analysis prior to chromatography. The electronic spectrum ($CH_2Cl_2$) shows five major absorptions: three ligand-to-ligand and two ligand-to-metal charge transfer bands (*10*).[1] This complex is an excellent substrate for electrochemical analysis because, unlike the tetramethyl analog, it does not electropolymerize on the electrode surface (*10*).[2]

## Experimental Procedure

1,2-Diaminobenzene, dibenzoylmethane, and alumina (activated, neutral, Brockmann I) were obtained from Aldrich and nickel acetate was purchased from Fisher Scientific. All reagents were used as received. A 900-W Sharp microwave oven with rotating carousel (Model R-5A84) was used. Reaction times may vary depending on the wattage of the microwave oven.

### *Preparation of [Ni($Ph_4Bzo_2$[14]tetraene$N_4$)]*

A 100-mL Pyrex beaker was charged with 1,2-diaminobenzene (2.16 g, 20.0 mmol), 1,3-diphenyl-1,3-propanedione (dibenzoylmethane) (4.49 g, 20.0 mmol), and several porcelain boiling chips (or glass beads). Before microwaving, the beaker with the reactants was placed in a 150 × 75 mm Pyrex dish containing 300–350 g of alumina and the entire assembly was put in the oven. The beaker was then heated at 100% power in the microwave oven *in a fume hood* until both the diamine and the diketone were completely melted (5–6 min). Nickel acetate (2.48 g, 10.0 mmol) was then immediately stirred into the melt and the flask was heated at 100% power for an additional 12–15 minutes.

**Note: Thick nonmelting gloves were used to avoid burns.**

After cooling, the mixture was dissolved in $CHCl_3$, filtered to remove undissolved solids, and then purified via column chromatography (325 × 41 mm, alumina, $CHCl_3$). The dark green band eluting first was collected, the solvent removed, and the residual oily material recrystallized from acetone/water to afford 50–100 mg (0.7–1.5%) dark green product.

$^1H$ NMR (250 MHz, $CDCl_3$, ppm): 5.18 (2H,s); 5.7, 5.9 (8H, d of q); 7.3, 7.4 (20H, m)

$^{13}C$ NMR (ppm): 113.83, 121.02, 122.04, 128.36, 138.98, 147.08, 157.19

## Acknowledgment

This work was supported by a Faculty Development grant from the College of Mount St. Joseph.

## Notes

1. Hochgesang and Bereman (ref *10*) report electronic absorption bands at the following wavelengths (log ε): 622 nm (3.04), 462 nm (4.11), 406 nm (4.30), 356 nm (3.88), and 266 nm (4.52). The bands at 622 and 462 nm were assigned as ligand-to-metal charge transfer and the other three bands as ligand-to-ligand charge transfer.

2. This compound is reported to have oxidation waves at 0.76 and 1.26 V and reduction peaks at −1.28 and −1.73 V (versus SCE, ±0.01 V) (ref *10*). The electrochemical measurement was done in 0.1 M tetraethylammonium perchlorate–dichloromethane solutions at 22 ± 2 °C using a platinum electrode and sweep rates of 200 mV/s.

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