

EXPERIMENTAL

All chemicals and reagents used were of analytical grade and purchased from commercial sources and used without further purification. The ligand PATH was provided by Dr. David Goldberg and his research group from the department of chemistry, The Johns Hopkins University. Milli-Q[®] water was used to prepare all solutions. A primary standard solution (HNO₃) was used to make secondary standard solutions for all standardizations.

¹H and ¹³C NMR spectra were recorded on a Bruker 400 MHz spectrometer. TMS in D₂O was used as an internal reference for ¹H measurements. A VWR SR60IC pH meter with an Orion PerpHecT ROSS pH electrode Model 8203BN was used for all pH and potential readings. All potential readings were measured to ±0.1 mV (±0.001 pH unit) and kept at a constant temperature of 25.0°C ± 0.05°C using a water circulating constant temperature bath and jacketed cell. Differential pulse voltammetry was carried out using Autolab software to control a Model 663 VA Stand (Metrohm). The multi-mode electrode was used as the working electrode in the static mercury dropping electrode (SMDE) mode. A silver/silver chloride electrode and a graphite electrode were used as the reference and auxiliary electrodes, respectively. A pulse height of 50 mV and step height of 4 mV were used. Pulse width and integration time were set to 200ms and 60ms, respectively. All solutions were degassed with prepurified N₂ gas and allowed to equilibrate before each measurement

All titration solutions were kept under prepurified nitrogen at 25 ± 0.05°C in an enclosed environment. A three-neck tapered jacketed flask was used for each titration.

All solution studies were carried out at $I = 0.10$ (NaNO_3). The pH meter was calibrated daily by using a standard HNO_3 solution titrated with a standardized NaOH solution. By plotting the potential vs. pH, a Nernstian slope was generated. All NaOH solutions were standardized by a previously standardized dilute solution of HNO_3 .

Cyclen (1, 4, 7, 10-tetraazacyclododecane) titrations

A solution of 0.0100 M cyclen (0.1723 g in 100 mL of H_2O) and 0.0900 M NaNO_3 (0.8499 g in 100 mL of H_2O) was used for each titration. A solution of 0.03333 M $\text{Zn}(\text{NO}_3)_2$ (0.4957 g in 50 mL of H_2O) was used for each titration. For each potentiometric titration, the ratio of cyclen: Zn was 1:1 (0.2 mmol: 0.2 mmol). All solutions were allowed to equilibrate for 60 minutes to ensure complete complexation of the Zn ion to the macrocycle, cyclen.

Titration of Cyclen, Zn, Triphenylphosphinobenzene-3-sulfonic acid

For this titration, a 1:1:1 ratio of cyclen: Zn: triphenylphosphinobenzene-3-sulfonic acid was used. A solution of 0.01000 M (0.5689 g, 1.001 mmol) triphenylphosphinobenzene-3-sulfonic acid and 0.06995 M (0.5945 g, 6.995 mmol) NaNO_3 was prepared. 20 mL of the above solution was added to 20 mL of 0.01 M cyclen and 0.09 M NaNO_3 along with 6 mL of 0.03335 M $\text{Zn}(\text{NO}_3)_2$ and 5 mL of 0.01 M HNO_3 and 0.09 M NaNO_3 . The solution was allowed to equilibrate for 60 minutes. This allows for complete equilibrium between the cyclen and Zn in solution. This solution was titrated with 1 mL additions of 0.01923 M (0.3916 g, 9.790 mmol) NaOH and 0.07998 M

(3.3986 g, 39.9882 mmol) NaNO_3 . Potentials were recorded in mV once the electrode came to equilibrium.

Titration of Cyclen, Zn, Iodide (I^-)

For this titration, a 1:1:10 ratio of cyclen: Zn: I was used. A solution of 0.1001 M (1.5008 g, 10.01 mmol) NaI was prepared. 20 mL of the NaI solution was added to 20 mL of the cyclen solution described above as well as 5.995 mL of the Zn solution previously described along with 5 mL of the HNO_3 solution. The solution was allowed to equilibrate for 60 minutes. The solution was titrated with 1 mL additions of the NaOH solution and the potential was recorded.

Titration of Cyclen, Zn, Thiourea

For this titration, a 1:1:10 ratio of cyclen: Zn: thiourea was used. A solution of 0.9997 M (7.6085 g, 99.97 mmol) thiourea and 0.1001 M (0.8504 g, 10.01 mmol) NaNO_3 was prepared. 2 mL of the thiourea solution, 5.995 mL of the Zn solution, and 5 mL of the HNO_3 solution were added to 20 mL of the cyclen solution. The solution was allowed to equilibrate for 60 minutes. The solution was then titrated with 1 mL additions of NaOH solution and the potential was recorded.

Titration of Cyclen, Zn, Cyanide (CN^-)

For this titration, a 1:1:1 ratio of cyclen: Zn: cyanide was used. A solution of 0.05012 M (0.2456 g, 5.011 mmol) NaCN and 0.4998 M (0.4248 g, 4.998 mmol) NaNO_3 was prepared. 3.990 mL of the cyanide solution, 5.995 mL of the Zn solution, and 5 mL

of the HNO_3 solution were added to 20 mL of the cyclen solution. The solution was allowed to equilibrate for 60 minutes. The solution was then titrated with 1 mL additions of NaOH solution and the potential recorded.

Titration of Cyclen, Zn, Azide (N_3)

For this titration, a 1:1:1 ratio of cyclen: Zn: azide was used. A solution of 0.09995 M (0.6498 g, 9.9954 mmol) NaN_3 was prepared. 2.005 mL of the azide solution, 5.995 mL of the Zn solution, and 5 mL of the HNO_3 solution were added to 20 mL of the cyclen solution. The solution was allowed to equilibrate for 60 minutes. The solution was then titrated with 1 mL additions of NaOH solution and the potential recorded.

Titration of Cyclen, Zn, Thiocyanate (SCN)

For this titration, a 1:1:1 ratio of cyclen: Zn: thiocyanate was used. A solution of 0.09943 M (0.8060 g, 9.943 mmol) NaSCN was prepared. 2.015 mL of the thiocyanate solution, 5.995 mL of the Zn solution, and 5 mL of the HNO_3 solution were added to 20 mL of the cyclen solution. The solution was allowed to equilibrate for 60 minutes. The solution was then titrated with 1 mL additions of NaOH solution and the potential recorded.

Titration of Cyclen, Zn, Chloride (Cl)

For this titration, a 1:1:1 ratio of cyclen: Zn: chloride was used. A solution of 0.1000 M (0.5846 g, 10.00 mmol) NaCl was prepared. 20 mL of the chloride solution, 5.995 mL of the Zn solution and 5 mL of the HNO_3 solution were added to 20 mL of the

cyclen solution. The solution was allowed to equilibrate for 60 minutes. The solution was then titrated with 1 mL additions of NaOH solution and the potential recorded.

Titration of Cyclen, Zn, Bromide (Br^-)

For this titration, a 1:1:1 ratio of cyclen: Zn: bromide was used. A solution of 0.1000 M (1.0282 g, 9.992 mmol) NaBr was prepared. 20 mL of the bromide solution, 5.995 mL of the Zn solution and 5 mL of the HNO_3 solution were added to 20 mL of the cyclen solution. The solution was allowed to equilibrate for 60 minutes. The solution was then titrated with 1 mL additions of NaOH solution and the potential recorded.

PATH (Pyridine-amine-thiolate ligand) Titrations

The PATH stock solution was kept at -80°C due to thermal decomposition. To reduce decomposition, all solutions were used within 1 hour of preparation. All titration solutions were kept under prepurified nitrogen and kept at a constant temperature of $25 \pm 0.05^\circ\text{C}$. A solution of 0.0100 M (0.5613 g, 2.501 mmol) PATH, 0.0900 M (1.9132 g, 22.51 mmol) NaNO_3 and 0.0100 N (26.235 mL of 0.0953 N HNO_3) HNO_3 was used for each potentiometric titration.

Titration of PATH and Zn

Three independent titrations were carried out at varying ratios of PATH: Zn. From a stock solution of 0.01 M PATH, 25 mL of the PATH solution was added to 5, 6, 7 mL of a 0.03440 M (0.5117 g, 1.720 mmol) $\text{Zn}(\text{NO}_3)_2$ solution. This corresponded to a PATH:Zn ratio of 1.67:1, 1.50:1, and 1.33:1, respectively. The titration began one hour

after the PATH solution was prepared. Once the electrode was calibrated, the solution was titrated with 1 ml additions of a standardized 0.02083 M (0.4488 g, 11.22 mmol) NaOH and 0.07984 M NaNO₃ (3.3926 g, 39.92 mmol) solution. The potential was measured and recorded in mV.

Titration of PATH and Nickel (Ni)

Three independent titrations were carried out at varying ratios of PATH: Ni. From a stock solution of 0.01 M PATH, 20 ml of PATH solution was added to 5, 6, and 7 ml of a 0.03310 M (0.9625 g, 3.310 mmol) Ni(NO₃)₂·6H₂O. This corresponded to a PATH: Zn ratio of 1.21:1, 1.01:1, and 0.86:1, respectively. The titration began one hour after the PATH solution was prepared. Once the electrode was calibrated, the solution was titrated with 1 ml additions of a standardized NaOH solution. The potential was measured and recorded in mV.

Titration of PATH and Indium (In)

Three independent titrations were carried out at varying ratios of PATH: In. From a stock solution of 0.01 M PATH, 20 ml of PATH solution was added to 8, 9, and 10 ml of a 0.01506 M (0.5887 g, 1.506 mmol) In(NO₃)₃·5H₂O and 0.01 N HNO₃. This corresponded to a PATH: In ratio of 1.66:1, 1.48:1, and 1.33:1, respectively. The titration began one hour after the PATH solution was prepared. Once the electrode was calibrated, the solution was titrated with 1 ml additions of a standardized NaOH solution. The potential was measured and recorded in mV.

Titration of PATH and Gallium (Ga)

Three independent titrations were carried out at varying ratios of PATH: Ga. From a stock solution of 0.01 M PATH, 20 ml of PATH solution was added to 8, 9, and 10 ml of a 0.01501 M (0.5190 g, 1.501 mmol) $\text{Ga}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ and 0.01 N HNO_3 . This corresponded to a PATH: Ga ratio of 1.67:1, 1.48:1, and 1.33:1, respectively. The titration began one hour after the PATH solution was prepared. Once the electrode was calibrated, the solution was titrated with 1 ml additions of a standardized NaOH solution. The potential was measured and recorded in mV.

Titration of PATH and Cadmium (Cd)

Three independent titrations were carried out at varying ratios of PATH: Cd. From a stock solution of 0.01 M PATH, 20 ml of PATH solution was added to 5, 6, and 8 ml of a 0.03350 M (1.0335 g, 3.350 mmol) $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. This corresponded to a PATH: Cd ratio of 1.19:1, 0.99:1, and 1.08:1, respectively. The titration began one hour after the PATH solution was prepared. Once the electrode was calibrated, the solution was titrated with 1 ml additions of a standardized NaOH solution. The potential was measured and recorded in mV.

Titration of PATH and Lead (Pb)

Two independent titrations were carried out at varying ratios of PATH: Pb. From a stock solution of 0.03 M (0.0631 g, 0.2812 mmol) PATH, 40 ml of PATH solution was added to 2 and 3 ml of a 0.03336 M (1.1049 g, 3.336 mmol) $\text{Pb}(\text{NO}_3)_2$. This corresponded to a PATH: Pb ratio of 1.80:1 and 1.33:1, respectively. The titration began

one hour after the PATH solution was prepared. Once the electrode was calibrated, the solution was titrated with 1 ml additions of a standardized NaOH solution. The potential was measured and recorded in mV.

Titration of PATH and Zinc (Zn)

Two independent titrations were carried out at varying ratios of PATH: Zn. From a stock solution of 0.01 M PATH, 25 ml of PATH solution was added to 6 and 7 ml of a 0.03440 M (0.5117 g, 1.7201 mmol) $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. This corresponded to a PATH: Zn ratio of 1.21:1, 1.04:1, respectively. The titration began one hour after the PATH solution was prepared. Once the electrode was calibrated, the solution was titrated with 1 ml additions of a standardized NaOH solution. The potential was measured and recorded in mV.

Recrystallization of Cyclen-Zn-Ligands (TPP, CN, I, Br, Thiourea)

All recrystallizations were prepared in a 1:1:1 (0.2 mmol: 0.2 mmol: 0.2 mmol) ratio of cyclen: Zn: L, where L = triphenylphosphinobenzene-3-sulfonic acid, CN^- , I^- , Br^- , and thiourea. The cyclen: Zn: L solutions were dissolved with ~20 ml of EtOH and remained undisturbed at room temperature (25°C) under N_2 during the recrystallization process. The weights of 3, 3', 3''-phosphinidynetris(benzene-sulfonic acid), CN^- , I^- , Br^- , and thiourea are 0.0525 g, 0.0098 g, 0.0299 g, 0.0206 g, and 0.0152 g, respectively. The weights of the cyclen and Zn are 0.0345 g and 0.0595 g, respectively. The solutions were allowed to remain undisturbed for 1 month. The resulting crystals were vacuum-filtered

and stored under N₂ gas. X-ray crystallographic analyses of crystals were carried out by the Department of Chemistry at Texas A & M.

Voltammetry of PATH with Metal Ions (Zn²⁺, Bi³⁺) and Cyclen with Zn²⁺

All solutions used for voltammetry were made with reagent grade chemicals and Milli-Q[®] water. The ionic strength of the solutions were kept constant at $I = 0.10$ with NaNO₃. In order to prevent trace metal contamination, all solutions were made at time of use and all glassware was cleaned with Milli-Q[®] water and standardized HCl. All reaction solutions were allowed to equilibrate and degas for 10 minutes in the absence of the mercury electrode, due to complexation of the PATH ligand with the mercury.

Voltammetry of Cyclen-Zn complex

A 2.5 mL aliquot of a solution of 0.001M cyclen in 1N HNO₃ was added to 5.0 mL of 500 μM Zn(ClO₄)₂ in 0.1M NaClO₄ and 42.5 mL of 0.1M NaNO₃. The pH of this solution was adjusted from pH 2 to 12 with standardized 0.1M NaOH, 0.01M NaOH/0.09M NaClO₄ and 0.001M NaOH/0.1M NaClO₄. In order to obtain adequate data points, polarograms were recorded at 0.2 pH intervals.

Voltammetry of PATH-Zn complex

A 25 mL aliquot of a solution of 50 μM PATH, 50 μM Zn(ClO₄)₂ and 0.09M NaClO₄ dissolved in standardized 0.1N HNO₃ was added to 25 mL of 0.1M NaNO₃. The pH of the solution was adjusted from pH 2 to 12 with standardized 0.1M NaOH, 0.01M

NaOH/0.09M NaClO₄ and 0.001M NaOH/0.1M NaClO₄. In order to obtain adequate data points, polarograms were recorded at 0.2 pH intervals.

Voltammetry of PATH-Bi complex

A 25 mL aliquot of a solution of 50 μM PATH, 50 μM Bi(NO₃)₃ and 0.09M NaClO₄ dissolved in standardized 0.1N HNO₃ was added to 25 mL of 0.1M NaNO₃. The pH of the solution was adjusted from pH 2 to 12 with standardized 0.1M NaOH, 0.01M NaOH/0.09M NaClO₄ and 0.001M NaOH/0.1M NaClO₄. In order to obtain adequate data points, polarograms were recorded at 0.2 pH intervals.