Inorg. Chem. **2006**, *45*, 6108−6110

Inorganic Chemistry
Communication

Electron Transfer vs Coordination Chemistry: Isomer-Specific Binding of Hg^{II} by an *ortho*-Wurster's Thiacrown Ether

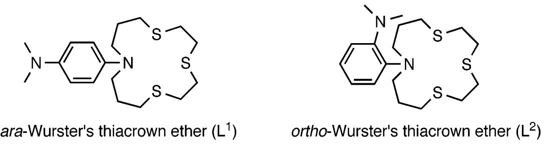
John W. Sibert,*,† Philip B. Forshee,† and Vincent Lynch‡

Department of Chemistry, The University of Texas at Dallas, Richardson, Texas 75083, and
Department of Chemistry and Biochemistry, The University of Texas at Austin,
Austin, Texas 78712

Received April 12, 2006

Isomeric *p*- and *o*-phenylenediamine-containing macrocyclic hosts (Wurster's thiacrown ethers $\mathbf{L^1}$ and $\mathbf{L^2}$, respectively) were prepared and studied as Hg^{II} ionophores. The distinct electrochemical properties of the two hosts allowed for the formation of a coordination compound with the *ortho*-Wurster's thiacrown ether but not the *para* isomer. In the latter case, the Hg^{II} ion served as an oxidant in an electron-transfer reaction with the host. Solutions of the Hg^{II} complex of $\mathbf{L^2}$ were studied by ^{13}C NMR spectroscopy and cyclic voltammetry and revealed a strong interaction between the redox-active phenylenediamine subunit and the bound metal cation. An X-ray analysis confirmed the participation of the three macrocyclic S atoms and both phenylenediamine N atoms in the stabilization of the complex.

The design of agents with an affinity for heavy-metal ions continues to be a research area of increasing importance because heavy-metal pollution has become a widespread global problem.[1] We are interested in electrochemically responsive ligand systems for Hg^{II}, which can provide a foundation for the development of sensors and switchable transport agents. While a large number of redox-active macrocycles have been reported in the literature,[2] the vast majority are based on crown ethers, a structural motif containing hard O donor atoms that supports the coordination of alkali- and alkaline-earth-metal cations. With the exclusion of a few notable examples,[3] those that target the binding of heavy-metal ions have received comparatively little attention.



para-Wurster's thiacrown ether (L^1) *ortho*-Wurster's thiacrown ether (L^2)

Figure 1. Wurster's thiacrown ethers used in this study.

Based on the rich coordination chemistry of thiacrown ethers with heavy-metal ions, we recently reported on the synthesis and coordination chemistry of two *para*-Wurster's thiacrown ethers, a redox-active crown and crownophane, which are formally derived from Wurster's reagent (*N*,*N*,*N′*,*N′*-tetramethyl-*p*-phenylenediamine or *p*-TMPD) and thiacrown ethers.[4] These hosts contain a *p*-phenylenediamine moiety within the macrocyclic framework such that direct interaction between the redox-active moiety and a bound guest is promoted. One of the structures, $\mathbf{L^1}$ (see Figure 1), formed a particularly stable complex with Pt^{II} and displayed a large anodic shift (>900 mV) upon coordination due to the presence of the phenylenediamine subunit in the coordination sphere. However, the heavy-metal ion coordination chemistry of $\mathbf{L^1}$ is limited by the relatively modest oxidation potential of the *p*-phenylenediamine subunit ($E_{1/2} = 135$ mV vs Ag/AgCl) and the oxidizing abilities of potential target ions (e.g., Hg^{II}).

In contrast to their *para* counterparts, the *ortho*-Wurster's crown ethers[5] are substantially more resistant to oxidation because of the pronounced steric effects associated with the disposition of two amino groups in an *ortho* position.[6] In addition, the *o*-phenylenediamine subunit can serve as a bidentate donor to further enhance the interaction between

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* To whom correspondence should be addressed. E-mail: sibertj@utdallas.edu.

† The University of Texas at Dallas.

‡ The University of Texas at Austin.

[1] For examples, see the following and references cited therein: (a) Yoon, S.; Albers, A. E.; Wong, A. P.; Chang, C. J. *J. Am. Chem. Soc.* **2005**, *46*, 16030−16031. (b) Zahir, F.; Rizwi, S. J.; Haq, S. K.; Khan, R. H. *Environ. Toxicol. Pharmacol.* **2005**, *20*, 351−360. (c) Baumann, T. F.; Reynolds, J. G. *J. Chem. Soc., Chem. Commun.* **1998**, 1637−1638.

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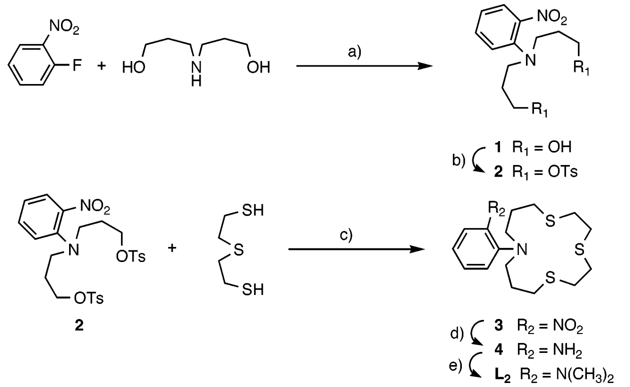
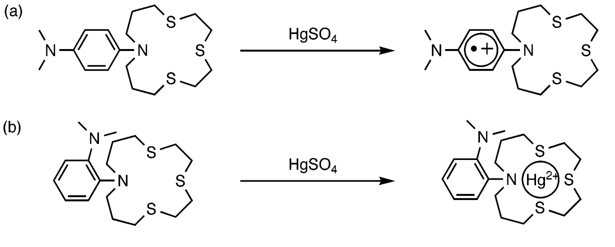
10.1021/ic060624r CCC: $33.50

Scheme 1[a]



[a] (a) Cs_2CO_3, 90 °C, 24 h, 92%. (b) TsCl, pyridine, CH_2Cl_2, 6 h, 79%. (c) Cs_2CO_3, DMF, 60 °C, 36 h, 55%. (d) H_2, Pd/C, EtOAc, 24 h, 60%. (e) CH_2O, H_2SO_4, $NaBH_4$, 89%.

Scheme 2



the redox and metal centers. Herein, we describe the synthesis and properties of the first *ortho*-Wurster's thiacrown ether (**L^2**), a host that combines the robust electrochemical properties of *N*,*N*,*N*′,*N*′-tetramethyl-*o*-phenylenediamine (or *o*-TMPD) with a mixed set of aza and thia donor functionalities suitable for the binding of softer metal ions, and compare its Hg^{II} coordination chemistry to that of the *para* isomer **L^1**.

The synthesis of ligand **L^1** has been previously described.[4] The synthesis of **L^2** (Scheme 1) was accomplished in a five-step scheme starting with a nucleophilic aromatic substitution reaction involving 2-fluoronitrobenzene and the commercially available bis(3-hydroxypropyl)amine. After tosylation of the resultant diol, cyclization with 2-mercaptoethyl sulfide in dimethylformamide (DMF) in the presence of Cs_2CO_3 afforded crown **3** in 55% yield. Reduction of the nitro functionality by catalytic hydrogenation followed by methylation gave the desired ligand in an overall yield of 21%.

The combination of equimolar amounts of **L^1** and mercury(II) sulfate in water resulted in the instantaneous formation of a deep-violet-blue solution. This color is characteristic of the radical cation of *p*-TMPD and, in fact, gives rise to its common name "Wurster's blue". Analysis by UV−visible spectroscopy confirmed the formation of the singly oxidized radical cation form of **L^1**. Thus, in this case, the Hg^{II} ion serves not as a Lewis acid in complex formation but, instead, as an oxidizing agent removing an electron from the π system of **L^1** (see Scheme 2). In sharp contrast, the addition of **L^2** to a warm equimolar aqueous solution of mercury(II) sulfate caused no change in the color of the solution. Upon treatment with excess NH_4PF_6, **L^2**·Hg$(PF_6)_2$ precipitated from solution as a crystalline white solid.

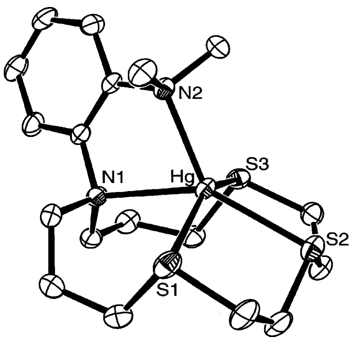


Figure 2. X-ray crystal structure of **L^2**·Hg$(PF_6)_2$ (H atoms and PF_6^- anions omitted for clarity). Thermal ellipsoids plotted at 50% probability.

X-ray-quality crystals of **L^2**·Hg$(PF_6)_2$ were obtained from the vapor diffusion of ethyl ether into an acetonitrile solution.[7] As shown in Figure 2, the five donor atoms of **L^2** form a distorted square-pyramidal geometry around the Hg^{II} center, with the dimethylamino group occupying the apical position and the cation residing 0.744 Å above the plane of the four macrocyclic donor atoms.[8] Similar to the previously reported Pt^{II} complex of **L^1**,[4] the S atoms of **L^2** have oriented themselves to form an endocyclic complex with an average Hg−S bond distance of 2.64 Å. Also noteworthy is the strong interaction of both the macrocyclic and pendant dimethylamino groups with the bound metal center as shown by the Hg−N distances [Hg−N1 = 2.474(2) Å; Hg−N2 = 2.299(2) Å] and complete pyramidalization of the aromatic N atoms ($C{-}N1_{avg} = 109.6°$ and $C{-}N2_{avg} = 110.5°$). The pyramidalization or rehybridization of the N donor atoms to greater sp^3 character upon complexation allows for their greater interaction with the Hg^{II} ion by freeing the lone pairs from interaction with the π system. Interestingly, this appears to be a general structural component present in metal complexes of both *o*-[5] and *p*-phenylenediamine-based[4] macrocycles and demonstrates the strong mutual interaction between the redox-active subunit in Wurster's crowns and their guests.

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(7) Crystal structure of **L^2**·Hg$(PF_6)_2$: $[(C_{18}H_{30}N_2S_3)Hg]^{2+}2(PF_6)^{-1}$, M_r = 861.15 g mol^{-1}, monoclinic, $P2_1/n$, $a = 9.6186(1)$ Å, $b = 16.4436(1)$ Å, $c = 17.1630(2)$ Å, $\beta = 92.539(1)°$, $V = 2711.91(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.109$ g cm^{-3}, $T = 153(2)$ K. A total of 406 frames of data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with Mo Kα radiation ($\lambda = 0.710\,73$ Å) using ω scans with a scan range of 1° and a counting time of 93 s per frame. Data reduction was performed using DENZO-SMN.[12] The structure was solved by direct methods using *SIR97*[13] and refined by full-matrix least squares on F^2 with anisotropic displacement parameters for the non-H atoms using *SHELXL-97*.[14] The data were corrected for absorption using the Gaussian integration method. The transmission factors ranged from 0.151 to 0.313. The H atoms were observed in a ΔF map and refined with isotropic displacement parameters. The function $\sum w(|F_o|^2 - |F_c|^2)^2$ was minimized, where $w = 1/[(s(F_o))^2 + (0.019P)]$ and $P = \sum w(|F_o|^2 - |F_c|^2)/3$. $R_w(F^2)$ was refined to 0.0545, with $R(F)$ equal to 0.0232 and a goodness of fit, S, equal to 1.02. Definitions used for calculating $R(F)$ and $R_w(F^2)$ are given below.[15] The data were corrected for secondary extinction effects. The correction takes the form $F_{corr} = kF_c/[1 + (2.9(1) \times 10^{-6})F_c^2l^3/(\sin 2q)]^{0.25}$, where k is the overall scale factor. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from ref 16.

(8) Five-coordinate Hg^{II} complexes are relatively uncommon. For an additional example, see: Blake, A. J.; Pasteur, E. C.; Reid, G.; Schroder, M. *Polyhedron* **1991**, *10*, 1545−1548.

A detailed computational study highlighting this interaction has been recently reported.[9]

^{13}C NMR spectroscopy ($CD_3CN/CDCl_3$, 9:1, as the solvent) was used to study the $\mathbf{L^2}\cdot Hg(PF_6)_2$ complex in solution. As expected, the ^{13}C NMR spectrum for free ligand **L²** is consistent with a hybrid structure of *o*-TMPD and a thiacrown ether. Downfield chemical shifts in the ^{13}C NMR resonances of thiacrown ether complexes relative to those of the corresponding free ligands are commonly observed and serve as a means to confirm binding between a crown and a metal center.[10] These shifts are attributed to inductive effects resulting from the close proximity of the crown to the positively charged cationic center. For the free ligand (**L²**), the methylene groups give rise to four distinct resonances in a tight cluster between 27.1 and 30.6 ppm. As expected, upon complexation all of these resonances shift downfield with the exception of one that shows an upfield shift. The upfield shift may be the result of distortion in the tetrahedral environment of one of the macrocyclic C atoms upon complexation, as has recently been described in detail for the $[Hg(9S3)_2](ClO_4)_2$ complex of Grant and co-workers.[10d] The CH_2-N and CH_3-N resonances are each shifted downfield in the complex by 10.1 ppm, reflecting a solution structure that involves coordination by all five donor atoms. Further, complex formation also causes a downfield shift in the aromatic C atoms of the phenylene moiety ($\Delta C_{avg} = 3.5$ ppm).

The electrochemical properties of **L²** and its Hg^{II} complex were studied by cyclic voltammetry (CH_3CN, 0.1 M $TEAPF_6$, 100 mV/s). The voltammogram of **L²** shows oxidations at 606 and 871 mV vs Ag/AgCl, with the first oxidation occurring at a potential 400 mV more anodic than that observed for the first oxidation of **L¹**. In contrast to *o*-TMPD and **L¹**, the oxidation of **L²** is irreversible at all scan rates. Electrochemical analysis of a sample of the preformed $\mathbf{L^2}\cdot Hg(PF_6)_2$ complex showed a completely suppressed oxidation wave for the host out to the sweep limit of 1.8 V. Such suppression has been previously noted for *p*-phenylenediamine-containing crown ethers upon encapsulation of alkaline-earth-metal cations.[11] This indicates that complexation of Hg^{II} by **L²** causes a shift in its oxidation potential in excess of +1.1 V. Given that the coordination of Pt^{II} produced a 900-mV shift upon complexation with **L¹**, a ligand that provides only one phenylenediamine donor atom for coordination to the cationic guest, such a large electrochemical response to Hg^{II} by **L²** is not wholly unexpected. In other words, the strong interaction with *both* N atoms of the *o*-phenylenediamine subunit in **L²** causes a substantially greater response versus the comparable *p*-phenylenediamine-based system, a trend previously noted for the *ortho*-Wurster's crown ethers.[5] Upon sweeping to negative potentials, the complex $\mathbf{L^2}\cdot Hg(PF_6)_2$ was degraded via metal-centered reduction and subsequent decomplexation, as evidenced by the formation of a new irreversible oxidation wave at 940 mV that occurs at the same potential as that observed in voltammograms of solutions containing only the starting Hg^{II} salt.

In summary, we describe here the synthesis of the first *ortho*-Wurster's thiacrown ether, **L²**, and demonstrate its use in the isomer-selective binding of Hg^{II}. The coordination of Hg^{II} by **L²** is due to the incorporation of the electrochemically compatible *ortho* isomer of phenylenediamine and contrasts with the oxidation of the *para* isomer **L¹** upon treatment with Hg^{II}.

Acknowledgment. The Robert A. Welch Foundation (Grant AT-1527) contributed financial support for this work.

Supporting Information Available: Experimental section, representative cyclic voltammograms, and X-ray crystallographic data for $\mathbf{L^2}\cdot Hg(PF_6)_2$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC060624R

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(15) $R_w(F^2) = \{\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(|F_o|^4\}^{1/2}$, where w is the weight given each reflection. $R(F) = \sum(|F_o| - |F_c|)/\sum|F_o|$ for reflections with $F_o > 4[\sigma(F_o)]$. $S = [\sum w(|F_o|^2 - |F_c|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

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