Results and Discussion
Preparation and Crystal Structure of [HgLCl\textsubscript{4}] (1).

By the reaction of HgCl\textsubscript{2} with L in methanol, the colorless crystalline complex 1 suitable for crystallography was obtained in nearly quantitative yield. The FAB mass and microanalysis data of the product are consistent with the formulation of 1. The crystal structure of 1 shows that the molecule has a C\textsubscript{3} axis and one half molecule occupies the asymmetric unit (Fig. 1). The mercury center is in a hexacoordinated environment and the coordination is best described as octahedral with some noticeable distortions. The bond angles around the mercury atom are extremely different each other; (Cl-Hg-Cl: 167.5(2)\(^\circ\)) > (S-Hg-S 160.6(1)\(^\circ\)) > (O-Hg-O 64.8(3)\(^\circ\)). The resulting open space between two S donors was not occupied by other species.

From the database of Cambridge Crystallographic Data Centre,\textsuperscript{7} four cases of the cyclic thiaoxa complexes with Hg\textsuperscript{2+} were extracted.\textsuperscript{8,12} To our best knowledge, this crystal structure is the first example of an acyclic thiaoxa ether complex with Hg\textsuperscript{2+}. Interestingly, the two O atoms are closely bound to Hg atom (Hg-O: 2.659(6) Å), but two S atoms marked less so (Hg-S: 3.079(2) Å).\textsuperscript{8} The Hg-S distances are longer than those of typical Hg-S bonds reported (2.50-2.70 Å).\textsuperscript{8,10} This preferential coordination by O donor is unusual since Hg\textsuperscript{2+} trends to bind to thioether S donors. Consequently, the unique coordination mode of 1, which shows the synergic effect\textsuperscript{13} of the mixed coordinating site via thiaoxa-donor set may serve as an evidence of the

Figure 1. Crystal structure of [HgLCl\textsubscript{4}] (1). Selected bond lengths (Å), bond angles (\(^\circ\)) and torsion angles (\(^\circ\)): Hg-C1 2.329(2), Hg-O1 2.659(6), Hg-S1 3.079(2), C1A-Hg-C1I 167.5(2), S1-Hg-S1A 160.6(1), C1I-Hg-O1I 101.8(2), C1I-Hg-O1A 89.7(2), C1I-Hg-S1 89.7(1), C1A-Hg-S1 88.2(1), O1-Hg-S1A 131.4(2), O1-Hg-O1A 64.8(3), O1-C2-C3-S1 65.9(9), O1-C1I-C1A-O1A -69.5(17). [Symmetry codes A: -x, -y+1, z].
high selectivity for Hg\textsuperscript{2+} as a modifier in this work (see below).

**L-Modified CPEs for Voltammetric Determination of Hg\textsuperscript{2+}**

As mentioned, the L-modified CPEs were prepared and the electrode characteristics were examined for the determination of Hg\textsuperscript{2+} by means of LSSV. No redox wave was observed except at the L-modified CPE, which had immersed into 0.50 mM Hg\textsuperscript{2+} (Fig. 2). Figure 2d shows a cathodic peak at $-0.02$ V and an anodic peak at $+0.40$ V vs. Ag/AgCl, suggesting the practical use of Hg\textsuperscript{2+} detection in the range used. From the standard addition of Hg\textsuperscript{2+} salt, the peaks were identified as the redox between Hg(0) and Hg\textsuperscript{2+}. The 50% composition of L offered the electrode with an optimum condition. Electrolysis time of 150 s was employed as an optimum condition from the effect of peak height on the electrolysis time. The effect of pH on the preconcentration was optimized and the peak currents were measured at pH 5.5.

The optimized parameters allow finding the most suitable condition for a quantitative analysis by calibration curves. The calibration graph for the proposed electrode was obtained by LSSV (Fig. 3). The anodic peak for the oxidation of Hg peak at $+0.04$ V was well defined and the peak heights of the CV and LSSV were linearly related to Hg\textsuperscript{2+} concentration from 5.0 μM up to 50.0 μM. The influence of the interfering species on the current response of Hg\textsuperscript{2+} was evaluated (Table 1). Most of the species show no effect on Hg\textsuperscript{2+} signal, with deviations less than 3%. Only Ag\textsuperscript{+} was found to interfere significantly by decreasing the Hg\textsuperscript{2+} signal, because Ag\textsuperscript{+} may form the complex with L\textsuperscript{4g,14} and prevent Hg\textsuperscript{2+} from the complexation and accumulation at the electrode surface. The possible interference of organic species, such as EDTA and oxalate was also tested and relatively low deviations (ca. 1-3%) were observed. Once again, it is noted that the preferential affinity of L to Hg center in the solid complex \textsuperscript{1} seems to be responsible for the selectivity of the proposed electrode system.

**Table 1. Effect of interference species on the determination of Hg\textsuperscript{2+} at the L-modified CPE**

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration</th>
<th>Interference (%)</th>
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<tbody>
<tr>
<td>Hg\textsuperscript{2+}</td>
<td>0.50 mM&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-2.27 mm</td>
</tr>
<tr>
<td>Cu\textsuperscript{2+}</td>
<td>0.50 mM&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-1.70 mm</td>
</tr>
<tr>
<td>Cd\textsuperscript{2+}</td>
<td>0.50 mM&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-1.14 mm</td>
</tr>
<tr>
<td>Zn\textsuperscript{2+}</td>
<td>0.50 mM&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-0.84 mm</td>
</tr>
<tr>
<td>Ag\textsuperscript{+}</td>
<td>0.50 mM&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-0.68 mm</td>
</tr>
<tr>
<td>Pb\textsuperscript{2+}</td>
<td>0.50 mM&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-0.27 mm</td>
</tr>
<tr>
<td>EDTA</td>
<td>0.50 mM&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-1.14 mm</td>
</tr>
<tr>
<td>oxalate</td>
<td>0.50 mM&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-1.14 mm</td>
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<sup>a</sup>[Hg\textsuperscript{2+}] = [interferent] = 0.50 mM; <sup>b</sup>[Hg\textsuperscript{2+}] = 0.50 mM, [interferent] = 1.0 mM

\[\text{Figure 2. Cyclic voltammograms taken at (a) CPE immersed in blank buffer solution (pH 5.5) and then in cell containing } 0.1 \text{ M KNO}_3, (b) same as (a) but immersed in 0.50 mM Hg\textsuperscript{2+}, (c) L-modified CPE immersed in blank buffer solution (pH 5.5) and then in cell containing 0.1 M KNO}_3, (d) same as (c) but immersed in 0.50 mM Hg\textsuperscript{2+}.\]

\[\text{Figure 3. Calibration curve for determination of Hg\textsuperscript{2+} at the L-modified CPE.}\]
Experimental Section

Materials. L was synthesized by slight modification of our previous method as follows. Benzylmercaptane (55 mmol) and NaOH (55 mmol) were dissolved in THF (150 mL). Under reflux condition, 1,8-dichloro-3,6-dioxaoctane (25 mmol) dissolved in THF (70 mL) was added dropwise. The mixture was refluxed for 5 h. After cooling to room temperature, the mixture was filtered and evaporated. The residue was dissolved in chloroform. To remove the unreacted thioli, the mixture was washed with dilute NaOH solution several times. The organic layer was dried over anhydrous NaSO₄, concentrated and purified by column chromatography over silica gel to obtain a pure product as anode scanning from all the experiments, the electrode surface was activated with + requires M value, 0.28). Yield 68%. 1H NMR (500 MHz, CDCl₃): δ 2.60 (t, 4H, J = 6.8 Hz, OCH₂CH₂S), 3.55 (s, 4H, OCH₂CH₂O), 3.58 (t, 4H, J = 6.8 Hz, OCH₂CH₂S), 3.74 (s, 4H, benzylic CH₂), 7.20-7.31 (m, 10H, aromatic). 13C{1H} NMR (125 MHz, CDCl₃): δ 30.64, 36.65, 70.27, 71.03, 126.98, 128.58, 129.11, 138.42. IR (KBr disc, cm⁻¹): 3058-3025 (CH, aromatic), 2957-2910 (CH, aliphatic), 2355, 1094 (COC), 3058-3025 (CH, aromatic), 2957-2910 (CH, aliphatic), 2355, 1094 (COC), 3052-3020 (CH, aromatic), 2957-2910 (CH, aliphatic), 2355, 1094 (COC), 3052-3020 (CH, aromatic), 2957-2910 (CH, aliphatic), 2355, 1094 (COC), 3052-3020 (CH, aromatic), 2957-2910 (CH, aliphatic), 2355, 1094 (COC).

Preparation of [Hg(L)Cl₂]. To a solution of L (0.28 mmol) in methanol (15 mL) was added an equimolar amount of HgCl₂. The reaction mixture was kept in the dark while being stirred at room temperature for 30 min. By slow evaporation of the methanol solution, 1 was isolated in nearly quantitative yield as colorless crystals suitable for X-ray diffraction. Mp. 94-95 ºC. 1H NMR (500 MHz, CDCl₃): δ 2.55 (t, 4H, J = 6.7 Hz, OCH₂CH₂S), 3.48 (s, 4H, OCH₂CH₂O), 3.53 (t, 4H, J = 6.7 Hz, OCH₂CH₂S), 3.77 (s, 4H, benzylic CH₂), 7.23-7.32 (m, 10H, aromatic). 13C{1H} NMR (125 MHz, DMSO-d₆): δ 30.53, 35.80, 69.88, 70.39, 127.14, 128.69, 129.24, 139.06. IR (KBr disc, cm⁻¹): 3052-3020 (CH, aromatic), 2957-2910 (CH, aliphatic), 2355, 1094 (COC), 3052-3020 (CH, aromatic), 2957-2910 (CH, aliphatic), 2355, 1094 (COC), 3052-3020 (CH, aromatic), 2957-2910 (CH, aliphatic), 2355, 1094 (COC), 3052-3020 (CH, aromatic), 2957-2910 (CH, aliphatic), 2355, 1094 (COC), 3052-3020 (CH, aromatic), 2957-2910 (CH, aliphatic), 2355, 1094 (COC), 3052-3020 (CH, aromatic), 2957-2910 (CH, aliphatic), 2355, 1094 (COC).

Electrode Preparation and Voltammetric Procedures. To prepare the coated graphite powder, the graphite powder washed with absolute ethanol and dried under vacuum was first mixed with the desired amount (10-60%) of modifier L to the weight of paste. The modified carbon paste was prepared by thorough mixing of 5 g of coated graphite powder and 3 mL of nujol oil in a mortar. Unmodified carbon paste was prepared by the same method from uncoated graphite powder. The electrode surfaces were subsequently conditioned by exposure to 0.1 M HNO₃ solution for 5 s. and then rinsed with distilled water. Before all the experiments, the electrode surface was activated with anode scanning from -0.4 to +1.0 V vs. Ag/AgCl. Acetate buffer (pH 5.5) was used to control pH. Supporting electrolyte for voltammetric measurements was 0.1 M KNO₃. CV and LSSV were performed with a Bioanalytical Systems Model BAS 100 voltammetric analyzer. For all voltammetric measurements, an Ag/AgCl electrode and a platinum wire were used as a reference and a counter electrode, respectively. After deposition, the electrodes were transferred to the cell containing 0.1 M KNO₃ supporting electrolyte solution to obtain CV and LSSV.

Supplementary Material. Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-186945). That data can be obtained free of charge via http://www.ccdc.cam.ac.uk/or deposit@ccdc.cam.ac.uk.

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References and Notes

6. A crystal was mounted on a Bruker SMART diffractometer equipped with a graphite monochromator Mo Ka (λ = 0.71073 Å) radiation source and a CCD detector. The frame data were processed to give structure factors using the program SAINT. The structure was solved by direct method and refined by full matrix least squares against F² for all data using SHELXTL software. All non-H atoms were refined with anisotropic displacement parameters. Crystal data for C₅₆H₅₆Cl₄O₂S₄M = 634.02, orthorhombic, a = 13.029(10) Å, b = 52.480(4) Å, c = 6.9913(5) Å, U = 47779(3) Å³, T = 298(2) K, space group Pn2₁2₁2₁, Z = 8, μ(Mo Kα) = 6.851 mm⁻¹, 7634 reflections measured, 2352 unique (Rint = 0.0798) which were used in all calculations. Refinement converged as a final R = 0.0391 (wR2 = 0.1032) for 2323 independent reflections [1≤F2<2σ(F2)].