

Synthesis and Crystal Structure of Hg²⁺ Complex with an S₂O₂ Donor Dipodal Ligand. A Search for New Voltammetric Sensor for Hg²⁺

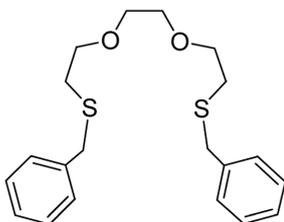
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Heavy metal complexations with host molecules have been received much attention, not only because of prime environmental concern,¹ but also the heavy metal binding is one of fundamental problems of molecular recognition.² Based on the optimal requirement of cooperative effect of the mixed coordinating sites *via* thioxa donor set for heavy metals,³ we have reported the solvent extraction, membrane transport and crystal structures of Ag⁺ and Pd²⁺ complexes with the new system of the cyclic and acyclic ionophores incorporating a potential thioxa donor system.⁴ Particularly, the acyclic thioxa ionophores can be obtained simply and cheaply because there is no need for expensive and time-consuming steps, such as high dilution or template methods, which is usually required in preparations of cyclic analogues. In the continuing work on the metal complexation,⁴ we were recently able to prepare the new Hg²⁺ complex of the S₂O₂ dipodal ligand **L** and have determined its X-ray crystal structure. Although the stability constant for the Hg²⁺ complex with **L** is not yet available, this result is enough to motivate the works on the stripping voltammetry by using the modified carbon paste electrode (CPE) as a more sophisticated detection procedure for Hg²⁺.⁵ Herein, we describe the preparation of the Hg²⁺ complex of **L** together with its crystal structure. In addition, the characteristics of the **L**-modified CPEs are presented in terms of the Hg²⁺ detection.



L

Results and Discussion

Preparation and Crystal Structure of [HgLCl₂] (1). By the reaction of HgCl₂ 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 C₂ axis and one half molecule occupies the asymmetric unit (Fig. 1).⁶ 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)^o) > (S-Hg-S 160.6(1)^o) > (S-Hg-O 131.4(2)^o) > (O-Hg-O 64.8(3)^o). The resulting open space between two S donors was not occupied by other species.

From the database of Cambridge Crystallographic Data Centre,⁷ four cases of the cyclic thioxa complexes with Hg²⁺ were extracted.⁹⁻¹² To our best knowledge, this crystal structure is the first example of an acyclic thioxa ether complex with Hg²⁺. 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).⁸ The Hg-S distances are longer than those of typical Hg-S bonds reported (2.50-2.70 Å).^{9,10} This preferential coordination by O donor is unusual since Hg²⁺ trends to bind to thioether S donor. Consequently, the unique coordination mode of **1**, which shows the synergic effect¹³ of the mixed coordinating site *via* thioxa-donor set may serve as an evidence of the

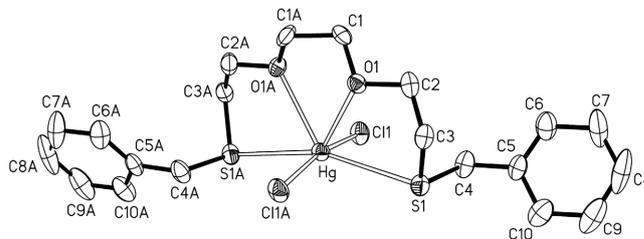


Figure 1. Crystal structure of [HgLCl₂] (**1**). Selected bond lengths (Å), bond angles (°) and torsion angles (°): Hg-Cl1 2.329(2), Hg-O1 2.659(6), Hg-S1 3.079(2), Cl1A-Hg-Cl1 167.5(2), S1-Hg-S1A 160.6(1), Cl1-Hg-O1 101.5(2), Cl1-Hg-O1A 89.2(2), Cl1-Hg-S1 89.7(1), Cl1A-Hg-S1 88.2(1), O1-Hg-S1A 131.4(2), O1-Hg-O1A 64.8(3), O1-C2-C3-S1 65.9(9), O1-C1-C1A-O1A -69.5(17) [Symmetry codes A: -x, -y+1, z].

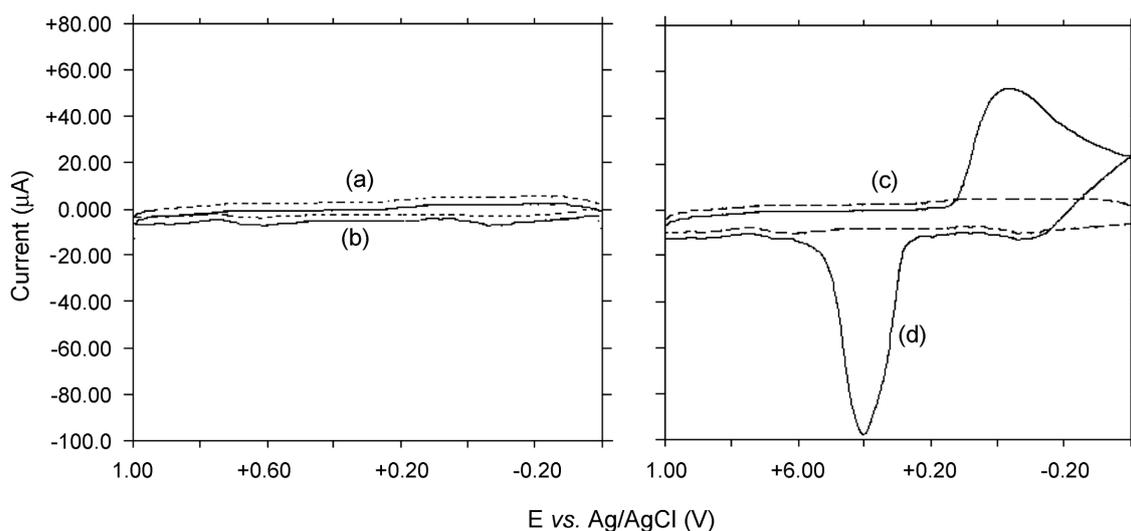


Figure 2. Cyclic voltammograms taken at (a) CPE immersed in blank buffer solution (pH 5.5) and then in cell containing 0.1 M KNO_3 , (b) same as (a) but immersed in 0.50 mM Hg^{2+} , (c) L-modified CPE immersed in blank buffer solution (pH 5.5) and then in cell containing 0.1 M KNO_3 , (d) same as (c) but immersed in 0.50 mM Hg^{2+} .

high selectivity for Hg^{2+} as a modifier in this work (see below).

L-Modified CPEs for Voltammetric Determination of Hg^{2+} . As mentioned, the L-modified CPEs were prepared and the electrode characteristics were examined for the determination of Hg^{2+} by means of LSSV. No redox wave was observed except at the L-modified CPE, which had immersed into 0.50 mM Hg^{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^{2+} detection in the range used. From the standard addition of Hg^{2+} salt, the peaks were identified as the redox between $\text{Hg}(0)$ and Hg^{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

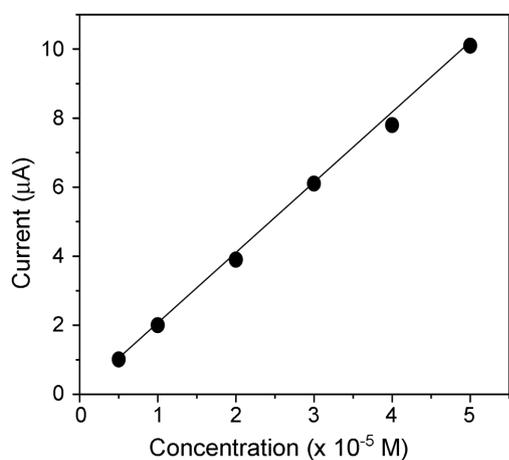


Figure 3. Calibration curve for determination of Hg^{2+} at the L-modified CPE.

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^{2+} concentration from $5.0 \mu\text{M}$ up to $50.0 \mu\text{M}$. The influence of the interfering species on the current response of Hg^{2+} was evaluated (Table 1). Most of the species show no effect on Hg^{2+} signal, with deviations less than 3%. Only Ag^+ was found to interfere significantly by decreasing the Hg^{2+} signal, because Ag^+ may form the complex with $\text{L}^{4g,14}$ and prevent Hg^{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 **1** seems to be responsible for the selectivity of the proposed electrode system.

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

Species	Concentration			
	0.50 mM ^a		1.0 mM ^b	
	I (µA)	Interference (%)	I (µA)	Interference (%)
Hg^{2+}	88	—	—	—
Cu^{2+}	86	-2.27	85.5	-2.84
Cd^{2+}	86.5	-1.70	85.3	-3.01
Zn^{2+}	87	-1.14	86.5	-1.70
Ag^+	83	-5.68	80	-9.09
Pb^{2+}	86	-2.27	85	-3.41
EDTA	87	-1.14	86	-2.27
oxalate ²⁻	87	-1.14	87	-1.14

^a $[\text{Hg}^{2+}] = [\text{interferent}] = 0.50 \text{ mM}$. ^b $[\text{Hg}^{2+}] = 0.50 \text{ mM}$, $[\text{interferent}] = 1.0 \text{ mM}$

Experimental Section

Materials. **L** was synthesized by slight modification of our previous method as follows.¹³ 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 thiol, the mixture was washed with dilute NaOH solution several times. The organic layer was dried over anhydrous Na₂SO₄, concentrated and purified by column chromatography over silica gel to obtain a pure product as colorless oil. Eluent: 20% ethylacetate/80% n-hexane v/v (R_f 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, cm⁻¹): 3058-3025 (CH, aromatic), 2911-2863 (CH, aliphatic), 1109 (COC), 702 (CSC). HRMS (EI) found: M⁺, 362.1375. C₂₀H₂₆S₂O₂ requires M⁺, 362.1374.

Preparation of [Hg(L)Cl₂] (1). 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 °C. ¹H NMR (500 MHz, DMSO-*d*₆): 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-*d*₆): 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), 1028, 701 (CSC). Found: C, 37.85; H, 4.32%. Calc. for C₂₀H₂₆S₂O₂HgCl₂: C, 37.89, H, 4.13%. FAB-MS: *m/z* 599 for [HgLCl]⁺.

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 voltam-

metric 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/perl/catreq.cgi> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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6. A crystal was mounted on a Bruker SMART diffractometer equipped with a graphite monochromated Mo K α (λ = 0.71073 Å) radiation source and a CCD detector. The frame data were processed to give structure factors using the program SAINT.¹⁵ The structure was solved by direct method and refined by full matrix least squares against F^2 for all data using SHELXTL software.¹⁶ All non-H atoms were refined with anisotropic displacement parameters. Crystal data for **1**: C₂₀H₂₆Cl₂HgO₂S₂, *M* = 634.02, orthorhombic, *a* = 13.0259(10) Å, *b* = 52.480(4) Å, *c* = 6.9913(5) Å, *U* = 4779.3(6) Å³, *T* = 298(2) K, space group *Fdd2*, *Z* = 8, μ (Mo K α) = 6.851 mm⁻¹, 7634 reflections measured, 2332 unique (R_{int} = 0.0798) which were used in all calculations. Refinement converged as a final *R* = 0.0391 (*wR*₂ = 0.1032) for 2332 independent reflections [*I* > 2 σ (*I*)].
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