

Macrocyclic Isomers with S₂O-Donor Set as Silver(I) Ionophores

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S₂O-donor macrocyclic isomers incorporating a xylyl group in *o*- (**L**¹), *m*- (**L**²) and *p*-positions (**L**³) extract no metal ions except silver(I) from aqueous to chloroform phase. And the magnitudes of %Ex for silver(I) are in the order of **L**¹ > **L**² > **L**³. Taking this result into account, **L**¹-**L**³ were utilized as membrane active components to prepare potentiometric silver(I)-selective electrodes. The proposed macrocycles-based electrodes E1 (**L**¹), E2 (**L**²) and E3 (**L**³) exhibited comparable results which show considerable selectivity toward silver(I) over alkali, alkali earth and other transition metal ions. Comparative NMR study on **L**¹-**L**³ and their complexes with silver(I) in solution was also accomplished. In addition, a unique sandwich-type complex [Ag(**L**¹)₂]ClO₄ was prepared from the assembly reaction of **L**¹ with AgClO₄ and structurally characterized by an X-ray diffraction analysis.

Key Words : Isomeric S₂O macrocycles, Solvent extraction, Ag(I)-ISE, NMR, Sandwich-type silver(I) complex

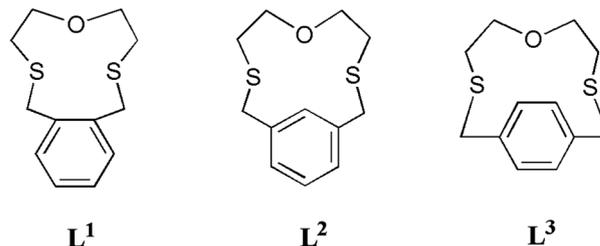
Introduction

There is growing interest for the thioxa-macrocyclic ionophores because of not only their role as a connection between thia-macrocycles and homoleptic oxygen-donor crown ethers¹⁻⁵ but also as versatile building blocks for the self-assembled supramolecular architectures.⁶⁻⁹ Recently, we have introduced the donor⁸ and anion⁹ effects, allowing diverse types of discrete or continuous types of supramolecular complexes assembled from the thioxa-macrocycles and silver(I) salts.

From the pioneering work of Casabo *et al.*,¹⁰ it has been noticed that some ionophores with thia or thioxa donor sets can act as sensing materials for soft metal ions¹¹ including silver(I). For examples, monobenzo thioxa-macrocycles show the excellent sensing components for the ion-selective electrodes (ISEs) due to the synergic coordination effect of the S/O donor set towards the silver(I).^{10,12} On the other hand, the macrocycles incorporating a rigid xylyl fragment, which was added in different substitution position such as, *o*-, *m*- and *p*-positions largely contribute to the overall structure of the macrocyclic rings.¹³⁻¹⁵ Thus the cation selectivity and/or coordination behavior of such positional isomers are expected to be dependent on the conformation of the free ligands. Recently, we reported the exo-coordination-based supramolecular silver(I) complexes in which their structural diversity depends highly on the ligand isomerism of **L**¹-**L**³.¹⁶

The influence of the positional isomerism of the ionophores on the metal ion selectivity in the area of sensing materials, however, is not well explored especially for such thioxa macrocycles.^{17,18} In connection with these demands, **L**¹-**L**³ were employed as candidate systems. In this paper, we report the results for the silver(I) ion-selective electrodes

together with solvent extraction, NMR spectra and a crystal structure of the related silver(I) complex.



Results and Discussion

Solvent Extraction. The affinities of **L**¹-**L**³ towards metal ions were examined by a solvent extraction experiment using water-chloroform biphasic system. The extracted amount of each metal ion by the macrocyclic extractant

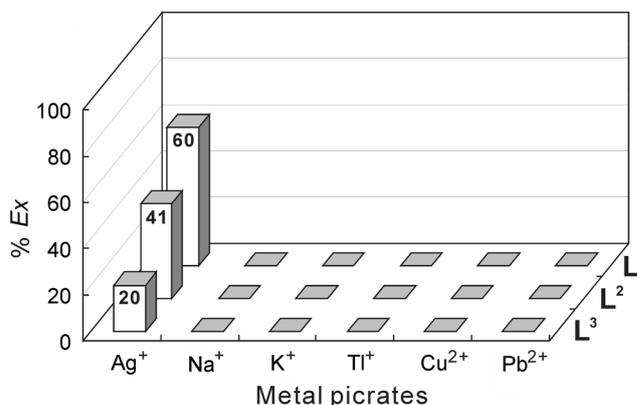


Figure 1. Percent extraction (%Ex) of metal picrates from aqueous to chloroform phase by **L**¹-**L**³.

was measured conveniently by the determination of picrate ion which extracted as a complexed ion-pair form, $M^{n+} \cdot L \cdot (\text{pic}^-)_n$.^{19,20} The extraction profiles conducted under the condition employed using equimolar amounts of the ionophores and single cations are shown in Figure 1.

The results show that no metal ions used were extracted except silver(I). And the extractability order for silver(I) is $L^1 > L^2 > L^3$. In general, the more stable the complexes with the metal ion, the more extractable it is.^{21,22} Thus, the increased extractability of silver(I) by L^1 is caused by more stable complexation due to the greater conformational flexibility than L^2 and L^3 . Taking the extraction results into account, the macrocycles L^1 - L^3 could be promising ionophores for silver(I) in the transport-assisted membrane-based ion-selective electrodes.

Silver(I)-Selective Electrodes. By employing L^1 - L^3 in conjunction with potentiometric PVC-membrane sensors, it was possible to observe silver(I) responses. Approximately 6.0 wt % of the ligand in PVC matrix yielded electrodes with almost Nernstian response toward silver(I) (55-60 mV/

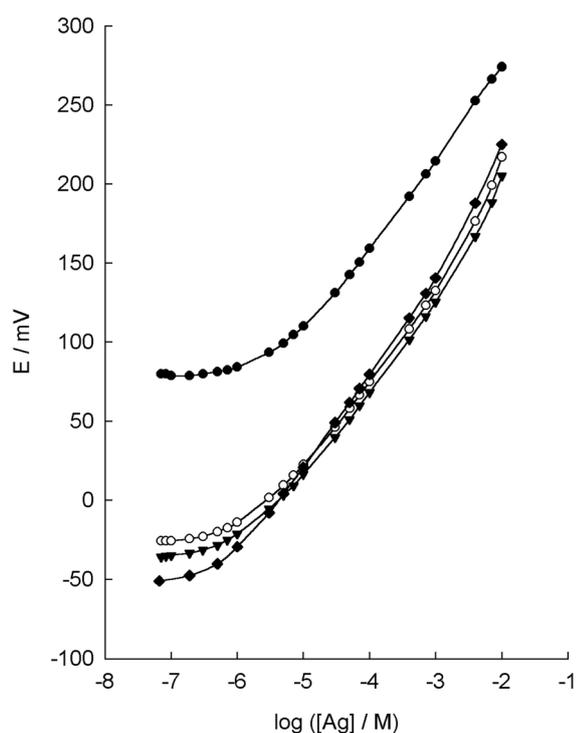


Figure 2. Potentiometric Ag(I) responses of the S₂O macrocycles-based electrodes: (●) E1, (○) E2, (▼) E3 and (◆) E4 in Table 1.

decade) over a wide range of the concentrations (Table 1). The equilibrium potentiometric responses of the proposed electrodes are shown in Figure 2. Almost Nernstian slopes are observed for silver(I) in 0.05 M Tris-nitric acid buffer, pH 9.0. Time required to reach 90% of the equilibrium mV values was less than 2 s. In terms of lifetime of the PVC membrane electrodes, more than 1 month of response stability was observed.

Table 2 provides the potentiometric selectivity coefficient data of the proposed membrane electrodes for the interfering cations relative to silver(I). Importantly, the data for the macrocycle-based electrodes such as E1 (L^1), E2 (L^2) and E3 (L^3) are comparable and show commonly excellent selectivity to silver(I) with respect to the most common monovalent and divalent metal cations investigated. It is also noted that the proposed electrodes show better or similar selectivity compared to the commercial Ag₂S-type electrode.²³ For example, the selectivity for the mercury(II) ($\log K_{\text{Ag}/\text{Hg}}$: -4.5 ~ -4.9) is obviously better than that of the Ag₂S-based one ($\log K_{\text{Ag}/\text{Hg}}$: -4.0). Doubtlessly, the mercury(II) is known as the most severely interfering ion for the silver(I)-selective membrane electrodes. These results may reflect, at least in part, that the magnitude of percent extraction for silver(I) less contribute to the silver(I) sensing than the extraction selectivity itself.

NMR Spectra of Complex System. The recognition properties of L^1 - L^3 toward silver(I) were investigated through the comparative ¹H NMR experiments²⁴ in CD₃CN

Table 2. Potentiometric selectivity coefficients, $\log k_{\text{Ag},Y}$ for the Ag(I)-ISEs

Cation	Electrode (Ionophore) ^a			Ag ₂ S
	E1 (L^1)	E2 (L^2)	E3 (L^3)	
Ag ⁺	0	0	0	0
NH ₄ ⁺	-4.9	-4.5	-4.6	-4.9
Na ⁺	-5.0	-4.9	-4.8	-5.1
K ⁺	-5.1	-4.9	-4.8	-4.9
Ba ²⁺	-5.0	-5.2	-4.9	-5.1
Ca ²⁺	-5.2	-5.0	-5.1	-5.2
Mg ²⁺	-5.3	-5.1	-5.1	-5.1
Cd ²⁺	-5.1	-5.1	-5.1	-5.1
Co ²⁺	-5.3	-5.2	-5.2	-5.2
Pb ²⁺	-4.46	-4.85	-4.75	-4.79
Hg ²⁺	-4.8	-4.5	-4.7	-4.0

^aAverage of three determinations.

Table 1. Formulation and electrochemical properties of Ag(I)-ISEs based on L^1 - L^3

Electrode No.	Membrane composition				Detection limit/ <i>M</i>	Slope/mV per decade ^c
	Ionophore ^{a,b}	PVC ^a	NPOE ^a	THF		
E1	2.0, L^1	32.0	66.0	1.5 mL	0.7×10^{-6}	56.1
E2	2.0, L^2	32.0	66.0	1.5 mL	1.0×10^{-6}	58.1
E3	2.0, L^3	32.0	66.0	1.5 mL	1.0×10^{-6}	62.5
E4	Ag ₂ S				0.8×10^{-6}	59.1

^aNumbers indicate mass-%. ^bE1-E3, average of three membranes; E4 is a Ag₂S-based solid-state electrode. ^cbetween detection limit and 1 mM.

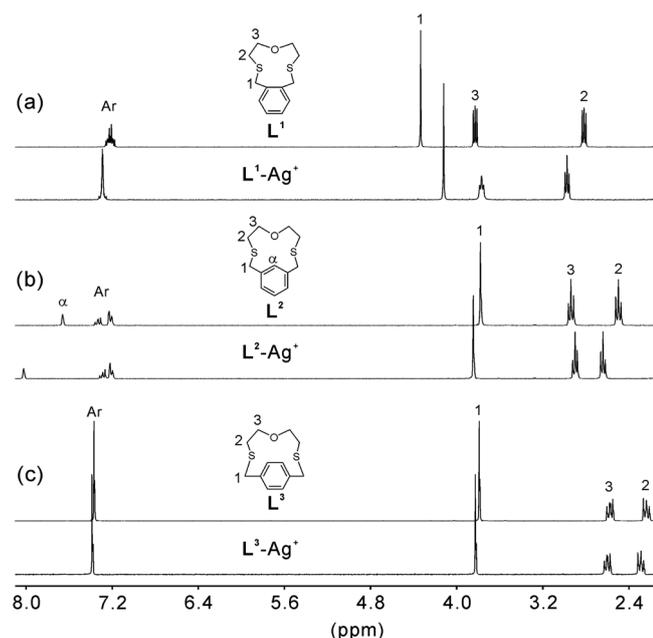


Figure 3. ¹H NMR spectra of (a) **L**¹ (top) and **L**¹-Ag⁺ (bottom), (b) **L**² (top) and **L**²-Ag⁺ (bottom), and (c) **L**³ (top) and **L**³-Ag⁺ (bottom) in CD₃CN. The complex solutions were prepared by dissolving equimolar amount of AgClO₄ in 10 mM solutions of each ligand.

(Fig. 3). The signals of three methylene (H_{1,3}) and aromatic (~7.4 ppm) protons for each free ligand were well resolved and identified. On complexation, commonly the peaks for H₁ and H₂ show relatively larger shift than those for H₃ and H_{ar} indicating that silver(I) is strongly coordinated by S donors, similar to the case in the solid state (see Fig. 5). In case of the triplet assigned to H₂ in each ligand, the order of magnitude of the lower field chemical shift variations is **L**¹ ($\Delta\delta = 0.16$) > **L**² ($\Delta\delta = 0.14$) > **L**³ ($\Delta\delta = 0.05$), which reflects the relative binding affinity of each ligand toward silver(I) in solution. This also agrees with the results from the extraction experiments and once again the relative binding affinity originated from the ligand isomerism less contribute to the silver(I) sensing.

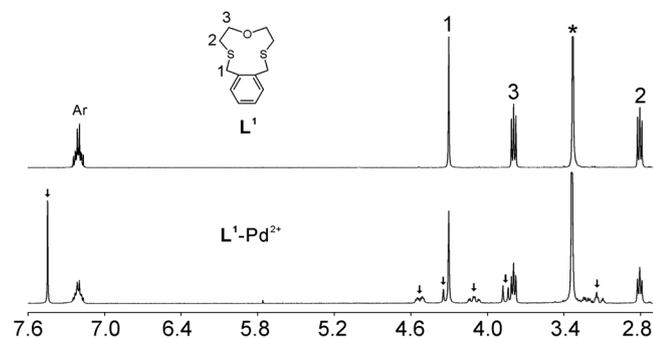


Figure 4. ¹H NMR spectra of **L**¹ (top) and **L**¹-Pd²⁺ (bottom) in DMSO-*d*₆. The complex solution was prepared by dissolving equimolar amount of K₂PdCl₄ in 10 mM solution of **L**¹. Complexed species is denoted by arrows. ‘*’ means water peak in DMSO-*d*₆. DMSO-*d*₆ used as solvent is due to the low solubility of the solutes in CD₃CN.

In addition, we also carried out the parallel NMR experiments for the **L**¹-Pd(II) complex system since the two Pd(II) complexes with **L**¹, *cis*-X₂**L**¹Pd(II) (X = NO₃, SCN) in solid state have been reported by us.²⁵ Partial ¹H NMR spectra for **L**¹, and an equimolar solution of **L**¹ and K₂PdCl₄ are shown in Figure 4. Contrary to the case of Ag(I) complexes presented in Figure 3, the Pd(II) complex shows the slow-exchange complexation on the proton NMR time scale. Two sets of peaks were found in the spectrum for **L**¹-Pd(II) complex. The complexed peaks (arrow marked) appear down field compared to those of free **L**¹ and broadened suggesting that the complex may exist in more complicated form in this solution. From the results, direct comparison of the complexation ability to those of Ag(I) complexes is not available. However we confirmed the **L**¹-Pd(II) complexation can occur in solution as well as in solid state.

Preparation and Crystal Structure of **L¹ Complex with AgClO₄.** Reaction of **L**¹ and AgClO₄ in molar ratio 1 : 1 in methanol afforded X-ray quality single crystals after slow evaporation of the solvent at room temperature. The crystal structure of the complex is shown in Figure 5. Selected geometric parameters are presented in Table 3. The crystallographic analysis of the complex reveals that its structure is a unique sandwich-type consisting of two macrocycles and one silver(I) center with formula [Ag(**L**¹)₂]ClO₄. The silver(I) center sits in a distorted tetrahedral coordination sphere with each ligand coordinated in bidentate fashion via two sulfur donor atoms to form a sandwich-type. The coordination of silver(I) center is particularly interesting as not only are four-coordinate silver(I) sandwich complex rare.²⁶⁻²⁸ The S-Ag-S bite angles vary considerably from S2-Ag1-S2A 95.81(3)° to S1-Ag1-S2A 115.31(2)°. The large deviation of the angles from tetrahedral coordination around Ag(I) may reflect the presence of additional long-range interactions between Ag atom and O-donors of the rings, which are slightly longer than the sum of Ag and O van der Waals radii (3.20 Å)²⁹ [Ag1...O1 3.284(2) Å]. The Ag-S distances range between 2.592(7) and 2.617(7) Å, which are slightly shorter than those of the similar system.²⁶⁻²⁸ Consequently, the metal center is completely shielded by two **L**¹s and therefore is unable to contact the anion or solvent.

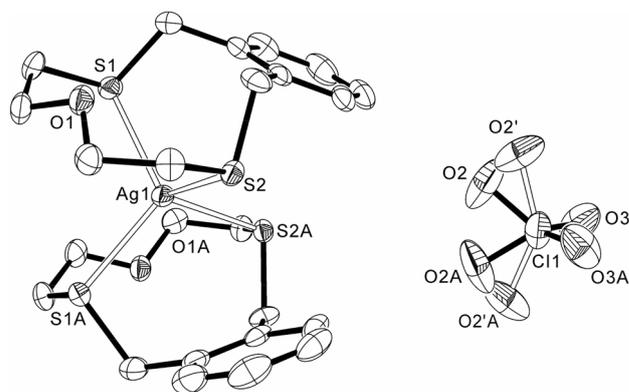


Figure 5. Sandwich structure of [Ag(**L**¹)₂](ClO₄). Hydrogen atoms are omitted. [Symmetry operation: $-x+1, y, -z+1/2$]

Table 3. Selected bond lengths (Å), bond angles (°) and torsion angles (°) for [Ag(L¹)₂]ClO₄

Ag(1)-S(1)	2.5618(7)	Ag(1)-S(2)	2.6172(7)
S(1)-Ag(1)-S(2)	107.80(2)	S(1)A-Ag(1)-S(1)	113.69(3)
S(2)-Ag(1)-S(2)A	95.81(3)	S(1)-Ag(1)-S(2)A	115.31(2)
S(1)-C(2)-C(1)-O(1)	58.46(32)	O(1)-C(12)-C(11)-S(2)	-57.10(30)

Symmetry operation: $-x+1, y, -z+1/2$

Conclusions

The S₂O-donor macrocyclic isomers L¹ (*o*-), L² (*m*-) and L³ (*p*-) were employed as a model system for silver(I) ionophores. No metal ions used were extracted except silver(I) by L¹-L³, and the extractivity (%*Ex*_{Ag}) associated with their complexation stability is in the order of L¹ > L² > L³. The result of comparative NMR study for the ligands and their silver(I) complexes in acetonitrile solutions also agree with that from the extraction experiments. The crystal structure for the sandwich-type complex of L¹ with silver(I) perchlorate, [Ag(L¹)₂]ClO₄ was also confirmed as an evidence of the strong complexation. Without exception the membrane electrodes based on these three macrocycles show excellent selectivity toward silver(I). From the comparable results we may conclude that the relative magnitude of extractivity or binding affinity of such macrocyclic isomers less contribute to the silver(I) sensing.

Experimental Section

Chemicals. All chemicals were of reagent grade and used without further purification. L¹ and L² were prepared according the literature method.^{12,30} L³ was synthesized from the reaction of 2-mercaptoethyl ether and α, α' -dichloro-*p*-xylene under high dilution condition. The detailed procedure will be reported elsewhere.

Solvent Extraction. A water-saturated chloroform solution of macrocycle (5.00 mL, 3.00 mM) and an aqueous solution of metal picrate (5.00 mL, 3.00 mM) were placed in a volumetric flask, and the flask was shaken in a thermostated water bath for 1 h at 25 ± 0.2 °C. After standing for 2 h, the concentration of metal picrate in the aqueous phase was determined at 356 nm with Scinco S-3100 UV/Vis spectrophotometer.

Preparation of Silver(I)-Selective Electrodes and Potentiometric Measurement. The ionophores (L¹-L³), PVC, and plasticizer (diisodecyl adipate) were used in the weight ratio of 2.0, 32.0, and 66.0. After allowing the membranes to cure, 5.5 mm diameter disks were cut out and placed in Phillips electrode bodies (ISE-561, Glasblaserei Moller, Zurich). As an internal filling solution, 1 mM AgNO₃ was used for all electrodes. Cell potentials were measured at ambient temperature (18 °C). The potentiometric cell used was as follows: Ag/AgCl(s)/4 M KCl saturated with AgCl/tris buffer/sample solution/ion-selective membrane/1 mM AgNO₃/AgCl(s)/Ag. The ion-selective and Ag/AgCl reference electrodes were connected through a high impedance

Table 4. Crystallographic data for [Ag(L¹)₂]ClO₄

Empirical formula	C ₂₄ H ₃₂ AgClO ₆ S ₄
Formula weight	688.06
Crystal system	Monoclinic
Space group	C2/c
<i>a</i> / Å	16.1634(8)
<i>b</i> / Å	13.1343(6)
<i>c</i> / Å	13.2017(6)
α / Å	101.1220(10)
<i>V</i> / Å ³	2750.0(2)
<i>Z</i>	4
<i>T</i> / K	173(2)
μ (Mo-K α)/mm ⁻¹	1.172
Reflections collected	8732
Independent reflections	3225 (<i>R</i> _{int} = 0.0887)
Final <i>R</i> 1, <i>wR</i> 2 indices [<i>I</i> > 2 σ (<i>I</i>)]	0.0364, 0.0785
<i>R</i> 1, <i>wR</i> 2 [all data]	0.0499, 0.0846

amplifier to an IBM AT-type computer equipped with an A/D converter. Sampling rate was adjusted to 1 Hz. This apparatus was used to determine the selectivity of each membrane toward silver(I) over other cations in the static mode. Selectivity coefficients, $k^{\text{pot}}_{\text{Ag}/\text{X}}$, were obtained by using the separate solution method at 1 mM cation concentration.

X-ray Crystallography. All data were collected on a Bruker SMART diffractometer equipped with a graphite monochromated MoK α ($\lambda = 0.71073$ Å) radiation source and a CCD detector. The frame data were processed to give structure factors using the program SAINT.³¹ The structure was solved by a direct method and refined by full matrix least squares against *F*² for all data using SHELXTL software.³² All non-H atoms were refined with anisotropic displacement parameters. A summary of data collection parameters is given in Table 4.

Supporting Information Materials. Crystallographic data for [Ag(L¹)₂]ClO₄ has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 601064.

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