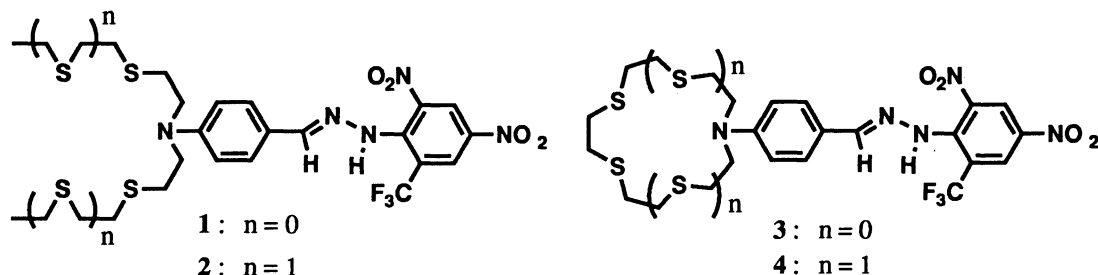


Silver Selectivity of Novel Monoazapolythioether Derivatives Bearing a Hydrazone Group in the Solvent Extraction

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Novel acyclic and cyclic monoazapolythioether derivatives incorporating a substituted hydrazone group were synthesized. The acyclic and the cyclic monoazapolythioether derivatives exhibited high Ag^+ ion selectivity in the extraction with 1,2-dichloroethane. The monoazapolythioether derivatives gave hypsochromic and bathochromic shifts in the visible absorption spectra when extracted Ag^+ ion from the aqueous phase of varying acidities into the organic phase.

Silver-selective ionophores have been investigated with thioether derivatives as neutral carriers for ion-selective electrodes,^{1,2)} and extractants.^{3,4)} The thioethers which have only sulfur atoms as coordination sites also form complexes with the other transition metal ions, such as Ni^{2+} , Cu^{2+} , Cu^+ , Zn^{2+} , Rh^{3+} , Cd^{2+} , Pt^{2+} , Co^{2+} , Hg^{2+} , etc. To improve the selectivity of silver ionophores, some sulfur atoms of a thioether were substituted for oxygen^{1,4)} and/or nitrogen atoms,⁵⁾ and some compounds with a variety of structures⁶⁾ were synthesized. Much attempts have been made to gain the highly ion-selective chromogenic crown compounds and to apply them to the determination of alkali metal ions.^{7,8)} Some silver-selective thiacyclic crown ethers with a chromophore, such as a picrylamino moiety, have also been presented.⁹⁾ It is well-known that hydrazone derivatives are a chromogen, exhibiting large bathochromic shifts of the absorption spectra caused by the deprotonation on the imino group, as well as a chromogenic complexing agent for certain transition metal ions. We have recently reported that oligoethylene glycol bis(hydrazone) derivatives exhibit high ion-selectivity and a large bathochromic shift (about 70 nm) accompanied by a great change in the molar absorptivity in the copper (II) ion extraction.¹⁰⁾ The incorporation of a 6-trifluoromethyl-2,4-dinitrophenylhydrazone moiety into acyclic and cyclic monoazapolythioether derivatives would lead to novel silver-selective chromoionophores.



The reactions of 1,5-diiodo-3-phenyl-3-azapentane with ethylmercaptane or ethyl 2-mercaptoethyl sulfide in the presence of Na metal in refluxing ethanol afforded the corresponding acyclic N-phenylmonoazapolythioethers. The cyclic analogues were synthesized by the cyclization reaction of 1,5-diiodo-3-phenyl-3-azapentane with 1,2-ethanedithiol or 3,6-dithia-1,8-octanedithiol in the presence of Cs_2CO_3 at 50-60 °C in DMF. Acyclic and cyclic monoazapolythioether hydrazones, **1-4**, were prepared by the formylation of the corresponding N-phenylmonoazapolythioethers with POCl_3 and DMF at room temperature, followed by the condensation reaction with 6-trifluoromethyl-2,4-dinitrophenylhydrazine in the presence of acetic acid in refluxing ethanol. These compounds were identified by the elemental analysis, infrared, ^1H -NMR and mass spectroscopic methods.¹¹⁾

In a 50 ml stoppered centrifuge tube were placed a 1,2-dichloroethane solution of monoazapolythioether derivative and an aqueous solution containing metal ion, and the mixture was shaken for 1 h at 25 ± 0.2 °C. The extraction behaviors of transition metal ions with the present thioether derivatives in 1,2-dichloroethane were studied by spectrophotometry for an organic solution. Figure 1 shows the metal ion extraction behavior with acyclic monoazatetrathioether **2** under the conditions where an aqueous solution contains a metal sulfate and is kept at pH 6.0, the compound **2** being dissolved in 1,2-dichloroethane. The high extraction selectivity of **2** for Ag^+ over Cu^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} and Tl^+ is exhibited. The molar absorptivities of **2** and Ag^+ -**2** complex are $2.4 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ at $\lambda_{\text{max}} = 439 \text{ nm}$ and $3.9 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ at $\lambda_{\text{max}} = 500 \text{ nm}$, respectively. This extraction selectivity was supported by atomic absorption spectrometry applied to the aqueous phase in the alternate extraction experiment, as shown in Table 1. The cyclic monoazatetrathioether **4** exhibited similar extraction selectivity. However, the Ag^+ extractability of **4** was less than that of the acyclic one **2**. This is probably because the sulfur atoms of the acyclic compound are able to provide preferable circumstances to associate Ag^+ compared to those of the cyclic one when they form complexes with Ag^+ , since the acyclic compound **2** has more flexible structure than the cyclic one **4**. Extractabilities of the acyclic and the cyclic monoazadithioethers, **1** and **3**, for Ag^+ ion are decreased dramatically compared to those of monoazatetrathioethers, due to poor cation-complexing abilities of the monoazadithioether moieties.

The extraction of Ag^+ with the acyclic monoazatetrathioether **2** was carried out under the different proton

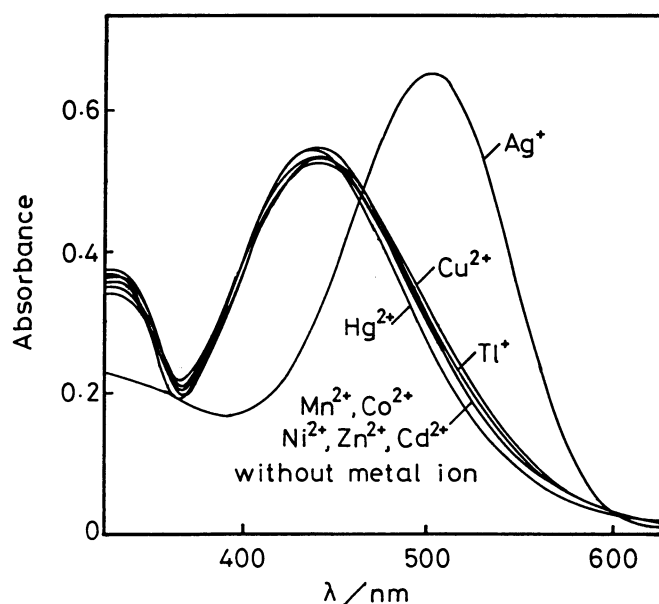


Fig.1. Spectral changes in the organic phase in the extraction of various metal ions with **2** at 25 °C. Organic phase: [**2**] = $2.0 \times 10^{-5} \text{ M}$ in 1,2-dichloroethane, 12 ml; aqueous phase: [metal ion] = $1.0 \times 10^{-3} \text{ M}$ using metal sulfate at pH 6.0, 12 ml. 1 M = 1 mol dm^{-3} .

Table 1. Solvent extraction of metal ions with thioether derivatives^{a)}

Compound	Extraction (%)							
	Mn ²⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺	Ag ⁺	Cd ²⁺	Hg ²⁺
1	0	0	0	0	0	0	0	<5
2	0	0	0	2	1	84	0	<5
3	0	0	0	0	0	0	0	<5
4	0	0	0	4	2	30	0	<5

a) Extraction conditions: organic phase: [compound] = 1.0×10^{-4} M. 5 ml; aqueous phase: [metal ion] = 2.0×10^{-5} M using metal sulfates except for HgCl₂ at pH 6.0. 5 ml. Metal ion in the aqueous phase were determined by the atomic absorption spectrophotometry except for Tl⁺ and Hg²⁺ which were detected by ICP-AES.

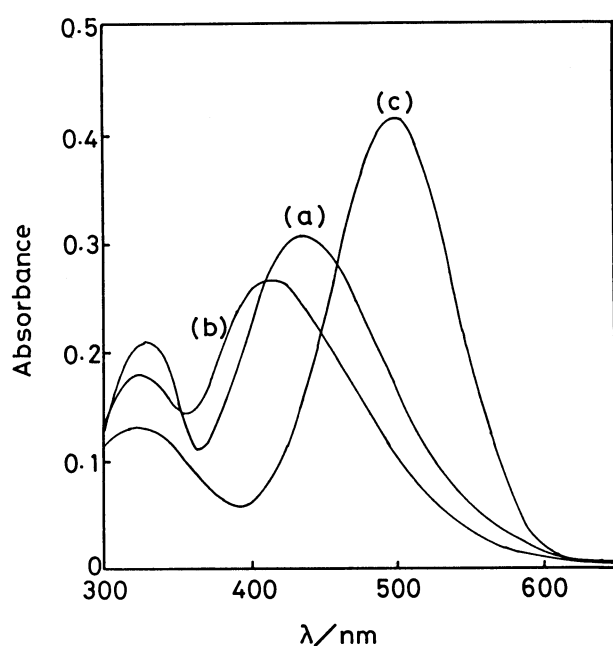


Fig. 2. Effects of pH in the aqueous solution on the spectra in the organic phase in the extraction of Ag⁺ with 2 at 25 °C. Organic phase: [2] = 1.1×10^{-5} M in 1,2-dichloroethane. 12 ml; aqueous phase: 12 ml (a) without metal ion, (b) [AgNO₃] = 2.0×10^{-4} M at pH 2.6, (c) [AgNO₃] = 2.0×10^{-4} M at pH 7.1.

concentrations (pH) in the aqueous solution containing AgNO₃. The interesting spectral changes in the organic solution are exhibited (Fig.2). In the extraction of Ag⁺ from an acidic aqueous solution (below pH 4.0), a hypsochromic shift, $\lambda_{\max} = 400$ nm, of the acyclic compound 2 in the visible region was observed in the organic solution. On the other hand, the extraction from a neutral solution (pH 6.0-7.0) exhibited a bathochromic shift, $\lambda_{\max} = 500$ nm, in the extract. It is explained that the hypsochromic and the bathochromic shifts are attributed to the formation of an ion-pair complex between a positively charged silver complex of the ligand and a NO₃⁻ and a complex between silver and the deprotonated form of the ligand, respectively. The bathochromic shifts are generally observed in the complexation of metal ion with chromoionophore bearing the proton-dissociable anionic chromophore.⁷⁾ The hypsochromic shift caused by complexation of 2 with Ag⁺ is similar to the spectral characteristics of donor-acceptor-type chromoionophores such as N-(4-nitrophenylazo)phenyl-aza-18-crown-6.⁸⁾ The cyclic compound 4 exhibited similar spectral changes as those of the acyclic one 2.

Further details of the investigation are in progress.

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- 11) Elemental analyses and spectroscopic data of the compounds, **1** - **4**, are as follows: **1**: MS (EI) $m/e=545$ (M^+); 1H -NMR ($CDCl_3$) $\delta=1.15-1.40$ (m, 6H), 2.44-2.81 (m, 8H), 3.48-3.70 (m, 4H), 6.58-7.70 (m, 4H), 7.88 (s, 1H), 8.69-9.17 (m, 2H), 11.13 (s, 1H); IR (KBr) (cm^{-1}): 3300, 2900, 1670, 1600, 1540, 1320, 1260, 1240; Anal Found: C, 48.28; H, 4.65; N, 13.05%. Calcd for $C_{22}H_{26}N_5O_4S_2F_3$: C, 48.43; H, 4.80; N, 12.84%. **2**: MS (EI) $m/e=665$ (M^+); 1H -NMR ($CDCl_3$) $\delta=1.15-1.40$ (m, 6H), 2.40-2.87 (m, 16H), 3.50-3.72 (m, 4H), 6.58-7.70 (m, 4H), 7.88 (s, 1H), 8.69-9.17 (m, 2H), 11.13 (s, 1H); IR (KBr) (cm^{-1}): 3300, 2900, 1670, 1600, 1550, 1330, 1270, 1240; Anal Found: C, 46.94; H, 5.12; N, 10.35%. Calcd for $C_{26}H_{34}N_5O_4S_4F_3$: C, 46.90; H, 5.15; N, 10.52%. **3**: MS (EI) $m/e=515$ (M^+); 1H -NMR ($CDCl_3$) $\delta=2.74-3.22$ (m, 8H), 3.71-3.88 (m, 4H), 6.80-7.70 (m, 4H), 7.95 (s, 1H), 8.69-9.20 (m, 2H), 11.13 (s, 1H); IR (KBr) (cm^{-1}): 3300, 2900, 1670, 1600, 1540, 1320, 1260, 1240; Anal Found: C, 46.20; H, 3.90; N, 13.48%. Calcd for $C_{20}H_{20}N_5O_4S_2F_3$: C, 46.60; H, 3.91; N, 13.59%. **4**: MS (EI) $m/e=635$ (M^+); 1H -NMR ($CDCl_3$) $\delta=2.67-2.88$ (m, 16H), 3.50-3.78 (m, 4H), 6.60-7.68 (m, 4H), 7.88 (s, 1H), 8.69-9.17 (m, 2H), 11.13 (s, 1H); IR (KBr) (cm^{-1}): 3300, 2900, 1670, 1600, 1550, 1330, 1270, 1240; Anal Found: C, 45.10; H, 4.34; N, 10.79%. Calcd for $C_{24}H_{28}N_5O_4S_4F_3$: C, 45.34; H, 4.44; N, 11.01%.

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