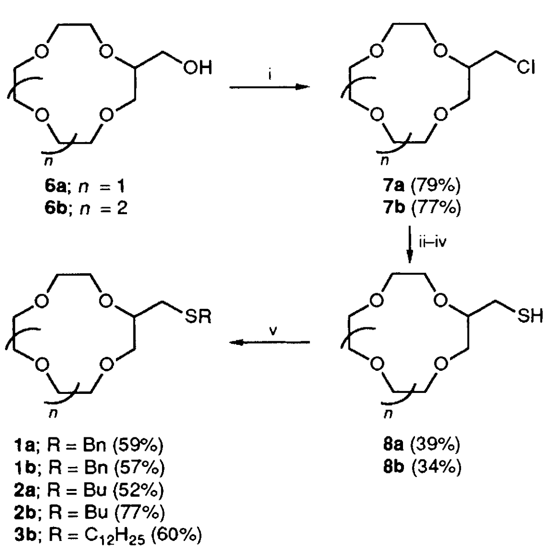
Remarkably Selective Binding of Silver Ion by Thiolariat Ether with a 15-Crown-5 Ring

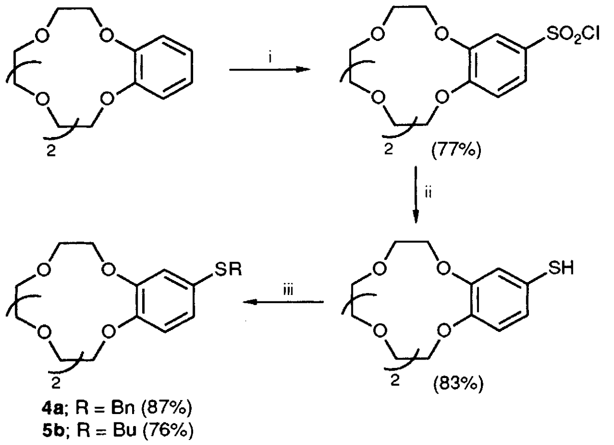
Tatsuya Nabeshima,* Katsunori Nishijima, Naoko Tsukada, Hiroyuki Furusawa, Toshiyuki Hosoya and Yumihiko Yano
Department of Chemistry, Gunma University, Kiryu, Gunma 376, Japan

The thiolariat ether, which is a lariat ether with an oxygen atom in the side arm replaced by a sulfur atom, exhibits a high selectivity to silver ion among alkali and heavy metal ions because of synergistic ligation of the crown ether and the one sulfur outside the ring.

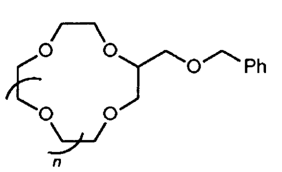
Crown ethers bearing side arm(s), such as lariat ethers and double armed crown ethers, reveal a selective binding affinity to a variety of metal ions, amino acids and cationic organic guests.[1,2] The affinity can be modulated effectively by simply changing the type of side arm, whereas the structure of the cyclic framework is maintained. The introduction of a side arm into a crown ring has been easily performed to give many kinds of lariat ethers.[3,4] No example, however, has been reported on thiolariat ethers, *i.e.* lariat ethers where the oxygen atom in the side arm is replaced by a sulfur atom. We report the first



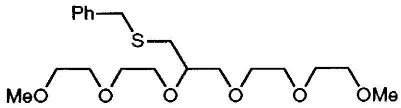
Scheme 1 *Reagents*: i, $SOCl_2$, py, PhH; ii, tu; iii, KOH; iv, HCl; v, RBr, EtONa, EtOH (R = Bn, Bu, $C_{12}H_{25}$)



Scheme 2 *Reagents*: i, $ClSO_3H$, $CHCl_3$; ii, LAH, tetrahydrofuran; iii, RBr, EtONa, EtOH (R = Bn, Bu)



9; n = 1
10; n = 2



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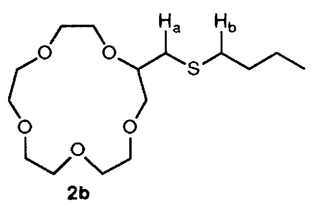

2b

Table 1 Solvent extraction of transition and heavy metal ions

	Extractability (%)[a]								
Host	Ag^+	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}	Hg^{2+}[b]
1a	25	1	5	2	1	1	2	1	38
1b	95	2	4	1	3	1	1	4	39
2a	24	2	3	2	2	2	3	3	37
2b	95	2	2	2	3	3	3	5	42
3b	97	2	2	2	3	4	3	5	46
4	10	2	3	3	3	2	2	4	32
5	11	–	–	–	–	–	1	2	33
9	5	2	1	1	1	1	1	3	33
10	28	1	3	1	2	3	1	6	31
11	55	2	2	2	4	2	4	4	53
12	12	–	–	–	–	–	–	–	33
none	2	1	3	1	1	1	1	2	31

[a] Org. layer (CH_2ClCH_2Cl): [host] = 1×10^{-4} mol dm^{-3}; aq. layer: [Pic^-H^+] = 3×10^{-5} mol dm^{-3} and [metal nitrate] = 0.01 mol dm^{-3}.
[b] Aq. layer: [Pic^-H^+] = 3×10^{-5} mol dm^{-3} and [$Hg(NO_3)_2$] = 5×10^{-4} mol dm^{-3}.

example of thiolariat ethers and their remarkably high Ag^+ selectivity, which is surprisingly achieved by the introduction of only one sulfur atom outside the 15-crown-5 cavity.

Thiolariat ethers (**1**–**5**) were synthesized by the reaction of the corresponding mercaptocrown ether with alkyl or benzyl (Bn) halides in the presence of EtONa in EtOH, as shown in Scheme 1. Hydroxymethylcrown ethers **6**[5] were converted into the corresponding chloromethylcrowns **7** by the treatment of $SOCl_2$ and pyridine (py) in benzene in good yields. Mercaptomethylcrown ethers **8** were prepared from **7** *via* thiuronium salt by using thiourea (tu). For **4** and **5**, 4′-mercaptobenzo-15-crown-5 was synthesized by lithium aluminium hydride (LAH) reduction of 4′-chlorosulfonylbenzo-15-crown-5, which was prepared from chlorosulfonic acid and benzo-15-crown-5 in $CHCl_3$ at 0 °C (Scheme 2).

Solvent extraction experiments ($ClCH_2CH_2Cl$–H_2O) were carried out to evaluate the affinity of **1**–**5** for metal ions. The selectivity sequence of the thiolariat ethers for alkali metal ions is almost the same as that of the corresponding lariat ethers (**9**, **10**).† This fact reveals that the sulfur atom in the side chain does not affect the affinity significantly[6–8] and that the selectivity results essentially from the crown ring as expected. In contrast, toward heavy metal ions only thiolariat ethers with a 15-crown-5 ring (**1b**–**3b**) exhibit quite high Ag^+ selectivity (Table 1). The extractabilities in **1b**, **2b** and **3b** are 95, 95 and 97%, respectively. However, affinity for Ag^+ is dramatically decreased in the thiolariat ether with a 12-crown-4 ring [extractability (ex) = 25% in **1a**, 24% in **2a**]. A linear compound **11** and dodecyl ethyl sulfide **12** also show a smaller extractability toward Ag^+ (ex = 55% in **11**, 12% in **12**). In addition the low affinity towards Ag^+ was also observed in **4** (ex = 10%). From the inspection of the space-filling model, the sulfur atom in **4** cannot coordinate Ag^+, when the ion is bound in the crown ring. Considerable decrease of affinity was also seen in the lariat ether (**9**, **10**), although Ag^+ is extracted most preferentially by **10** (ex = 28%) among the heavy metals.[8,9] Much lower extractability is found when the cyclic framework of **10** is changed into smaller one **9**, a 12-crown-4 derivative (ex = 5%). Hence, the extraction experiments clearly indicate that the extremely high Ag^+ selectivity is achieved by synergistic coordination of a suitable sized 15-crown-5 and the sulfur atom. Noteworthy is that thiolariat ethers (**1b**–**3b**) exhibit very low affinity to Pb^{2+} and Hg^{2+}, when the extractability in the absence of the crown ethers is taken into account (ex = 31%, Hg^{2+}). It is usually very difficult to obtain a high preference of Ag^+ over Pb^{2+} and Hg^{2+} by using crown ether derivatives, though hetero atoms,

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† Org. layer (CH_2ClCH_2Cl): [host] = 1×10^{-4} mol dm^{-3}; aq. layer: [Pic^-M^+] = 3×10^{-5} mol dm^{-3} and [metal chloride] = 0.10 mol dm^{-3}; *e.g.* extractabilities (%) in **1b** and **10** are 16 and 21 for Na^+; 19 and 20 for K^+; 15 and 17 for Rb^+, respectively. ex(%) = 100 (3×10^{-5} – [Pic^-M^+]$_{aq}$)/3×10^{-5}. (Pic = picrate).

such as sulfur and nitrogen, in a crown ring play a significant role to bind heavy metals specifically. For instance, thiacrowns, crown ethers having sulfur atoms in the ring, are known to show high and specific binding behaviour to heavy metal ions, such as Hg^{2+} and Ag^+.[7,8,10–12] Therefore, it is a surprising phenomenon that the high selectivity is caused by a synergistic coordination of a usual 15-crown-5 ring and only one sulfur atom located in the vicinity of and outside the cyclic recognition site.[13] The cooperative ligation is also supported strongly by ^1H NMR spectroscopy. Addition of an excess amount of silver nitrate gives rise to noticeable spectral changes, *e.g.* the down field shift of H_a and H_b of **2b** (0.28 and 0.17 ppm, respectively) in $CDCl_3$.

The interesting framework of thiolariat ether will open a variety of applications to novel detection and recovery methods of Ag^+, which are under investigation in our group.

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