Solvent Extraction of Transition Metal Ions with Acyclic Polyethers Incorporating Several Heteroatoms and Bearing Heterocyclic Moieties as End Groups

Hidefumi Sakamoto,* Shigeki Ito, and Makoto Otomo
Department of Applied Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466

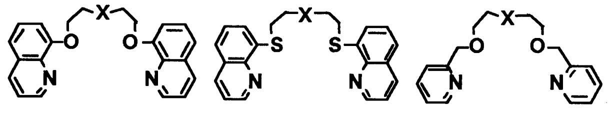
(Received October 3, 1994)

Nine acyclic polyethers incorporating oxygen, nitrogen and/or sulfur atoms were synthesized, which possess two heterocyclic groups at both ends of an ether chain, and metal ion extractabilities of these compounds were estimated using 1,2-dichloroethane - H_2O system. On the solvent extraction of some transition metal ions as the nitrates, Ag^+, Cu^+ and Hg^{2+} were more effectively extracted with most of the reagents than the other metal ions. Addition of picrate ion into the aqueous phase of $AgNO_3$ increased Ag^+ extractability remarkably.

Some complexation studies of acyclic polyether, which contains the same kind of hetero-atoms such as oxygen, sulfur and nitrogen atoms, with metal ions have been investigated. Acyclic polyethers incorporating only oxygen atom which is known as a hard donor atom have complexability with alkali metal and alkaline earth metal ions.[1,2] On the other hand, complexabilities with transition metal ions were presented for acyclic polythioethers[3-5] and polyamines[6,7] which contain softer donor atoms. Complexes of acyclic polyethers containing mixed heteroatoms with metal ions, however, have not been reported so much.[8-12] Especially, mixed-donor acyclic polyethers incorporating sulfur and nitrogen atoms have been rarely presented while analogous cyclic polyethers have been vigorously investigated by Lindoy and co-workers.[13,14]

We previously reported Ag^+ selective extraction using novel acyclic monoazapolythioether hydrazones.[15] In this paper, extraction behaviors of nine acyclic polyethers incorporating oxygen, nitrogen and/or sulfur atoms toward transition metal ions are described.

The reactions of 3-phenyl-1,5-bis(*p*-toluenesulfonyloxy)-3-azapentane with oxine or thiooxine in the presence of sodium ethoxide in refluxing ethanol afforded **1a** and **1b**, respectively. **2a** and **2b**, and **3a** and **3b** were synthesized by the reactions of 1,5-dichloro-3-oxapentane with oxine or thiooxine, and of 1,5-dibromopentane with oxine or thiooxine, respectively, in a similar manner as noted above. The reaction of 2-chloromethylpyridine hydrochloride with the appropriate diol derivatives in the presence of NaH in refluxing 1,4-dioxane yielded **1c**, **2c** and **3c**. These compounds were purified with alumina or silica-gel column chromatography, vacuum distillation and/or recrystallization techniques and were identified by the elemental analysis, ^1H-NMR and mass spectroscopic methods.



-X-			
Ph-N< :	**1a**	**1b**	**1c**
-O- :	**2a**	**2b**	**2c**
$-CH_2-$:	**3a**	**3b**	**3c**

In a 50 ml stoppered centrifuge tube were placed 1,2-dichloroethane solution of ligand and aqueous solution which contained metal nitrate except for Cu^+ and which was kept at pH 6.0 by MES-KOH buffer solution except for Ag^+ of which extraction was carried out at pH 9.0, being adjusted by CHES-tetramethylammonium hydroxide (TMAOH) buffer solution. On the extraction of Cu^+, hydroxylamine sulfate was further added into the aqueous solution containing $Cu(NO_3)_2$ to reduce Cu^{2+} to Cu^+. In order to estimate the effect of picrate ion on a Ag^+ extraction from an aqueous into an organic phase, picric acid was added into the aqueous phase containing $AgNO_3$. The mixture of the organic and the aqueous solutions was shaken for 1 h at 25.0±0.2 °C. The concentration of metal ion extracted into the organic phase was evaluated by that of metal ion remaining in the aqueous phase determined with atomic absorption spectrophotometry or ICP-AES for Hg^{2+}, Tl^+ and Pb^{2+}. The distribution of any ligand into the aqueous phase was rarely observed.

Percent extractions of transition metal ions as nitrates with the ligands are summarized in Table 1. It is shown that Cu^+, Ag^+ and Hg^{2+}, being classified into soft metal ion, were extracted by all of the ligands from the aqueous into the organic phase. These extraction behaviors of the ligands would be dependent on the complexabilities of the ligands with metal ions. Nitrogen atom of the terminal quinolyl and pyridyl groups are known to have high affinitiy for some transition metal ions. For 3-phenyl-3-aza-pentane derivatives, **1b** exhibited higher extractability toward these metal ions than **1a** and **1c** which had similar extractabilities each other. The ligands, **1b**, **2b** and **3b**, incorporating sulfur atom which is classified into soft donor atom extracted these metal ions more effectively than the other ligands. Such a high extractability toward Cu^+ is attributed to the high affinity of sulfur atom for class b metal ion; being well-known for cyclic- and acyclic-polythioethers as well.[4] **1b** and **3b** exhibited extractabilities toward Pb^{2+}, and only **1b** showed a little extractability toward Cu^{2+}. Among the ligands incorporating sulfur atom, **2b** extracted Cu^+ most effectively and **1b** and **3b** exhibited similar extractabilities each other.

Determination of extraction constants (K_{ex}) of $AgNO_3$ with the ligands were carried out by keeping $AgNO_3$ concentration constant and changing the ligand concentration. The value of the extraction constant was obtained graphically from the plots of $\log D/[NO_3^-]$ *vs.* $\log[\text{ligand}]_o$ according to the following equation: $\log D/[NO_3^-] = \log K_{ex} + m\log[\text{ligand}]_o$, where D, K_{ex}, and m mean distribution constant of Ag^+, extraction constant and the number of ligand bonded to a Ag^+, respectively. The subscript "o" denotes an organic phase. For all of the ligands, straight lines with a slope of unity, $m = 1$, were obtained, meaning extractions of 1:1 complex of Ag^+ and ligand from the aqueous into the organic phase. The extraction constants are summarized in Table 2. Thioether derivatives exhibited higher Ag^+ extractability, which decreased in the order **2b** ≥ **1b** > **3b**, than the other kinds of ligands, as mentioned above.[4,15,16] On the comparison of Ag^+ extractabilities among the ligands bearing the

Table 1. Extraction (%) of metal nitrates with some ligands[a]

Ligand	Extraction (%)									
	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{+}	Cu^{2+}	Zn^{2+}	Ag^{+b}	Hg^{2+}	Tl^{+}	Pb^{2+}
1a	1	0	0	8	0	0	1	7	0	0
1b	0	0	1	43	7	0	34	21	0	12
1c	0	0	1	4	0	0	6	5	0	0
2a	1	0	1	5	0	0	4	7	0	0
2b	1	0	1	52	0	0	54	14	0	0
2c	0	0	1	6	0	0	5	5	0	0
3a	1	0	1	4	2	0	1	4	0	0
3b	0	0	2	42	1	0	6	12	0	7
3c	0	0	1	5	0	0	2	3	0	0

[a]Extraction conditions: organic phase: [ligand] = 7.0×10^{-5} M, 5 ml; aqueous phase [metal nitrate] = 7.0×10^{-5} M, pH 6.0, 5 ml. The errors were less than ±3%. [b]Extraction conditions: organic phase: [ligand] = 1.0×10^{-4} M, 5 ml; aqueous phase $[Ag^+]$ = 1.0×10^{-4} M, [TMAOH] = 1.0×10^{-3} M, pH 9.0, 5 ml. The errors were less than ±4%.

Table 2. Extraction constants (K_{ex}) of ligands toward silver nitrate[a] and picrate[b]

Ligand	Extraction constant of $AgNO_3$ ($\log K_{ex}$)	Extraction constant of AgPic[c] ($\log K_{ex}$)
1a	5.5±0.2	8.4±0.2
1b	6.7±0.1	8.8±0.1
1c	5.7±0.1	8.1±0.1
2a	5.5±0.1	8.3±0.2
2b	7.1±0.1	9.2±0.1
2c	5.7±0.2	8.3±0.2
3a	5.1±0.1	7.8±0.2
3b	5.8±0.2	8.2±0.2
3c	5.2±0.1	7.6±0.1

[a]Extraction conditions: organic phase: [Ligand] = 1.0×10^{-4} – 3.0×10^{-3} M ; aqueous phase: $[AgNO_3]$ = 1.0×10^{-4} M, [TMAOH] = 1.0×10^{-3} M, pH 9.0. [b]Extraction conditions: organic phase: [Ligand] = 1.0×10^{-5} – 1.8×10^{-4} M ; aqueous phase: $[AgNO_3]$ = 1.0×10^{-4} M, [picric acid] = 2.0×10^{-4} M, pH 9.0. [c]AgPic is silver picrate.

same terminal units, the tendency of **1a**, **2a** > **3a**, which carry 8-quinolyloxy moiety, is similar to that of **1c**, **2c** > **3c** which have 2-pyridylmethoxy moiety instead of 8-quinolyloxy moiety as the terminal unit. It is obvious from these results that nitrogen and oxygen atoms on the bridge chains relate to the coordination to the silver ion.

On the addition of picrate ion into the aqueous phase, the extraction constants were also determined in a similar manner as described above, and were furthermore determined by keeping ligand concentration constant and changing picrate ion concentration according to the following equation: $\log D/[\mathrm{ligand}]_o = \log K_{ex} + n\log[\mathrm{picrate\ ion}]$, where n is the number of picrate ion extracted with a complex ion of a ligand and Ag^+. The plots of $\log D/[\mathrm{ligand}]$ *vs.* log[picrate ion] also gave a straight line with a slope of 1, that is $n = 1$, for all of the ligands. These results demonstrate the extraction of 1:1:1 complexes of Ag^+, ligand and picrate ion into the organic phase. The addition of picrate ion into the aqueous phase increased extractability of Ag^+ as shown in Table 2. Such an enhancement of the Ag^+ extraction is because the distribution of an ion-pair of Ag^+-ligand complex ion and counter anion into the organic phase is increased due to much higher lipophilicity of picrate ion than that of nitrate ion.[17]

The present work was partially supported by Salt Science Research Foundation.

References and Notes

1 R. Wakita, K. Fujiwara, Y. Nakatsuji, and M. Okahara, *Chem. Lett.*, **1990**, 1897.
2 F. Vögtle and E. Weber, *Angew. Chem., Int. Ed. Engl.*, **18**, 753 (1979).
3 Z. Brzozka, *Analyst (London)*, **114**, 1431 (1989).
4 K. Chayama and E. Sekido, *Anal. Sci.*, **3**, 535 (1987).
5 K. Chayama, Y. Tamari, H. Tsuji, Y. Kusaka, and E. Sekido, *Anal. Sci.*, **7 (Supplement)**, 57 (1991).
6 R. D. Hancock and A. E. Martell, *Chem. Rev.*, **89**, 1875 (1989) and references cited therein.
7 J. Aragó, A. Bencini, A. Bianchi, E. Garcia-España, M. Micheloni, P. Paoletti, J. A. Ramirez, and P. Paoli, *Inorg. Chem.*, **30**, 1843 (1991).
8 M. G. B. Drew, D. A. Rice, and K. M. Richards, *J. Chem. Soc., Dalton Trans.*, **1980**, 2503.
9 M. Kodama, T. Koike, N. Hoshiga, R. Machida, and E. Kimura, *J. Chem. Soc., Dalton Trans.*, **1984**, 673.
10 B. Adhikary and C. R. Lucas, *Inorg. Chem.*, **33**, 1376 (1994).
11 D. Parker, J. -M. Lehn, and J. Rimmer, *J. Chem. Soc., Dalton Trans.*, **1985**, 1517.
12 S. Liu, C. R. Lucas, R. C. Hynes, and J. -P. Charland, *Can. J. Chem.*, **70**, 1773 (1992).
13 K. R. Adam, M. Antolovich, D. S. Baldwin, P. A. Duckworth, A. J. Leong, L. F. Lindoy, M. McPartlin, and P. A. Tasker, *J. Chem. Soc., Dalton Trans.*, **1993**, 1013.
14 L. F. Lindoy, *Pure & Appl. Chem.*, **61**, 1575 (1989).
15 H. Sakamoto, J. Ishikawa, T. Mizuno, K. Doi, and M. Otomo, *Chem. Lett.*, **1993**, 609.
16 S. S. Lee, J. H. Jung, S. B. Cho, J. S. Kim, J. Kim, and S. -J. Kim, *Bull. Korean Chem. Soc.*, **13**, 704 (1992).
17 O. Heitzsch, K. Gloe, H. Stephan, and E. Weber, *Solvent Extr. Ion. Exch.*, **12**, 475 (1994).