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An Aminimide as an Extractant for Heavy- and Transition Metal Cations

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The compounds possessing two aminimide groups directly attached to each other showed moderate affinity toward heavy- and transition metal cations on the liquid-liquid extraction. It is thought that this takes the five membered ring chelation which results in high lipophilic complexations to extract the cations into the organic phase.

Since the first aminimides were prepared in 1930 by Curtius1-5) by the reaction of sulfonyl azides with pyridine, aromatic and aliphatic aminimides have been extensively examined on their syntheses, properties, and some applications.6) We have dealt with aliphatic aminimides containing a quaternary ammonium nitrogen bound to a carbonyl stabilized imino nitrogen, and have examined their phase transfer catalytic ability,7) nonionic surfactant properties,8) and micellar catatytic ability.9) Although their aromatic derivatives can make complexes with heavy- and transition metal cations, they hardly extract the metal cations into nonpolar solvents probably due to their high hydrophilicities. In this communication, we would like to report the relationships between their metal-ion extractabilities and the structures.

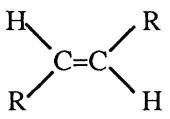
All aminimides were prepared by the reaction of carboxylic acid ester with aminimine derived from 1,1-dimethylhydrazine and epoxide (Slagel's method).10) Aminimides **1** to **7** have been already prepared and used as phase transfer catalysts,7) but bisaminimides **8** and **9** were newly prepared and showed expected analytical data including characteristic infrared absorption bands (C=O) at 1570-1585 cm^{-1} which are lower by 145-155 cm^{-1} than those of the esters used as starting materials. Analytical data of the new compounds are given.11) Only fumarate derivative of bisaminimide **8** were quantitatively formed even if Slagel's reaction was carried out by using maleic acid ester. Apparently, cis-trans isomerization occur during the reaction at room temperature in 2-propyl alcohol. Investigation of the reaction mechanism is now in progress. Synthesis of *o*-isomer of **9** was not achieved by Slagel's reaction under a variety of conditions probably due to the steric hindrance. It formed monosubstituted aminimide ester and its hydrolysis product predominantly. Aminimides obtained were used as solvent extractants. Thus, a dichloromethane solution of an aminimide (1×10^{-4} mol dm^{-3}, 5.0 ml) and an aqueous metal nitrate solution (1×10^{-3} mol dm^{-3}, 5.0 ml) buffered to pH 5.3 (CH_3COOH-CH_3COONa, 0.1 mol dm^{-3}) were shaken for 2 h at ambient temperature (20-22°C). After the mixture was separated, an aliquot of the organic layer was evaporated, and dilute HNO_3 aqueous solution was added to the residue, and finally the extracted cation was analyzed by atomic absorption analysis. Results are summarized in Table 1.

Four cations, Cu^{2+}, Ni^{2+}, Ag^{+}, and Pb^{2+} were chosen for preliminary experiments by the following reasons: *i.e.,* copper ion is known to complex with aromatic aminimides.[12] Nikel ion can complex with an aminimide because it belongs to the same periodic group VIII in the periodic table as palladium and platinum which form complexes with aromatic aminimides and their analogs, sulfilimines, respectively.[12-16] Both silver and lead cations show high affinity toward nitrogen atom contained in host ligands.[17]

Table 1. Extraction of metal cations with lipophilic aminimides[a]

Compound[b]	$R^1Me_2\overset{+}{N}\overset{-}{N}COR^2$		Extractability /%			
	R^1	R^2	Cu^{2+}	Ni^{2+}	Ag^{+}	Pb^{2+}
1	$HOCH_2CH_2$	$C_{11}H_{23}$	0	0	0	0
2	$C_{10}H_{21}CH(OH)CH_2$	CH_3	0	0	0	0
3	$C_{10}H_{21}CH(OH)CH_2$	C_2H_4OH	0	0	0	0
4	$C_6H_{13}CH(OH)CH_2$	$CO\overset{-}{N}\overset{+}{N}Me_2CH_2CH(OH)C_6H_{13}$	13	16	17[c]	2
5	$C_6H_{13}CH(OH)CH_2$	$(CH_2)_2CO\overset{-}{N}\overset{+}{N}Me_2CH_2CH(OH)C_6H_{13}$	0	0	0	0
6	$C_6H_{13}CH(OH)CH_2$	$(CH_2)_4CO\overset{-}{N}\overset{+}{N}Me_2CH_2CH(OH)C_6H_{13}$	0	0	0	0
7	$C_6H_{13}CH(OH)CH_2$	$(CH_2)_8CO\overset{-}{N}\overset{+}{N}Me_2CH_2CH(OH)C_6H_{13}$	0	0	0	0

a) Aq. phase, [metal nitrate] = 1×10^{-3} mol dm^{-3}. Org. phase, CH_2Cl_2, [ligand]= 1×10^{-4} mol dm^{-3}. b) See Ref. 7). c) When picric acid (1×10^{-4} mol dm^{-3}) was added, extractability of Ag^{+} increased to 53%.



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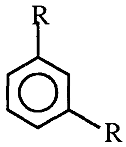

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$$R= CO\overset{-}{N}\overset{+}{N}Me_2CH_2CH(OH)C_6H_{13}$$

Compounds **1** to **3** with one aminimide group and hydroxyl group(s) did not extract any cation under the conditions applied. Although reagents **5** to **9** with two aminimide groups, which are located on each end of spacers such as alkane, ethylene, and benzene moieties, did not either extract any cation, **4** with the functional aminimide groups directly attached to each others now extracted Cu^{2+}, Ni^{2+}, and Ag^{+}. When picric acid was added to the extraction system, the percent extractions of these cations with **4** were markedly increased (see Table 1), most likely due to formation of high lipophilic ternary complexes composed of the bisaminimide, the cation, and picrate anion. In order to clarify the stoichiometry of these complexes, a continuous variation method was performed on the extractability. Fig. 1 shows the plots of extractabilities against the mol fraction of metal cations.

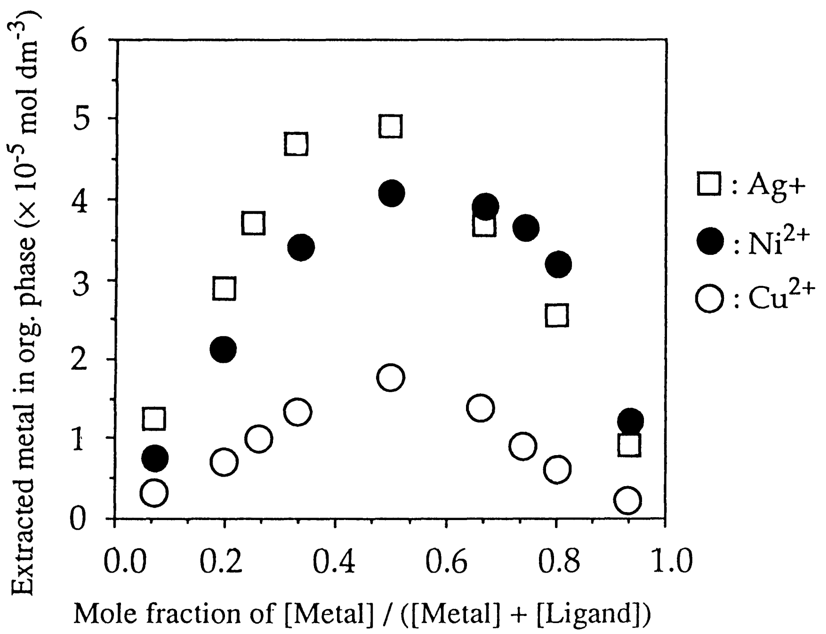

Fig. 1. Continuous variation plots of the extraction of cation with **4**. [Metal] + [Bisaminimide **4**] = 1.0 x 10^{-3} mol dm^{-3}. pH 5.3 (0.1 mol dm^{-3} acetate buffer).

The plots of all systems gave maximum extractabilities at 0.5 mol fraction of the metal cations, indicating the predominant formation of 1 : 1 complexes. The complexation is believed to take five-membered ring chelation as shown in Fig. 2.

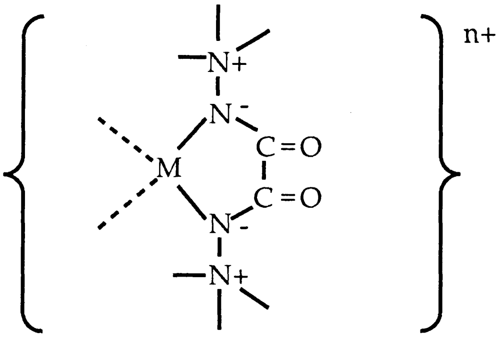

Fig. 2. Schematic representation of five membered chelation for the bisaminimide with metal cation.

Thus, the ligand acted as extractant for heavy- and transition metal cations, while in the same conditions using nitrate salts it did not extract any alkali metal and alkaline earth metal cation. These facts suggest that the aminimide is an useful material for recovering heavyand transition metal cations from the natural water and sea water which contain a plenty of alkali and alkaline earth metal cations.

Consequently, an easily available aliphatic aminimide showed moderate extractability toward Cu^{2+}, Ni^{2+}, and Ag^+. Its polypendant analogs, having polystyrene or polyethylene skeletons and preorganized cyclic aromatic oligomers such as calixarenes, would show an efficient extractability toward valuable metal cations. Furthermore, some modification of this aliphatic aminimide could result in a liquid membrane extractant to concentrate some metal cations.[17, 18)

References

1) T. Curtius, *J. Prakt. Chem.*, [2] **125**, 303 (1930).
2) T. Curtius and J. Risson, *J. Prakt. Chem.*, [2] **125**, 311 (1930).
3) T. Curtius and G. Kraemer, *J. Prakt. Chem.*, [2] **125**, 324 (1930).
4) T. Curtius and K. Vorbach, *J. Prakt. Chem.*, [2] **125**, 340 (1930).
5) T. Curtius, H. Bottler, and W. Raudenbusch, *J. Prakt. Chem.*, [2] **125**, 380 (1930).
6) W. J. McKillip, E. A. Sedor, B. M. Culbertson, and S. Wawzonek, *Chem. Rev.*, **73**, 155 (1973).
7) S. Inokuma, E. Kameyama, and T. Kuwamura, *Yukagaku*, **32**, 332 (1983).
8) S. Inokuma and T. Kuwamura, *Nippon Kagaku kaishi*, **1983**, 1494.
9) T. Kuwamura, Y. Yano, S. Inokuma, Y. Takenouchi, and H. Tokue, *Chem. Lett.*, **1986**, 1519.
10) R. C. Slagel, *J. Org. Chem.*, **33**, 1374 (1968).
11) Melting point and ^1H NMR spectroscopic data ($CDCl_3$, 500 MHz)—**8**: mp 193.5-194.5°C; δ 6.70 (2H, s), 4.16 (2H, dd, *J*=12.9 & 8.9 Hz), 3.56 (12H, s), 3.42 (2H, dd, *J*=12.9 & 9.5 Hz), 3.05 (2H, d, *J*=12.9 Hz), 1.29 (20H, m), 0.89 (6H, t, *J*=5.0 Hz). **9**: mp 76.0-77.0°C; δ 8.21 (1H, t, J=1.5 Hz), 7.76 (1H, dd, *J*=7.7 & 1.6 Hz), 7.27 (1H, t, *J*=7.9 Hz), 4.23 (2H, m), 3.55 (12H, d, *J*=12.5 Hz), 3.41 (4H, m), 1.47-1.31 (20H, m), 0.90 (6H, t, *J*=5.0 Hz).
12) L. Y. Chia, S. A. Dias, and W. R. McWhinnie, *Inorg. Nucl. Chem.*, **38**, 1263 (1976).
13) S. A. Dias, A. W. Downs, and W. R. McWhinnie, *J. Chem. Soc., Dalton*, **1975**, 162.
14) M. Seno and S. Tsuchiya, *J. Chem. Soc., Dalton* , **1977**, 751.
15) H. Kise, H. Endo, and M. Seno, *Bull. Chem. Soc. Jpn.*, **50**, 3245 (1977).
16) S. Tsuchiya and M. Seno, *J. Chem. Soc., Dalton Trans.*, **1984**, 731.
17) R. M. Izatt, G. C. LindH, R. L. Bruening, P. Huszthy, C. W. McDaniel, L. C. Bradshaw, and J. J. Chritensen, *Anal. Chem.*, **60**, 1694 (1988).
18) Y. Li, A. Wang, J. C. Van Loon, and R. R. Barefoot, *Talanta*, **39**, 1337 (1992).

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