Lipophilic Aminimides Possessing an Additional Ligating Group as Extractants for Heavy Metal Cations

SEIICHI INOKUMA[1], HIROKO SATOH[1], KAORI HASEGAWA[1],
TAKAO SHIBUSAWA[2] and JUN NISHIMURA[1,*]

[1]*Department of Chemistry, Gunma University, 1-5-1 Tenjin-cho, Kiryu 376, Japan.* [2]*Department of Biological and Chemical Engineering, Gunma University, 1-5-1 Tenjin-Cho, Kiryu 376, Japan.*

Abstract. The title compounds were prepared in good yields by Slagel's method. All compounds obtained were used as agents for liquid–liquid extraction. They showed high affinity for certain heavy metal cations and their extractability depended to a great extent on the ligand structure. This dependence is believed to be due to the chelation of the metal cations between the imino nitrogens and the additional ligating site.

Key words: Aminimide, extraction, heavy metal cations.

1. Introduction

Aminimides containing a quaternary nitrogen attached to the imino nitrogen, which is stabilized by an adjacent carbonyl group, show high hydrophilicity [1, 2], reactivity [3], and cation-ligating ability toward certain metals [4–7]. It has been discovered that aminimides act as phase transfer catalysts [8] or cation carriers via an interaction between aminimide group(s) and alkali metal cations [9]. Although complexes of aromatic aminimides with heavy metal cations have been isolated [5], they have not yet been utilized as carriers or extractants for the metal cations. This may be due to their low distribution coefficients to nonpolar organic solvents. Recently we found that in a series of simple bisaminimides with no other additional ligating site, only those compounds possessing two aminimide groups attached to each other showed a certain affinity for such heavy metal cations such as Ag^+, Ni^{2+}, and Cu^{2+} [10]. On the other hand, crown ethers [11, 12] and acyclic polyethers [13, 14] possessing additional binding site(s) have been extensively studied and found to extract or transport valuable metal cations. Although aminimides bearing a picolyl residue formed complexes with Pd^{2+} and Pt^{2+} [7], their complexing behavior with other metal cations have not been well explored. Thus we have synthesized some aminimides possessing a methylthiomethyl, 2-thienyl,

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* Author for correspondence.

or dimethylaminomethyl group, or an aromatic residue as an additional ligating site, since we expected them to exhibit good extraction abilities.

Stimulated by this investigation, we studied the effects of the additional ligating group on the affinity toward metal cations. In this paper, we describe in detail the synthesis and structural effects of lipophilic aminimides with an additional ligating site.

2. Experimental

2.1. APPARATUS

^{1}H-NMR spectra were recorded on a Varian Gemini-200 FT NMR spectrometer, using TMS as internal standard. Metal cations in aqueous solution were analyzed by a Hitachi 170-50 atomic absorption spectrophotometer.

2.2. REAGENTS

Isopropyl alcohol, *tert*-butyl alcohol, hexane, benzene, and acetone were purified by distillation. Guaranteed reagent grade CH_2Cl_2 was distilled before use.

The highest commercially available grade of $AgNO_3$, $Cu(NO_3)_2$, $Pb(NO_3)_2$, and $Ni(NO_3)_2$ were used with no further purification. All aqueous solutions were prepared from distilled, deionized water.

2.3. PREPARATION OF AMINIMIDES 1–15

Aminimides **1–3** and **7–11** were prepared by the method reported previously [8]. Compounds **4–6** and **12–15** were newly prepared by Slagel's method [15,16]. All compounds were purified by recrystallization from a mixed solvent of hexane and acetone, except for **12**, which was column chromatographed on silica gel using a gradient solution of benzene–acetone as an eluent.

2.3.1. *Aminimide 4*

Yield, 56%; mp 89.0–90.0 °C. IR (characteristic absorption of aminimide), 1605 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 7.52 (1H, dd, 3.6 and 1.3), 7.26 (1H, dd, 5.0 and 1.3), 6.99 (1H, dd, 5.0 and 3.6), 4.27 (1H, m), 3.67 (6H, s), 3.52 (1H, m), 3.07 (1H, br. d, 12.4), 1.68–1.17 (18H, m), 0.88 (3H, t, 6.5). *Anal. Calcd.* for $C_{19}H_{34}O_2N_2S$: C, 64.37; H, 9.67; N, 7.90; S, 9.04. *Found:* C, 64.53; H, 9.72; N, 7.90; S, 8.83.

2.3.2. *Aminimide 5*

Yield, 47%; mp 27.0–28.0 °C. IR (characteristic absorption of aminimide), 1590 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 4.20 (1H, m), 3.55 (6H, s), 3.42 (1H, m), 3.05 (2H, s), 3.02 (1H, br. d, 12.2), 2.17 (3H, s), 1.65–1.19 (18H, m), 0.88 (3H, t, 6.5), 0.88

(3H, t, 6.5). *Anal. Calcd.* for $C_{17}H_{36}O_2N_2S$: C, 61.40; H, 10.91; N, 8.42; S, 9.64. *Found:* C, 61.09; H, 11.04; N, 8.29; S, 9.41.

2.3.3. *Aminimide* 6

Yield, 56%; mp 62.0–63.0 °C. IR (characteristic absorption of aminimide), 1590 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 4.18 (1H, m), 3.55 (6H, m), 3.45 (1H, m), 3.01 (1H, br. d, 12.4), 2.84 (2H, s), 2.29 (6H, s), 1.64–1.16 (18 H, m), 0.88 (3H, t, 6.5). *Anal. Calcd.* for $C_{18}H_{39}O_2N_3$: C, 65.61; H, 11.23; N, 12.75. *Found:* C, 65.23; H, 11.42; N, 12.51.

2.3.4. *Aminimide* 12

Yield, 59%; Transparent viscous oil. IR (characteristic absorption of aminimide), 1585 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 8.53 (1H, br. d, 7.7), 7.61 (1H, td, 7.7 and 1.8), 7.30 (1H, dd, 7.7 and 1.8), 7.12 (1H, t, 7.7), 4.11 (1H, m), 3.59 (2H, s), 3.51 (6H, s), 3.39 (1H, m), 3.06 (1H, br. d, 12.5), 1.58–1.18 (18 H, m), 0.88 (3H, t, 6.4). *Anal. Calcd.* for $C_{21}H_{37}O_2N_3$: C, 69.98; H, 10.26; N, 11.56. *Found:* C, 69.66; H, 10.41; N, 11.78.

2.3.5. *Aminimide* 13

Yield, 52%; mp 66.0–67.0 °C. IR (characteristic absorption of aminimide), 1580 cm^{-1}. ^{1}H-NMR (CDCl$_3$); δ 7.78 (1H, d, 7.6), 7.59 (1H, t, 7.6), 7.15 (1H, d, 7.6), 4.30 (1H, m), 3.69 (6H, s), 3.10 (1H, br. d, 12.2), 2.58 (3H, s), 1.59–1.15 (18H, m), 0.88 (3H, t, 6.4). *Anal. Calcd.* for $C_{21}H_{37}O_2N_3$: C, 69.38; H, 10.26; N, 11.56. *Found:* C, 69.21; H, 10.50; N, 11.61.

2.3.6. *Aminimide* 14

Yield, 51%; mp 34.0–35.0 °C. IR (characteristic absorption of aminimide), 1590 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 8.64 (1H, br. d, 7.2), 8.05 (1H, br. d, 7.2), 7.72 (1H, td, 7.2 and 1.8), 7.25 (1H, t, 7.2), 3.88 (2H, m), 3.47 (6H, s), 1.79 (2H, s), 1.41–1.17 (20H, m), 0.88 (3H, t, 6.4). *Anal. Calcd.* for $C_{20}H_{35}ON_3$: C, 72.03; H, 10.58; N, 12.60. *Found:* C, 71.83; H, 11.01; N, 12.29.

2.3.7. *Aminimide* 15

Yield, 48%; mp 63.0–64.0 °C. IR (characteristic absorption of aminimide), 1585 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 7.81 (1H, d, 7.3), 7.60 (1H, t, 7.3), 7.15 (1H, d, 7.3), 3.86 (2H, m), 3.52 (6H, s), 2.64 (3H, s), 1.82 (2H, s), 1.44–1.19 (20H, m), 0.88 (3H, t, 6.6). *Anal. Calcd.* for $C_{21}H_{37}ON_3$: C, 72.58; H, 10.73; N, 12.09. *Found:* C, 72.41; H, 10.98; N, 11.88.

2.4. SOLVENT EXTRACTION OF HEAVY METAL CATIONS

A CH_2Cl_2 solution of aminimide (1×10^{-4} M, 5.0 mL) and an aqueous metal nitrate solution (1×10^{-3} M, 5.0 mL, buffered by acetate adjusted at pH 5.3) were shaken at ambient temperature (18–20 °C) for 2 h in a 20 mL test tube fitted with a ground-glass stopper. The two liquid phases were separated, and the equilibrium pH of the aqueous phase was measured. An aliquot (2 mL) of the organic phase was evaporated under reduced pressure, and then dilute aqueous HNO_3 (2 mL) was added to the residue. Finally the extracted cation was analyzed by the atomic absorption method.

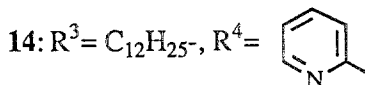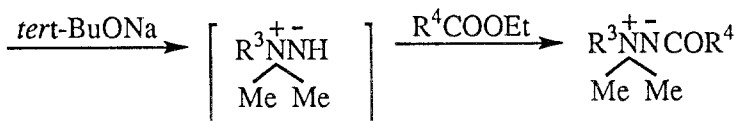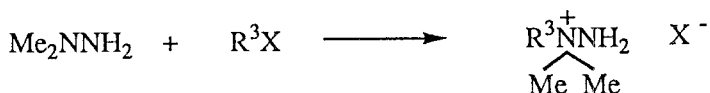## 3. Results and Discussion

3.1. SYNTHESIS OF AMINIMIDES

Lipophilic aminimides with a hydroxyl group were easily prepared by Slagel's method [16] in isopropyl alcohol at room temperature. The aminimides with no hydroxyl group were also prepared by Slagel's method [15] using the corresponding ester and the hydrazinium salt in the presence of potassium tert-butoxide in refluxing tert-butyl alcohol. The yields were fairly good and the purification was relatively simple (Scheme I). Their specific IR spectral band ranged from 1580 to 1605 cm^{-1}, which is characteristic of aminimides (—N—C=O) and different from esters (ca. 1740 cm^{-1}).

3.2. EXTRACTION OF METAL CATIONS BY AMINIMIDES

The aminimides obtained were used as solvent extractants: the results are summarize in Table I.

Four heavy metal cations (Ni^{2+}, Cu^{2+}, Ag^+, and Pb^{2+}) were chosen for the following reasons. Some copper cation complexes with aromatic aminimides were isolated from solutions of ethyl alcohol [5]. Nickel cation can complex with an aminimide because it belongs to the same periodic Group VIII as palladium and platinum, which also form complexes with aromatic aminimides and their analogs, sulfur ylides, respectively [5–7, 17]. Both silver and lead cations show high affinity toward nitrogen- and sulfur-containing host ligands [18–21]. From the practical point of view, copper is an important me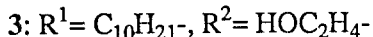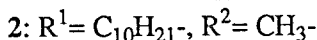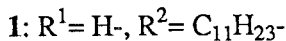tal, which shows good thermal and electric conductivity (ranked next to silver), and is an essential transition element for vital functions, similar to iron and zinc. Silver is the most important metal in the photographic industries and its complete recovery from the photographic waste stream is vital in connection with saving of resources and environmental protection [22].

In a preliminary experiment, none of the aminimides listed in Table I extracted any alkali metal nitrate under the conditions shown in Table I, nor significant amounts of the metal picrates (extractability < 10%) (organic phase, CH_2Cl_2,

$$Me_2NNH_2 \;+\; R^1CH\text{-}CH_2\;\diagdown\!\!O \longrightarrow \left[R^1\underset{OH}{\overset{|}{C}}HCH_2\overset{+}{\underset{\underset{Me\;Me}{\wedge}}{N}}\overset{-}{NH} \right]$$

$$\xrightarrow{R^2COOEt} \; R^1\underset{OH}{\overset{|}{C}}HCH_2\overset{+}{\underset{\underset{Me\;Me}{\wedge}}{N}}\overset{-}{N}\,COR^2$$

1: R^1= H-, R^2= $C_{11}H_{23}$-

2: R^1= $C_{10}H_{21}$-, R^2= CH_3-

3: R^1= $C_{10}H_{21}$-, R^2= HOC_2H_4-

4: R^1= $C_{10}H_{21}$-, R^2= [thiophene-S]

5: R^1= $C_{10}H_{21}$-, R^2= CH_3SCH_2-

6: R^1= $C_{10}H_{21}$-, R^2= $(CH_3)_2NCH_2$-

7: R^1= $C_{10}H_{21}$-, R^2= [phenyl]

8: R^1= $C_{10}H_{21}$-, R^2= [2-hydroxyphenyl, OH]

9: R^1= $C_{10}H_{21}$-, R^2= [3-methylpyridin-N]

10: R^1= $C_{10}H_{21}$-, R^2= [pyridin-4-yl, N]

11: R^1= $C_{10}H_{21}$-, R^2= [6-methylpyridin-2-yl, N]

12: R^1= $C_{10}H_{21}$-, R^2= [pyridin-2-yl-CH_2-, N]

13: R^1= $C_{10}H_{21}$-, R^2= [6-methylpyridin-2-yl, N, CH_3]

$$Me_2NNH_2 \;+\; R^3X \longrightarrow R^3\overset{+}{\underset{\underset{Me\;Me}{\wedge}}{N}}NH_2 \;\; X^-$$

$$\xrightarrow{\textit{tert}\text{-BuONa}} \left[R^3\overset{+}{\underset{\underset{Me\;Me}{\wedge}}{N}}\overset{-}{NH} \right] \xrightarrow{R^4COOEt} R^3\overset{+}{\underset{\underset{Me\;Me}{\wedge}}{N}}\overset{-}{N}COR^4$$

14: R^3= $C_{12}H_{25}$-, R^4= [pyridin-2-yl, N]

15: R^3= $C_{12}H_{25}$-, R^4= [6-methylpyridin-2-yl, N, CH_3]

Scheme I. Syntheses of aminimides.

[aminimide] = 1×10^{-4} M, 5 mL; aqueous phase, [MOH] = 1×10^{-3} M and [picric acid] = 1×10^{-3} M, 5 mL). As shown in Table I, simple aminimides **1**, **2**, **3**, **7**, and **8**, having no additional group other than a hydroxyl, extracted hardly any heavy metal cation examined. The extractabilities of the lipophilic aminimides possessing a sulfide (**4** and **5**) or tertiary amine (**6**) residue toward the heavy metal cations were not so high under the conditions used.

TABLE I. Extraction of metal cations with
lipophilic aminimides[a].

| Ligand	Extractability (%)			
	Ni^{2+}	Cu^{2+}	Ag^+	Pb^{2+}
1	0	0	0	0
2	0	0	0	0
3	0	0	0	0
4	8	2	1	2
5	7	13	1	2
6	8	2	5	2
7	0	0	7	0
8	2	0	0	2
9	0	0	0	0
10	0	0	6	0
11	41	98	66	0
12	0	22	11	0
13	9	70	60	0
14	29	35	54	2
15	9	52	65	1

[a] Extraction conditions: Aq. phase, [metal
nitrate] = 1×10^{-3} M, 5 mL; Org. phase,
Ch_2Cl_2, [ligand] = 1×10^{-4} M, 5 mL.

Since a 2-pyridyl group was recently found to bind Ag^+ cation cooperatively with a cyclic polyether in crownophane systems [23, 24], the pyridyl-substituent effect on the extractability has also been examined with these aminimides. Although 9, having a 3-pyridyl group, did not extract any cation, and 10, having a 4-pyridyl group, scarcely did, isomer 11, having a 2-pyridyl group, efficiently extracted Cu^{2+} and Ag^+ ions. Thus, the complexation behavior of 11 with these cations was elucidated by the continuous variation method during the extraction. As shown in Figure 1, the extractabilities of the ligand for both silver and copper cations reached maxima at 0.5 mole fraction. This is thought to involve a five-membered chelation, shown in Figure 2, which results in the endowment of lipophilicity on the complexes. It can make the transportation of the cation to the organic phase facile.

To increase the extractability toward Ag^+ ion, we prepared aminimide 12, bridged by a methylene group between the pyridyl and aminimide groups. Aminimide 12 was expected to form a more stable chelate: i.e., generally a six-membered chelate is more stable and favorable than a five-membered one with regard to Ag^+ chelation. The design, however, failed in both selective and effective extraction of Ag^+ ion. Moreover, in extractability toward Ni^{2+}, the introduction of a methyl group on the 6-position of the 2-pyridyl group (13 and 15) significantly decreased
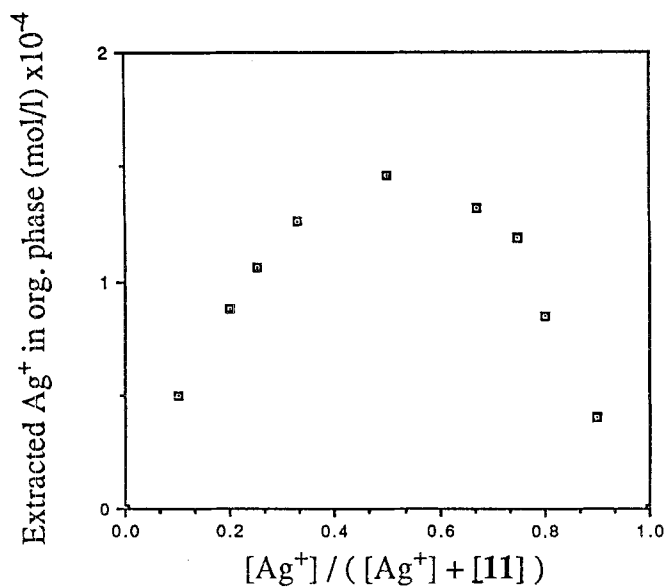
$[Ag^+]+[11] = 1 \times 10^{-3}$ mol/l. pH5.3 (0.1M acetic acid-sodium acetate buffer solution).
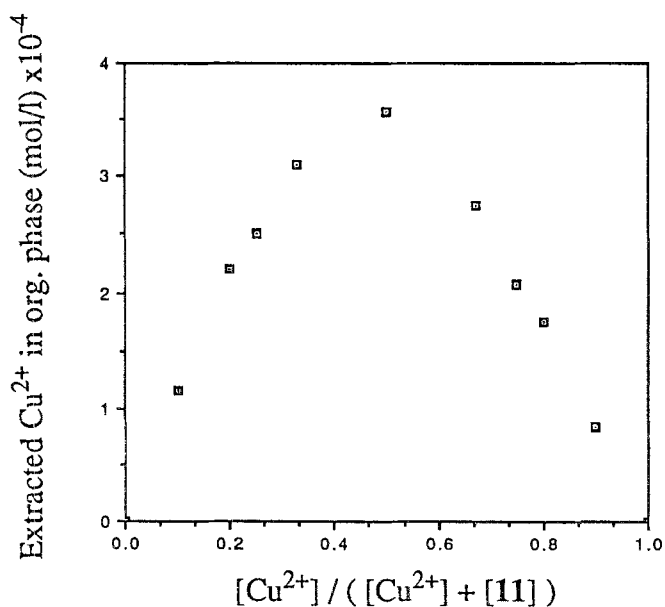
$[Cu^{2+}]+[11] = 1 \times 10^{-3}$ mol/l. pH5.3 (0.1M acetic acid-sodium acetate buffer solution).

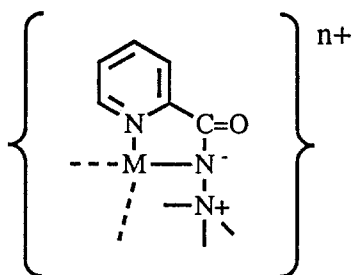Fig. 1. Continuous variation plots for the formation of metal complexes.

Fig. 2.   Proposed five-membered chelate between aminimide **11** and a metal cation.
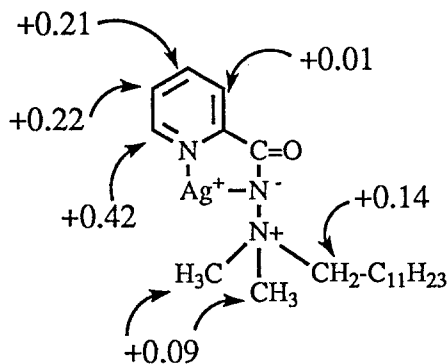

Fig. 3. Ag^+ induced changes in ^1H-NMR chemical shifts (ppm) of aminimide **14** (2 equiv. $AgClO_4$ was added in CD_3CN solution of the aminimide).

due to a steric factor, although the substituent was thought to enhance the electron density on the pyridine nitrogen. A comparison of the results of **11** and **13**, with those of **14** and **15**, respectively, showed that the hydroxyl group on the β position of the quaternary nitrogen enhances the extractability toward Cu^{2+}. The hydroxyl groups play an important role in making a Cu^{2+} complex more stable than other additional ligating groups. In general, Cu^{2+} forms many kinds of complexes with a variety of coordination numbers, depending on the stereochemical and electronic characters of the ligands employed [25, 26].

The complexing behavior of aminimides **11**, **13**, and **14** with Ag^+ cation was also examined by ^1H-NMR titration in homogeneous (methanol-d_4) solutions, the results being entirely different from those of the extraction experiments. The titration plots of these compounds with Ag^+ ion showed 1 : 1 complexation in the solvent, which is the same as that in dichloromethane (see above). Unfortunately, the titration with Ni^{2+} and Cu^{2+} cations could not be carried out using NMR spectroscopy because of the paramagnetic properties of the metal ions.
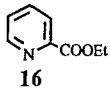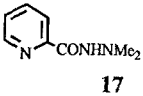
Figure 3 shows Ag^+-induced downfield shifts of the signals of **14** as a typical example. The proton at the 6-position on the pyridine ring was significantly shifted, indicating the coordination of the pyridine nitrogen to silver.

TABLE II. Association constants in methanol.[a]

Aminimides	log K		
	Ni^{2+}	Cu^{2+}	Ag$^+$
11	4.28	4.02	4.29
13	4.11	4.27	4.32
14	4.27	4.04	3.93

[a] Metal perchlorates were used for titration by UV spectroscopy.

TABLE III. Extraction of metal cations with lipophilic aminimides.[a]

Entry	Ligands	Extractability (%)			
		Ni^{2+}	Cu^{2+}	Ag$^+$	Pb^{2+}
1	7 + 16	3	2	1	2
2	17	0	0	0	0

[a] Aq. phase, [metal nitrate] = 1×10^{-3} mol dm^{-3}. Org. phase, CH$_2$Cl$_2$,[ligand] = 1×10^{-4} mol dm^{-3}.

Generally speaking, the extractability of metal cations is influenced by the association constant of a ligand and the distribution coefficient of the complex between organic and aqueous phases. In order to reveal which property of complexes in a solution govern the extractability, the association constants of compounds 11, 13, and 14 with Ni^{2+}, Cu^{2+}, and Ag$^+$ in methanol were measured by UV spectroscopy [27]. The data are shown in Table II. The association constants of the three metal cations were almost the same in this homogeneous system, despite the remarkable difference in the percentage extraction (see Table I). Thus, the extractabilities observed in this work are considered to be governed by the distribution coefficients. Several examples of such behavior are known. Pedersen pointed out that the distribution coefficient is a dominant factor for extraction with a crown ether: i.e., although the stability constant of dicyclohexano-18-crown-6, a typical crown compound, with K$^+$ ion is much larger than that with Na$^+$ ion (ca. 100 times) [28], the difference in its extractability toward the two cations is not very significant [29], because the distribution coefficients of the alkali metal cation complexes between organic and aqueous phases have a predominant effect on the extraction [30].

In order to clarify the importance of the intramolecular imino nitrogen–pyridyl nitrogen cooperation, a mixture of **7** and ethyl 2-pyridinecarboxylate **16** (entry 1), and 1,1-dimethyl-2-(2-pyridinecarbonyl)hydrazine **17** (entry 2) alone were used as extractants (Table III). The result (entry 1) suggests the necessity of their intramolecular cooperation, because the extractability could not exceed that of **7**. Apparently, the imino nitrogen is essential for the coordination to metal cation, since **17** (entry 2) did not show any extractibility. In fact, as shown in Table I, when these two nitrogen ligands were properly arranged in a molecule like **11**, an excellent extractability toward the heavy metal cations was recorded.

In summary, lipophilic aminimides have been conveniently prepared in good yields. An additional ligating site in the aminimides acted as a cooperative cation-binding site for Ni^{2+}, Cu^{2+}, and Ag^+ cations in liquid–liquid extraction.

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