# Ag$^+$-Selective Bisaminimides Possessing Oligo(oxyethylene) Linkages

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Lipophilic aromatic bisaminimides with three or five ethereal oxygens in the linkages were prepared. The structural effects of the aminimides on the extraction abilities were examined for some heavy metal nitrates in the liquid-liquid systems. The bisaminimides other than *p*-isomer showed Ag$^+$-selectivity, and the percent extraction of *o*-isomers about two times larger than that of *m*-isomers.

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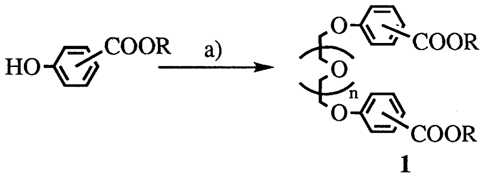
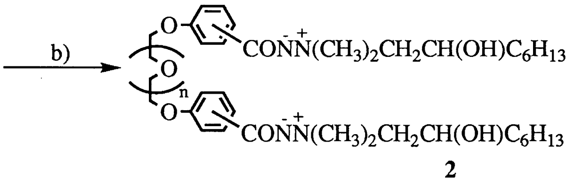
Acylic polyether derivatives have attracted much attention due to their mobility for guest induced-fit and structural resemblance to antibiotics.[1] Differed from those of natually occurring ionophores, however, almost all the compounds have the same functionalized groups at the both termini due to easy preparation. Acyclic polyethers having soft atoms in the terminal groups and/or central position complex not only with alkali and alkaline earth metal cations but also with heavy metal, lantanoid, and actinoid ions.[2] In other words, they cannot distinguish them with reasonable selectivity. Recently, we have found that aminimide group extracts some heavy metal cations in distinction from alkali metal cations when it is arranged properly; *i.e.*, two aminimide groups are linked directly,[3] or it has an additional group at a suitable position.[4]

In this communication, we would like to describe an excellent Ag$^+$-selectivity of bisaminimides possessing oligo(oxyethylene) linkages with lipophilic moieties on the quaternary ammonium nitrogens over other heavy metal, alkali and alkaline earth metal cations.



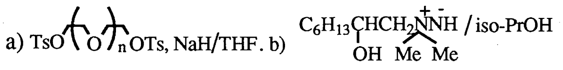
**1**

**a**: n=1, *o*-, R = Et ; **b**: n=1, *m*-, R = Me; **c**: n=3, *o*- , R = Et; **d**: n=3, *m*-, R=Me; **e**: n=3, *p*- , R=Et



**2**

**a**: n=1,*o*- ; **b**: n=1, *m*-; **c**: n=3, *o*-; **d**: n=3, *m*-; **e**: n=3, *p*-



a) TsO(CH$_2$CH$_2$O)$_n$OTs, NaH/THF. b) $\underset{\text{OH}}{\text{C}_6\text{H}_{13}\text{CHCH}_2}\overset{+\,-}{\underset{\text{Me Me}}{\text{NNH}}}$ / iso-PrOH

**Scheme 1.** Synthesis of the aminimides.

**Table 1.** Extraction of heavy metal cations with the ligands

| | Percent extraction[a] | | | | |
|---|---|---|---|---|---|
| Ligands | Ag$^+$ | Cu$^{2+}$ | Pb$^{2+}$ | Ni$^{2+}$ | Zn$^{2+}$ |
| **2a** | 61(5.1) | 9(4.4) | 3(4.4) | 0(6.8) | 1(5.5) |
| **2b** | 33(5.7) | 0(4.5) | 1(4.6) | 2(6.8) | 1(5.5) |
| **2c** | 78(4.6) | 5(4.2) | 17(4.5) | 3(6.7) | 1(5.4) |
| **2d** | 36(4.7) | 0(4.2) | 0(4.5) | 8(6.8) | 6(5.5) |
| **2e** | 1(4.7) | 1(4.3) | 0(4.5) | 1(6.4) | 0(5.2) |
| **1c** | 7(4.5) | 0(4.7) | 0(3.9) | 0(4.2) | 0(6.0) |
| **1d** | 8(4.5) | 2(4.4) | 0(4.6) | 0(6.9) | 0(5.8) |
| **1e** | 7(4.7) | 1(4.4) | 0(4.6) | 0(6.6) | 0(5.8) |

[a] Extraction conditions: Aq. phase, [metal nitrate] = $1 \times 10^{-1}$ M, 5 mL; org. phase, CH$_2$Cl$_2$, [ligand] = $1 \times 10^{-4}$ M, 5 mL. Values in parentheses are equilibrium pH of the aqueous phase.

The bisaminimides were readily prepared by the known method in 2-propyl alcohol at ambient temperature for 2 days.[3] The purification of crude products was carried out by the silica gel column chromatographic technique using gradient solution of benzene-acetone as an eluent. The analytical data of the compounds are given.[5] All aminimides obtained were used as extractant for heavy metal cations in a liquid-liquid system together with reference compounds. A CH$_2$Cl$_2$ solution of a host compound (1 x $10^{-4}$ mol dm$^{-3}$, 5 ml) and an aqueous metal nitrate solution (0.1 mol dm$^{-3}$, 5 ml), whose pH value was adjusted as high as possible, were shaken in a 20-ml test tube equipped with a ground glass stopper at room temperature (20-22 °C) for 2 h. After two liquid phases were separated, an aliquot (2 ml) of the organic phase was evaporated, and then HNO$_3$ solution (0.1 mol dm$^{-3}$, 2 ml) was added to the residue. Extracted cation in the acidic aqueous solution was analyzed by atomic absorption spectroscopy. Results are summarized in Table 1.

Precursor α,ω–bisbenzoates **1c**, **d**, and **e** hardly extracted any heavy metal cation except for Ag$^+$ ion. The lower extractability toward Ag$^+$ can be explained by means of ion-dipole interaction between the cation and ethereal oxygens without any aid of carboxylate groups from the fact that cyclic polyethers, crown ethers, are known to extract the cation very slightly.[6] It was found that some aminimides efficiently extracted Ag$^+$ ion with high selectivity, and the extractability of the compounds remarkably depended on their structures; *i.e.*, positions of the functional groups and oxyethylene units. Effect of the regio-isomerism was higher than that of the oxyethylene chain length on the Ag$^+$-extractability. As known well, the larger lipophilicity of a complex resulted in the higher distribution coefficient. Silver cation seems to be wrapped into the pseudo cavity constructed by the two aromatic aminimide groups with longer alkyl chains and an oligo(oxyethylene) chain. This makes the complexes highly lipophilic. It is not so difficult to predict that the lipophilicity of **2a**-Ag$^+$ and **2c**-Ag$^+$ complexes is higher than that of **2b**-Ag$^+$ and **2d**-Ag$^+$ ones, respectively, according to the frame-work examination of these complexes. Indeed, the former recorded

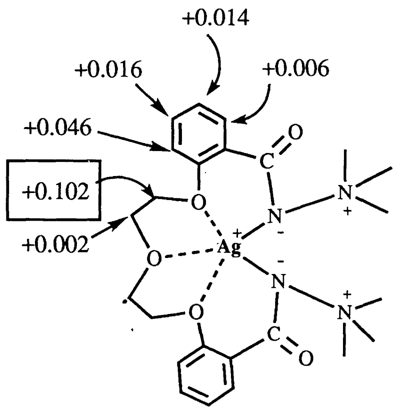


**Figure 1.** $Ag^+$-Induced changes in $^1H$-NMR chemical shifts (ppm) of aminimide **2a** (2 equiv. $AgClO_4$ was added in $CD_3CN$ soln. of the aminimide).

twice as much value as later on the percent extraction. In order to make the complex structures more clear, we spectroscopically investigated the interaction between *o*-isomer **2a** and $Ag^+$ ion in $CD_3CN$ (Figure 1 ).

Down-field shifts were observed in each signals of **2a** at the addition of $AgClO_4$. Methylene protons attached to the phenyloxy oxygens are most significant. Thus, it was clarified the contribution of the oxyethylene moiety cooperatively with aminimide groups on the complexation. Furthermore, the behavior of **2a** to $Ag^+$ ion was examined by $^{13}C$ NMR titration method. As shown in Figure 2, the chemical shift of its aromatic carbon attached to carbonyl group significantly changed with increasing the amount of $AgClO_4$ added to the host solution, until host/guest molar ratio became one, which strongly illustrates the 1:1 complexation.

Job plots on the liquid-liquid extraction using $CH_2Cl_2$ as organic media also gave the maximum at 0.5 mol fraction of metal cation for $Ag^+$-**2a** and **2c** systems (Figure 3 shows the **2c** system as representative one). This again clearly indicates the 1:1 complexation. Thus, the same complexing fashion was observed even in different kinds of solvent-systems.

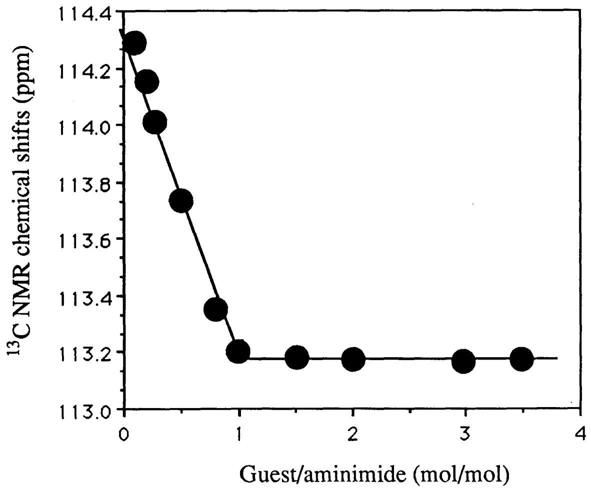
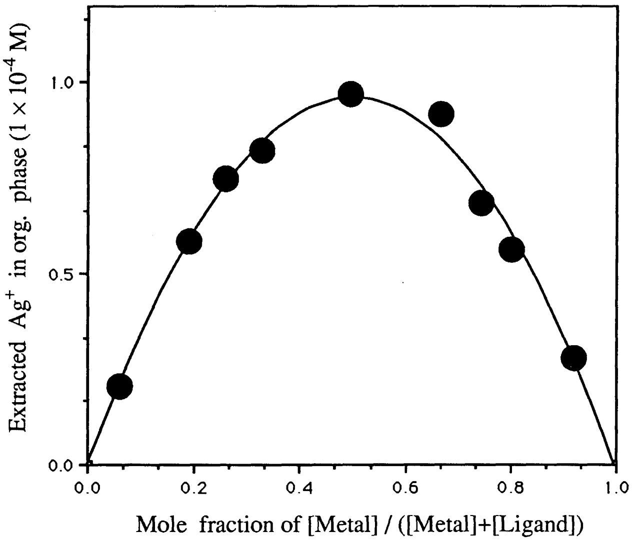


**Figure 2.** $Ag^+$-Induced changes in $^{13}C$ NMR chemical shifts of aminimde **2a** ($CD_3CN$ solution); The aromatic carbon attached carbonyl group was employed.



pH 5.3 (0.1 M acetate buffer)

[Metal] + [Ligand] = $1 \times 10^{-3}$ M

**Figure 3.** Job plots of the extractions of $Ag^+$ by **2c**.

Thus, the bisaminimides effectively and selectively extracted $Ag^+$ ion, while they did not extract any alkali and alkaline earth metal cation in the same conditions. This suggests that the aminimides are useful ligands for recovering $Ag^+$ ion from photographic waste stream which contains a plenty of alkali metal cations.

## References and Note

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5 All new compounds were colorless viscous liquid and gave satisfactory microanalytical data. $^1$HNMR spectroscopic data ($CDCl_3$, 500 $MH_z$): **2a**; δ 7.44 (2H, dd, *J* = 7.6 & 1.2), 7.21 (2H, t, *J* = 7.3), 6.90 ( 2H, t, *J* = 7.2), 6.86 (2H, d, *J* = 8.3), 4.18 (6H, m ), 3.96 (4H, m), 3.57 (6H, m), 3.53 (6H, d, *J*= 7.3), 3.45 (2H, dd, *J*=22.4 & 9.9), 3.16 (2H, dd, *J* = 12.6 & 7.7), 1.61-1.29 (20H, m), 0.88 (6H, t, *J* = 6.9). **2b**; δ 7.45 (2H, s), 7.41 (2H, m), 7.20 (2H, m), 6.94 (2H, m), 4.25 (2H, m), 4.18 (4H, m), 3.91 (4H, m), 3.65 (12H, m), 3.53 (2H, m), 3.13 (2H, m), 1.61-1.30 (20H, m), 0.88 (6H, t, *J* = 7.1). **2c**; δ 7.77 (2H, d, *J* = 7.6), 7.38 (2H, m), 6.94 (2H, m), 6.83 ( 2H, d, *J* = 8.3), 4.14 (6H, m), 3.88 (4H, m), 3.70-3.62 (12H, m), 3.55 (2H, s), 3.51 (2H, s), 3.30 (4H, m), 1.48-1.28 (20H, m), 0.88 (6H, t, *J* = 6.9). **2d**; δ 7.44 (2H, d, *J* = 2.7), 7.39 (2H, s), 7.21 (2H, t, *J* = 7.8), 6.94 (2H, m), 4.27 (2H, m), 4.16 ( 4H, t, *J* = 4.8), 3.84 (4H, t , *J* = 4.8), 3.71 ( 8H, m), 3.66 (12H, s), 3.54 (2H, m), 3.14 (2H, d, *J* = 11.7), 1.43-1.30 (20H, m), 0.88 (6H, t, *J* = 6.8). **2e**; δ 7.97 (2H, ABq, *J* = 8.8), 6.91 (4H, ABq, *J* = 8.8), 5.21 (2H, m), 4.27 (2H, m), 4.14 (4H, m), 3.85 (4H, m), 3.72-3.66 (20H, m), 3.55 (2H, m), 3.08 (2H, m), 1.34 (20H, m), 0.89 (6H, t, *J* = 7.2).
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