

Ag⁺-Selective Bisaminimides Possessing Oligo(oxyethylene) Linkages

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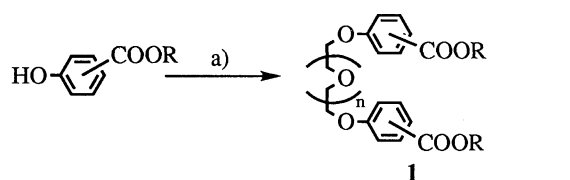
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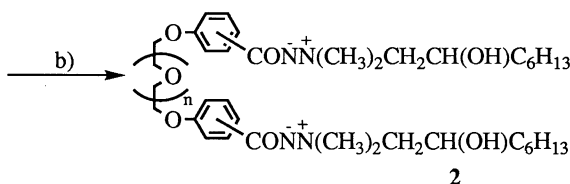
Lipophilic aromatic bisaminimides with three or five ethereal oxygens in the linkages were prepared. The structural effects of the aminimides on the extraction abilities were examined for some heavy metal nitrates in the liquid-liquid systems. The bisaminimides other than *p*-isomer showed Ag⁺-selectivity,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

Acyclic polyether derivatives have attracted much attention due to their mobility for guest induced-fit and structural resemblance to antibiotics.¹ Differed from those of naturally 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, lanthanoid, 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.

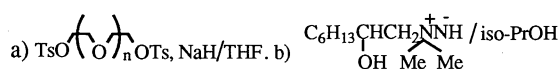
The bisaminimides were readily prepared by the known method in 2-propyl alcohol at ambient temperature for 2 days.³ The purification of crude products was carried out by the silica gel column chromatographic technique using gradient solution of benzene-acetone as an eluent. The analytical data of the



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



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



Scheme 1. Synthesis of the aminimides.

Table 1. Extraction of heavy metal cations with the ligands

Ligands	Percent extraction ^a				
	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] = 1×10^{-1} M, 5 mL; org. phase, CH₂Cl₂, [ligand] = 1×10^{-4} M, 5 mL. Values in parentheses are equilibrium pH of the aqueous phase.

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 CH₂Cl₂ solution of a host compound (1×10^{-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 HNO₃ 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 regioisomerism 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

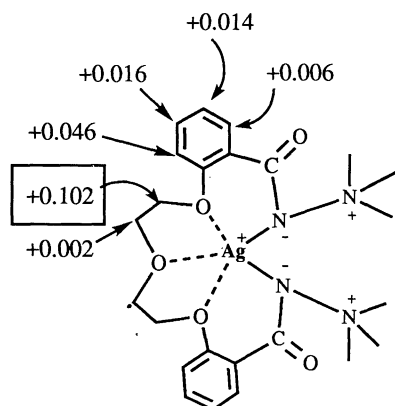


Figure 1. Ag^+ -Induced changes in ^1H -NMR chemical shifts (ppm) of aminimide **2a** (2 equiv. AgClO_4 was added in CD_3CN soln. of the aminimide).

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 phenoxy 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.

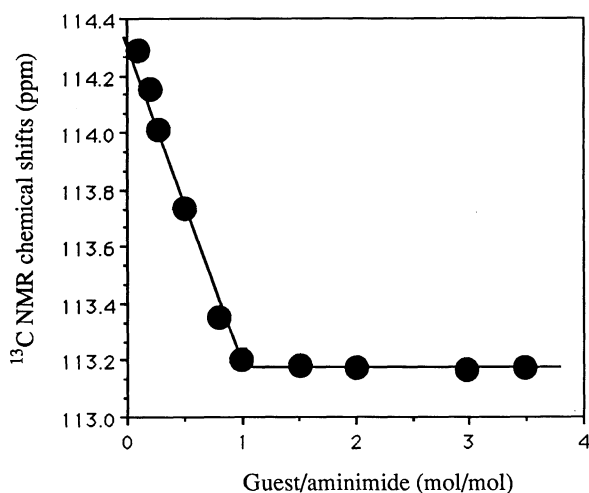


Figure 2. Ag^+ -Induced changes in ^{13}C NMR chemical shifts of aminimide **2a** (CD_3CN solution); The aromatic carbon attached carbonyl group was employed.

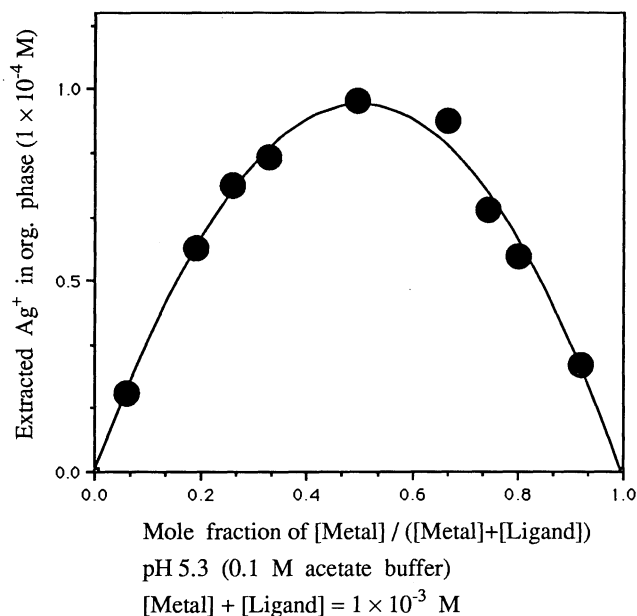


Figure 3. Job plots of the extractions of Ag^+ by **2c**.

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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- All new compounds were colorless viscous liquid and gave satisfactory microanalytical data. ^1H NMR spectroscopic data (CDCl_3 , 500 MHz): **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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