

Selective Extraction of Silver(I) Ion by a New Acyclic Diazapolyether Compound Bearing Dicarboxylate Functional End-Groups

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Interest in the development of techniques for the separation of heavy metal ions has been increased in recent years. Acyclic polyethers have been considerably studied due to their excellent complexation behavior with several metal ions as do cyclic polyethers.^{1,2} Some of the ligands and metal complexes have several potential applications, including medical treatment, imaging, analytical separation of metal cations and ion selective electrodes.^{3,4} Over the years, a large number of molecules featuring proper binding sites, particularly crown ethers or acyclic polyethers, have been synthesized and demonstrated to act as selective carriers of transition metal ions across a membrane.^{5,6} Theoretical models aimed at correlating the efficiency and selectivity of the extraction with the structure of the carrier molecules have been also proposed and experimentally tested.⁷ Specifically, strong silver ion recognition is very important for silver-based radioimmunotherapy⁸ and probably useful for photographic industry and recovery of silver ion from wastewater in environment. Several Ag(I) ion complexing ligands have been investigated such as crown ethers containing sulfur atom(s) in the cyclic structure,^{9,10} doubled armed¹¹ or multi-armed macrocycles.¹² Recently Nabeshima *et al.*¹³ found remarkable high Ag(I) selectivity among heavy metal ions in solvent extraction and transport across a liquid membrane using thio-lariat ethers which possess a sulfide side chain introduced in a framework of a crown ether with a 15-crown-5 ring as carriers. Lerchi *et al.*¹⁴ also used a new thio-carbamate derivative in polymeric sensing films together with a lipophilic chromoionophore for determining Ag(I) at submicromolar level.

In this work, a new acyclic azapolyether, *N,N*-diethyl-2,7-dihexyl-3,6-diazaoctanoic acid (**1**), which contains dicarboxylate functional end-groups and 1,5-bis[2-(2'-carboxypentadecyloxy) phenoxy]-3-oxapentane (**2**) were synthesized and investigated its binding property for various heavy metal cations by solvent extraction with a water-chloroform biphasic

system. Evaluation for the modification of metal binding sites and efficiency by changing the ligating atoms in main frame or in side chains for selective silver extraction was carried out.

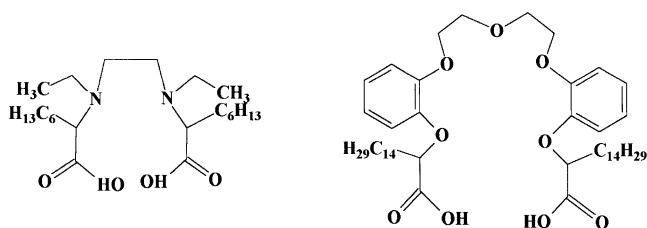
Experimental Section

Reagents and instrumentation. All stock solutions of Al(III), Cr(III), Fe(III), Cd(II), Pb(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Ag(I) ions were prepared from the corresponding metal nitrates (Aldrich, 99.99%) and standardized by titration with EDTA using xylenol orange as an indicator. All solutions were made in deionized water. All other chemicals were of reagent grade and were used without further purification. A Perkin Elmer Atomic Absorption Spectrophotometer was used for the determination of metal ion concentrations in solution. Melting points were taken by the use of a Mel-Temp of Fisher-Johns melting point apparatus without any correction. IR spectra were obtained with a Perkin-Elmer 1600 Series FT-IR on a KBr pellet and recorded in reciprocal centimeters. ¹H NMR spectra were also obtained with an AF-300 spectrometer with the chemical shifts (δ) reported downfield from the internal standard, tetramethylsilane (TMS). Elemental analysis was performed by a CHNS-O EA 1108-Elemental Analyzer from Carlo Erba Instruments in the Agency for Defence Development, Taejeon, Korea.

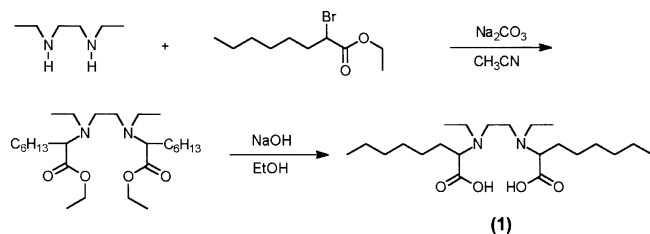
Synthesis.

***N,N*-Diethyl-2,7-dihexyl-3,6-diazaoctanoic acid diethyl ester.** Under dry nitrogen, ethyl -bromooctanoate (1.48 g, 12.80 mmol) and *N,N*-diethylenediamine (0.68 g, 5.90 mmol) were dissolved in 60 mL of acetonitrile containing excess sodium carbonate (8.40 g) and heated to reflux for 12 hrs. After cooling, the solution was filtered and the solvent was removed *in vacuo* to give the crude diester which was chromatographed on silica gel with *n*-hexane:ethyl acetate (4 : 1) as an eluent to yield 2.00 g (74%) as a colorless oil. IR (neat): 1733 (C=O). ¹H NMR (CDCl₃) δ 0.89 (t, 6H), 1.20-2.11 (m, 32H), 2.45 (q, 4H), 3.21 (d of t, 4H), 3.35 (t, 2H), 4.16 (q, 4H). Anal. Calcd for C₂₆H₅₂N₂O₄: C, 68.42; H, 11.40. Found: C, 68.37; H, 11.10.

***N,N*-Diethyl-2,7-dihexyl-3,6-diazaoctanoic acid (1).** Hydrolysis of diester 1 (2.00 g, 4.38 mmol) was carried out in refluxing ethanol: 10% NaOH (1 : 1) for 12 hrs, followed by removal of the ethanol *in vacuo* and acidification by the



Scheme 1



Scheme 2

addition of 50 mL of a dioxane: 6 N HCl (1 : 1) mixture. The mixture was refluxed for 3 hrs, and the dioxane removed *in vacuo* during which time a white precipitate formed. The precipitate was filtered through a medium glass frit followed by washing with 50 mL of water and drying under vacuum to yield 1.43 g (82 %) of **1** as a white solid. Mp 175-177 °C. IR (neat): 1713 (C=O). ¹H NMR (CDCl₃) δ 0.88 (t, 6H) 1.22-2.15 (m, 26H), 2.44 (q, 4H), 3.27 (d of t, 4H), 3.36 (t, 2H). Anal. Calcd for C₂₂H₄₄N₂O₄: C, 66.00; H, 11.00. Found: C, 66.10; H, 10.97.

Scheme 2 shows the synthetic routes followed to obtain the *N,N*-diethyl-2,7-dihexyl-3,6-diazaoctanoic acid (**1**). 1,5-Bis[2-(2'-carboxypentadecyloxy)phenoxy]-3-oxapentane (**2**) were also synthesized according to a synthesis procedure reported elsewhere.^{15,16}

Solvent extraction. Solvent extractions were carried out by shaking vigorously equal volumes (10 mL) of 1.5×10⁻⁴ M of organic ligands in chloroform and 3.0×10⁻⁴ M of metal cations in aqueous solution placed in a stopped test tube for 30 min at 30 °C. The two phases were allowed to separate and then the organic layer was kept aside. The extractability of each metal ion was estimated from the decrease of metal ion concentration in aqueous phase determined by Perkin Elmer AA-3300 atomic absorption spectroscopy. Each metal ion concentration in aqueous solutions was calculated using an established calibration curve with five different corresponding solutions (1.0×10⁻⁵ M-3.0×10⁻⁴ M). Counter ion effect in a silver ion extraction was investigated by the use of various counter ions, *i.e.* iodide, nitrate, phosphate, sulfate, *p*-toluenesulfonate.

Results and Discussion

The affinities of *N,N*-diethyl-2,7-dihexyl-3,6-diazaoctanoic acid (**1**) and 1,5-bis[2-(2'-carboxypentadecyloxy)phenoxy]-3-oxapentane (**2**) and various heavy metal ions were examined by solvent extraction experiment using a chloroform-water biphasic system. An aqueous phase of metal nitrate solution (3.0×10⁻⁴ M) was employed as an aqueous phase. A chloroform solution of ligand (1.5×10⁻⁴ M) was used as an organic phase. A 1.5×10⁻⁴ M organic solution of ligand in CHCl₃ was equilibrated against aqueous phase and the amount of metal extracted in CHCl₃ was determined. Extraction selectivity was investigated by mixing an aqueous solution containing each Al(III), Cr(III), Fe(III), Cd(II), Pb(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Ag(I), and an organic solution of ligands in CHCl₃. Extraction efficiency was found to be independent on pH over the range of 2.0-

10.0. From the organic phase, extracted metal ions can be stripped easily with 0.1 M HNO₃/0.1 M H₂SO₄ (1 : 1).

Figure 1 shows the extraction efficiency of various heavy metal ions from aqueous phase into chloroform layer using the compound (**1**) at 30 °C. Since the Ag(I) ion is softer than other metal ions, we would expect nitrogen complexes to overwhelmingly dominate silver(I) ion. Relative extraction efficiency of metal ions was determined in percent based on total extracted metal ion concentration, 3.0×10⁻⁴ M. As can be seen from Figure 1, compound (**1**) extracted Ag(I) ion with the highest efficiency (95.2%) assuming 2 : 1 (metal ion : ligand) stoichiometry. While, little affinities of compound (**1**) toward other metal ions were observed except copper(II) (38.4 %). The concentration ratio of extracted Ag(I) to compound(**1**) is nearly 2.0, which indicates the 2 : 1 stoichiometry of the complex. In general, the metal cation complexes of synthetic acyclic polyethers have lower stability and less ability to extract metal cations from aqueous solution compared to those of cyclic polyethers.¹⁷ However compound (**1**) shows very high selectivity and extractability of silver ions over other 10 elements used in this work due to the enhanced dynamic structural adaptability and the formation of 2 : 1 metal ion-acyclic multidentate complexes. The energy-minimized plausible molecular structure of the compound (**1**) and the structure of the proposed binding of silver ion to the ligand, drawn by *Hyperchem* molecular modeling program is illustrated in Figure 2. The calculated bond length of nitrogen and oxygen(a) and oxygen(b) is 2.45 Å and 3.31 Å, respectively. The distance between two neighboring oxygens is 2.29 Å. Complexation structure can be predicted by simply placing metal ion in this structure in such a way to give the largest number of donor atoms with acceptable distance to metal ion. As can be seen, two carboxylate end groups and a nitrogen atom are located near in

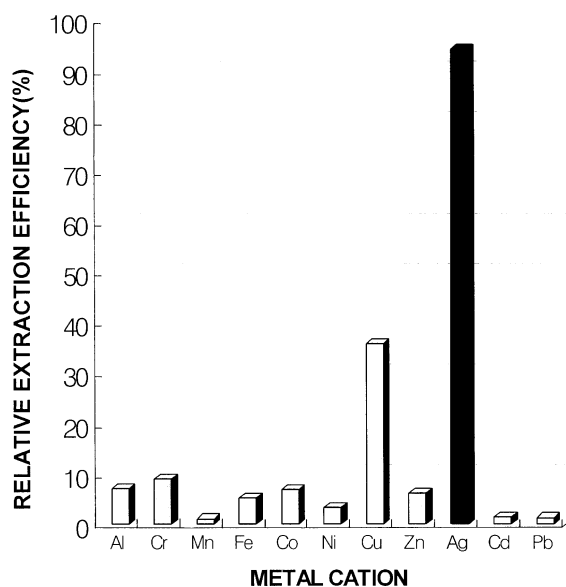


Figure 1. Profile for extraction efficiency of various heavy metal ions from aqueous phase into chloroform layer using the compound (**1**) at 30 °C and pH 6.80. Metal aqueous solution = 3.0×10⁻⁴ M, Organic solution (in chloroform) = 1.5×10⁻⁴ M.

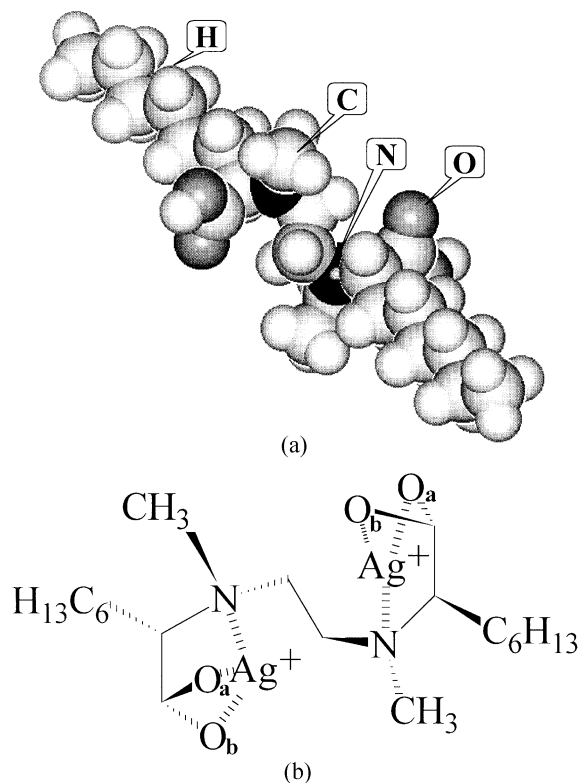


Figure 2. Schematic illustration of Energy minimized structure of Ag(I) selective acyclic azapolyether, compound (1); (a) and The structure of the proposed binding of silver ion to compound (1); (b).

the molecular structure and therefore can coordinate to the metal ion. The remarkably high Ag(I) preference of compound (1) is probably due to effective coordination of the nitrogen to Ag(I) and larger ionic size of Ag(I) (ionic radii of Ag(I) : 1.13 Å)¹⁸ compared to other metal ions. Probably the binding of one nitrogen atom into Ag(I) leads to the formation of pseudocavity by participating with two carboxylate end groups. The result suggested that the selectivity results from the hard and soft acid/base principle which probably reflects the increased covalent character between soft acid and soft base in a Ag(I) complex of a ligand containing a nitrogen atom.

Comparative work on the extraction efficiency of compound (1) and compound (2) was investigated for Ag(I), Pb(II) and Ni(II) metal ions. The compound (2) contains oxygen atoms in the frame and showed excellent extraction efficiency for alkali and alkaline earth metal ions especially for calcium cations through their free electron pairs.⁶ The Profiles for the extraction of three ions in an aqueous with two different ligands for 30 min at 30 °C are shown in Figure 3. As it is seen, compound (1) showed higher extractability than compound (2) especially for silver ion as expected. The effect of counter anion for silver(I) extraction with compound (1) was also performed and illustrated in Table 1. The metal ion concentration in aqueous solution was measured at 30 min after the mixing. The order of extractability of silver(I) in aqueous solution with compound (1) for various counter anions was $I^- > NO_3^- > CH_3C_6H_4SO_3^- > SO_4^{2-} >$

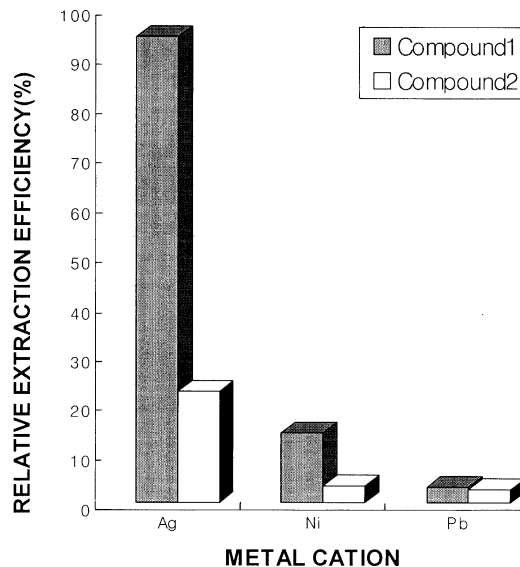


Figure 3. Comparative Profile for the extraction of Ag(I), Pb(II), Ni(II) ions in an aquatic environment with *N,N*-diethyl-2,7-dihexyl-3,6-diazaoctanoic acid (1) and 1,5-bis[2-(2'-carboxypentadecyloxy) phenoxy]-3-oxapentane (2). Metal aqueous solution = 3.0×10^{-4} M, Organic solution (in chloroform) = 1.5×10^{-4} M, for 30 min, at 30 °C.

PO_4^{3-} .

In conclusion, synthesis of a new acyclic azapolyether, *N,N*-diethyl-2,7-dihexyl-3,6-diazaoctanoic acid (1), which contains two nitrogen atoms in main frame and dicarboxylate functional end-groups was successfully accomplished with yields greater than 80% and their cation-binding properties for eleven metal cations including lead, nickel, chromium, silver and cobalt were elucidated by solvent extraction with a water-chloroform system. Control of high selective silver ion recognition over other ten heavy metal cations was achieved using this new acyclic azapolyether compound based on the two phase extraction system. The highly selective extraction of Ag(I) with remarkable efficiency over a broad range of pH (2.0-10) makes this new acyclic azapolyether compound attractive both for analytical and preparative scale separations.

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Table 1. Effect of counter anion for Ag(I) extraction with compound (1) at 30 °C and pH 6.80. Metal aqueous solution = 3.0×10^{-4} M, organic solution = 1.5×10^{-4} M

Metal Compound	Normalized Extraction Efficiency (%)
AgI	95.2
AgNO ₃	94.1
CH ₃ C ₆ H ₄ SO ₃ Ag	87.5
Ag ₂ SO ₄	84.1
Ag ₃ PO ₄	82.2

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