Solvent Extraction of Precious Metals with Quinolinocalix[4]arene

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Quinolinocalix[4]arene (abbreviated as Oct[4]CH₂²Qu) and a corresponding monomer have been prepared to investigate their extraction behavior for precious metals, together with a pyridinocalix[4]arene derivative for comparison. The present Oct[4]CH₂²Qu is not very soluble in an acidic aqueous solution of 2 mol dm⁻³ nitric acid. Slightly structural differences between quinolyl and pyridyl groups causes significant differences in the extraction behavior of platinum. Selective separation of palladium and silver over various metals was easily achieved with Oct[4]CH₂²Qu.

1. Introduction

Calixarenes are phenolic cyclic oligomers and are well-known as very attractive and interesting host compounds. [1-3] A number of review articles have been published on ion recognition. [4-7] The authors have been also attracted to this ion recognition property and have employed these compounds as solvent extractant reagents. [8] In our previous work, some specific extraction behavior involving ion discrimination by using such host compounds with certain size cavities has been observed. For example, among cyclic hexameric, cyclic tetrameric, linear trimeric, and monomeric carboxylate derivatives, the tetramer was found to be the most effective for the extraction of trivalent rare earth metal ions. [8a] It was also found that functional groups and ring size are very important factors for selective and effective extraction. In the previous work, ketone derivatives showed high silver selectivity, although the ketone compound seemed to be unsuitable for the uptake of silver due to the hardness of the ketonic oxygen as the coordinating atom. [8c] In order to further investigate the silver extraction behavior, the other work was carried out by using pyridyl derivatives providing soft functional groups. [9]

In the present work, a quinolinocalix[4]arene derivative with a soft quinolyl nitrogen as the coordinating atom in cone conformation has been prepared to investigate the extraction of silver and other precious metals as soft metals. Effect of structure on the extraction behavior has been discussed compared with those of the corresponding monomer and the pyridyl tetrameric derivative.

2. Experimental

2.1 Reagents

5,11,17,23-Tetrakis(1,1,3,3-tertamethylbutyl)calix[4]arene-25,26,27,28-tetrol (Oct[4]H) was
synthesized in a manner similar to that reported in a previous paper. [8a]

The preparation of 2-(chloromethyl)quinoline was carried out as follows: To 2-(chloromethyl)quinoline hydrochloride salt (25.3 g, 118 mmol) in 170 cm$^3$ dry $N, N$-dimethylformamide (DMF) was added triethylamine (12.1 g, 120 mmol) in 150 cm$^3$ dry DMF. After removal of the hydrochloride salt of triethylamine by filtration, the DMF solution of 2-(chloromethyl)quinoline was obtained. 25,26,27,28-Tetrakis(2-quinolylmethoxy)-5,11,17,23-tetrakis(1,1,3,3-tetramethylbutyl) calix[4] arene (tOct[4]CH$_2^2$Qu) in the cone conformation has been synthesized by interacting tOct[4]H with the corresponding chloromethyl quinoline as previously described for the preparation of pyridyl compounds. [9-12]


Under a nitrogen atmosphere, tOct[4]H (5.16 g, 5.91 mmol) was added to 120 cm$^3$ dry DMF. In a salt ice bath, sodium hydride (5.76 g, 144 mmol, 62.7% in oil) was added to the mixture and stirred for 3 h at room temperature. Then, 2-(chloromethyl)quinoline in dry DMF (118 mmol in 170 cm$^3$, 20 mol eq) was carefully added dropwise to the mixture, also in a salt ice bath and stirred for 1 h at 293 K and for 54 h at 318 K. After adding methanol to the mixture to deactivate excess sodium hydride, the solvent was evaporated in vacuo. Chloroform was added to the residue. The solution was neutralized by adding 1 mol dm$^{-3}$ hydrochloric acid and then the solution was washed with distilled water three times. The solution was dried over anhydrous magnesium sulfate. After filtration, the solvent was evaporated and the residue was recrystallized from methanol to yield 5.22 g of a pale yellow powder (70%), TLC(SiO$_2$, chloroform, $R_f = 0.10$), $^1$H-NMR (300 MHz, $\delta$, CDCl$_3$, TMS, 25°C), 0.63 (36H,s,(CH$_3$)$_3$), 1.14 (24H,s,(CH$_3$)$_2$), 1.54 (8H,s,C-CH$_2$-C), 3.06 (4H,d,ArCH$_2$Ar(exo)), 4.53 (4H,d,ArCH$_2$Ar(endo)), 5.15 (8H,s,OCH$_2$), 6.85 (8H,s,ArH), 7.34 (8H,t+t,3,4-QuArH), 7.46 (4H,d,8-QuArH), 7.59 (4H,d,5-QuArH), 7.68 (4H,d,7-QuArH), 7.68 (4H,d,2-QuArH)


25,26,27,28-Tetrakis(2-pyridylmethoxy)-5,11,17,23-tetrakis(1,1,3,3-tetramethylbutyl)calix[4]arene (tOct[4]CH$_2^2$Py) was synthesized in a manner similar to that reported in the previous paper. [9]

$p$-(1,1,3,3-tetramethylbutyl)phenoxy methyl-2-Quinoline ($^1$Oct[1]CH$_2^2$Qu)

Under a nitrogen atmosphere, $p$-(1,1,3,3-tetramethylbutyl)phenol (3.03 g, 14.7 mmol) was added to 60 cm$^3$ dry DMF. In a salt ice bath, sodium hydride (3.20 g, 80.0 mmol, 62.7% in oil) was added to the mixture and stirred for 2 h at room temperature. Then, 2-(chloromethyl)quinoline in dry DMF (72.4 mmol in 140 cm$^3$, 5 mol eq) was carefully added dropwise to the mixture, also in a salt ice bath and stirred for 1 h at 293 K and for 67 h at 318 K. After adding methanol to the mixture to deactivate excess sodium hydride, the solvent was evaporated in vacuo. Chloroform was added to the residue. The solution was neutralized by addition of 1 mol dm$^{-3}$ hydrochloric acid and then the solution was washed with distilled water three times. The solution was dried over anhydrous magnesium sulfate. After filtration, the solvent was evaporated and the residue was recrystallized from methanol to yield 1.58 g of a yellow powder (30.9%), TLC(SiO$_2$, chloroform : methanol = 10 : 1, $R_f = 0.86$), $^1$H-NMR (300 MHz, $\delta$, CDCl$_3$, TMS, 25°C), 0.71
(9H,5(CH3)3), 1.32 (6H,5(CH3)2), 1.69 (2H,5-C-CH2-C), 5.36 (2H,5-OCH2), 6.92 (2H,d,ArH), 7.26 (2H,d,ArH), 7.52 (1H,d,4-QuArH), 7.69 (2H,t+t,3,8-QuArH), 7.81 (1H,d,5-QuArH), 8.09 (1H,d,7-QuArH), 8.18 (1H,d,2-QuArH).

The chemical structures and the synthetic scheme for the extractants are shown in Figs. 1 and 2.

Fig. 1 Chemical structures of the extractants prepared in the present work.

Fig. 2 Synthetic scheme for the extractants.

2.2 Distribution test of 4-Oct[4]CH22Qu into aqueous phase

Organic solutions were prepared by diluting the extractant in analytical grade chloroform to the desired concentrations. Aqueous solutions were prepared by dissolving analytical grade HEPES (2-[4-(2-hydroxyethyl)-1-piperazinyl]-ethanesulfonic acid) or by diluting nitric acid to the desired concentrations. Both solutions were arbitrarily mixed to adjust pH and the nitric acid concentration. Equal volumes (5 cm3) of both phases were mixed and vigorously shaken at 303 K for 20 h. After phase separation, the extractant concentration distributed into the aqueous phase was measured by ultraviolet-visible spectrophotometry (Hitachi, UV-VIS U-3310).

2.3 Extraction study

Organic solutions were prepared by diluting each extractant with analytical grade chloroform to the desired concentration. Aqueous solutions were prepared by dissolving palladium and platinum chlorides to the desired concentration in aqueous nitric and hydrochloric acids (at pH < 1.2) or in a mixture of 0.1 mol dm−3 hydrochloric acid and 0.1 mol dm−3 HEPES solution (at pH > 1.2). Equal volumes (5 cm3) of both phases were mixed and vigorously shaken at 303 K for more than 24 h, which was sufficient to attain equilibrium. After phase separation, the pH was measured using a pH meter (Orion, model 720A+). Concentrations of metal ions were measured by ICP-AES (Shimadzu ICPS-8100). The amounts of the extracted metal ions were calculated from the differences of the metal concentrations in the aqueous phase before and after equilibrium. In the continuous variation method, the experiment was carried out keeping the total concentration of metal ion and the extractant constant at 5 mmol dm−3.

2.4 Proton nuclear magnetic resonance study

The organic solution was prepared by dissolving each extractant into analytical grade deuterated chloroform to the desired concentration. The aqueous solution was prepared by dissolving silver nitrate into an analytical grade deuterium oxide solution of nitric acid. Appropriate volumes of both phases were mixed...
and vigorously shaken at 303 K for more than 24 h. After phase separation, the spectra of ’Oct[4]CH$_2$2Qu in the organic phase were measured using a proton nuclear magnetic resonance spectrometer (Jeol, JNM-GX270).

3. Results and Discussion

3.1 Distribution of ’Oct[4]CH$_2$2Qu into the aqueous phase

The effect of pH and nitric acid concentration on the distribution of the extractant into the aqueous phase is shown in Figs. 3 (a) and (b), where the % distribution, $\%E_D$, is defined by eq.(1): 

$$
\%E_D = \frac{[R]_{aq}}{[R]_{ini}} \times 100
$$

(1).

where $[R]_{ini}$ and $[R]_{aq}$ are the initial extractant concentration in organic phase and the equilibrium extractant concentration in the aqueous phase. Figures 3 (a) and (b) show that only negligible distribution of the extractant was observed under almost all conditions, although slight distribution was observed at nitric acid concentrations above in 3 mol dm$^{-3}$. Since the $\text{pK}_a$ value of quinoline is approximately 4.5, the present extractant is largely insoluble in aqueous solution even in acid solutions. This is because the calix[4]arene derivatives are large molecule themselves and have four stepwise acid dissociation constants (this means that the charge per molecule of the calix[4]arene compound would be smaller than that of the corresponding monomer.), together with the fact that the polar groups are quire localized due to the cone conformation in which the functional groups point in the same direction.

![Fig.3 Effect of pH (a) and nitric acid concentration (b) on the % distribution of ’Oct[4]CH$_2$2Qu into the aqueous phase. [Extractant] = 5 mmol dm$^{-3}$.](image)

3.2 Extraction of precious metals

The effect of hydrochloric acid concentration on the percentage extraction of Pd (II) and Pt (IV) with the ’Oct[4]CH$_2$2Qu is shown in Fig. 4. The extractant strongly extracts both metals at high hydrochloric acid concentration, while the extraction percentages of Pt (IV) gradually decrease due to a decrease in the chloride anion concentration at low hydrochloric acid concentration. Although the extraction region for palladium overlapped that of platinum at high hydrochloric acid concentration, since palladium is more selectively extracted over platinum especially at low hydrochloric acid concentration, the separation of palladium from platinum using the quinolyl extractant employed in the present work could be achieved at low hydrochloric acid concentration. In order to investigate the influence of the media, the following experiment was carried out.
The effects of nitric acid concentration on the percentage extraction of Pd (II) and Pt (IV) with three extractants are shown in Figs. 5 (a)-(c), which show significant differences in the extraction of Pd (II) and Pt (IV) with the extractants. Both calix[4]arene types of extractants effectively extract palladium at all nitric acid concentrations, while extraction with the quinolyl monomer decreases at high nitric acid concentration due to protonation of the quinolyl nitrogens. The platinum extraction ability of \( ^1 \text{Oct}[4]\text{CH}_2^2\text{Qu} \) is quite poor compared with \( ^1 \text{Oct}[4]\text{CH}_2^2\text{Py} \). It is notable that a slight structural difference based on the absence or presence of the extended aromatic ring causes such a significant difference in the extraction behavior of Pt (IV). Therefore, it is concluded that the structural effect of the coordination site significantly affects the extraction behavior.

Furthermore, platinum extraction with \( ^1 \text{Oct}[4]\text{CH}_2^2\text{Qu} \) in nitrate media was significantly different from that in chloride media. It may be because the extracted platinum species were different which means platinum was extracted as a cation in nitrate media, while as an anion in chloride media.

Fig. 4 Effect of hydrochloric acid concentration on the \% extraction of Pd (II) and Pt (IV) with \( ^1 \text{Oct}[4]\text{CH}_2^2\text{Qu} \). [Extractant] = 5 mmol dm\(^{-3}\), [Metal] = 0.1 mmol dm\(^{-3}\).

Fig. 5 Effect of nitric acid concentration on the \% extraction of Pd (II), Ag(I) and Pt (IV) with three extractants. [Metal] = 0.1 mmol dm\(^{-3}\), \( ^1 \text{Oct}[4]\text{CH}_2^2\text{Qu} \) and \( ^1 \text{Oct}[4]\text{CH}_2^2\text{Py} = 5 \text{ mmol dm}^{-3}\), \( ^1 \text{Oct}[1]\text{CH}_2^2\text{Qu} = 20 \text{ mmol dm}^{-3}\).
Since the concentration of the monomeric compound was 4 times greater than that of the cyclic tetrameric calix[4]arene derivatives, the amount of functional groups were the same for all extractants. The extractants strongly extract silver at all nitric acid concentrations. On careful evaluation, however, it can be seen that the extraction % of silver with 'Oct[4]CH₂₂Qu is slightly lower than that with 'Oct[1]CH₂₂Qu and 'Oct[4]CH₂₂Py. This may be because the quinoline in 'Oct[4]CH₂₂Qu suppressed the complexation with silver due to the steric hindrance of the extended aromatic ring. Although silver extraction with the cyclic quinoline compound was suppressed, it is suggested that the compounds with a steric ally hindered quinoline group possibly contribute with regard to metal separation.

3.3 Determination of the structure of the silver complex with 'Oct[4]CH₂₂Qu

In order to determine the structure of the silver complex with 'Oct[4]CH₂₂Qu, the stoichiometric relation between silver and the reagent was examined by means of a loading test and the continuous variation method. The loading test for silver extraction with 'Oct[4]CH₂₂Qu is shown in Fig.6. The experimental result shows that the ratio of the initial extractant concentration to the loaded silver ion concentration gradually approaches 1.0 with increasing initial silver concentration. The result supports the formation of a 1:1 metal:reagent complex. The present stoichiometry is the same as that for silver extraction with ketones, [8e] amides [8f] and pyridyl [9] derivatives of calix[4]arene. These derivatives were found to form complexes with silver surrounded by carbonyl and phenoxy oxygens, while the phenoxy oxygens of the pyridyl derivative do not participate in silver extraction.

Fig.6 Loading test for silver extraction with 'Oct[4]CH₂₂Qu. 0.1 mol dm⁻³ HNO₃, ['Oct[4]CH₂₂Qu] = 1 mmol dm⁻³.

Fig.7 ¹H-NMR spectra of 'Oct[4]CH₂₂Qu before (a) and after (b) complexation with silver.
In order to determine the silver complex structure with 1-Oct[4]CH$_2$Qu, a proton nuclear magnetic resonance study was carried out. The $^1$H-NMR spectra of 1-Oct[4]CH$_2$Qu before (a) and after (b) the complexation with silver are shown in Fig.7. Since the chemical structures and the coordinating properties of 1-Oct[4]CH$_2$Qu and 1-Oct[4]CH$_2$Py are similar, it was expected that the coordination sites would consist of only four quinolyl and pyridyl nitrogens but not phenoxy oxygens, which would cause structural change with four electron pairs vertically coordinated directly to the silver ion as reported for 1-Oct[4]CH$_2$Py. [9] For silver uptake with 1-Oct[4]CH$_2$Qu, however, since the methylene peak next to the phenoxy oxygen shifted to around 5.15 ppm (whereas the methylene peak of 1-Oct[4]CH$_2$Py was not observed), the participation of phenoxy oxygens was indicated. It may be attributed to the steric ally hindered structure of the quinolyl extended aromatic ring.

### 3.4 Extraction of other metal ions

In order to selectively separate and recover palladium and silver from other metal ions, the extraction of various other metal ions was also tested. The effect of pH on the percent extraction of some metals with 1-Oct[4]CH$_2$Qu is shown in Fig.8. The present extractant shows only poor extraction ability for other metal ions, such as copper (II), lead (II), indium (III). The selective separation of palladium and silver from these metal ions is easily achieved with 1-Oct[4]CH$_2$Qu.

### 4. Conclusion

Quinolinocalix[4]arene and a corresponding monomer have been prepared to investigate the extraction behavior for precious metals. The work showed that silver and palladium are selectively extracted. Slight differences in the extractant structure based on the absence or presence of quinoline causes significant differences in the extraction behavior for Pt (IV). Determination of the structure of the silver complex with 1-Oct[4]CH$_2$Qu was discussed. The complex structure, however, was not determined. From a selective extraction point of view, selective separation of palladium and silver from copper (II), lead (II), and indium (III) was easily achieved with 1-Oct[4]CH$_2$Qu. The compounds with steric ally hindered quinolyl groups possibly provide an opportunity for metal separation.

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### References