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Relationship between chemical structure and extraction efficiency toward palladium with ketonic derivatives of *p*-tert-octylcalix[4]arene in nitric acid media

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Abstract A *p*-tert-octylcalix[4]arene derivative with four phenyl ketonic side arms has been synthesized as a solvent extraction reagent for precious metal ions in order to compare the extraction behavior with that of the corresponding methyl ketonic derivative of *p*-tert-octylcalix[4]arene in nitric acid media. The extraction efficiency of the phenyl ketonic derivative for palladium was superior to that of the methyl ketonic one over the whole nitric acid concentration range. Silver and platinum were also moderately extracted by the phenyl ketonic derivative in low nitric acid concentration. The results demonstrated that the extraction behavior of the ligands towards precious metals is related to several structural factors, such as the flexibility of the side arms, the electric charge on the carbonyl oxygen atoms and the lipophilic properties. This work also determined the extraction mechanism of palladium with the phenyl ketonic derivative of *p*-tert-octylcalix[4]arene based on slope analysis and the peak shift for the FT-IR spectra of the ligand before and after the metal loading. Stripping from the organic phase after forward extraction was performed to separate palladium and silver.

Keywords Ketonic derivatives of *p*-tert-octylcalix[4]arene · Palladium · Solvent extraction · Chemical structure

Introduction

Precious metals such as gold(III), palladium(II) and platinum(IV) are important rare metals that are indispensable to high-technology industries as raw materials for catalysts, electronic materials and so on [1–3]. Although the selective separation and recovery of precious metals from aqueous solutions are of great importance in hydrometallurgy and wastewater treatment, the separation and purification of these metals are very difficult processes with insufficient separation efficiency due to their similar chemical properties. Consequently, it is a high requirement to develop more efficient recovery and separation processes [4–6]. A solvent extraction process is a potential alternative refining technology as is an ion-exchange process. Solvent extraction has become an advanced technique for the recovery and separation of precious metals including palladium(II), gold(III), and platinum(IV) [3, 7]. One of the most important factors in metal extraction is selectivity of the ligand towards certain target metal ions. Calix[4]arenes are phenolic macrocyclic host compounds [8–14] with their metal discriminating ability being one of their remarkable features making them suitable as specific receptors [15]. The authors have also been attracted by such ion discriminating property and have employed these compounds as solvent extraction reagents [16–20].

In our former works, some specific extraction behavior involving ion discrimination using the above host compounds with particular size cavities has been observed. For example, among acetic acid derivatives of *p*-tert-octylcalix

The present paper is dedicated to Prof. Jack Harrowfield and Dr. Jacques Vicens on the celebration of their 70th birthday.

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[6] arene and *p*-*tert*-octylcalix[4]arene, a corresponding linear trimer and monomer, the cyclic tetramer was found to be the most effective for the extraction/separation of trivalent rare earth metal ions due to the size fitting effect [15]. In our previous work, methyl ketonic *p*-*tert*-octylcalix[4]arene showed high silver selectivity, although the ketonic compound was not expected to be suitable for silver uptake due to the hard nature of the ketonic oxygen atom based on HSAB theory [17]. In the present work, the phenyl ketonic derivative of *p*-*tert*-octylcalix[4]arene with rigid and bulky aromatic rings in a cone conformation has been prepared in order to investigate the extraction behavior of the selected precious metals, and to discuss structural effects on the extraction behavior of precious metals in comparison with the corresponding methyl ketonic derivative.

Experimental

Reagents

All chemicals were employed as commercially received without further purification. Deuterated chloroform from Wako chemicals was used for NMR spectroscopy. The following metal chloride and nitrate salts were used for extraction experiments: $\text{H}_4\text{PtCl}_6 \cdot 5\text{H}_2\text{O}$, $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, $\text{RhCl}_3 \cdot 5\text{H}_2\text{O}$, AgNO_3 , $\text{Pd}(\text{NO}_3)_2$.

Synthesis

The chemical structures of cone conformational *p*-*tert*-octylcalix[4]arene derivatives are shown in Fig. 1, together with their abbreviations. The syntheses of the original *p*-*tert*-octylcalix[4]arene (TOC) [17] and methyl ketonic derivative of *p*-*tert*-octylcalix[4]arene (MKTOC) [21] were carried out by following the published procedures.

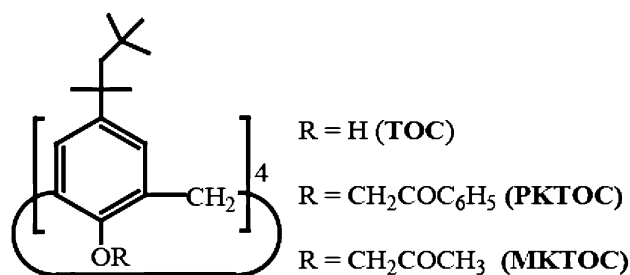


Fig. 1 Chemical structures and the abbreviations of original *p*-*tert*-octylcalix[4]arene (TOC) and cone conformational *p*-*tert*-octylcalix[4]arene derivatives with phenyl ketone (PKTOC) and methyl ketone (MKTOC)

The synthesis of cone conformational 25,26,27,28-tetrakis(2-oxo-2-phenylethoxy)-5,11,17,23-tetrakis(1,1,3,3-tetramethylbutyl)calix[4]arene (PKTOC)

Sodium iodide (1.35 g, 9.00 mmol) and phenacyl chloride (1.39 g, 9.00 mmol) were added under a nitrogen stream to 5 cm³ of dry acetone and the mixture was stirred for 20 min at room temperature. TOC (1.00 g, 1.14 mmol), potassium carbonate (1.30 g, 9.00 mmol) and 50 cm³ of dry acetone were added to the solution which was refluxed for 24 h. Then, the solvent was evaporated to obtain the crude compound which was dissolved in chloroform (150 cm³). The organic phase was washed twice with saturated sodium thiosulfate solution, once with distilled water, twice with 1 M ($\text{M} = \text{mol dm}^{-3}$) hydrochloric acid solution and twice again with distilled water (30 cm³). The solution was dried over anhydrous magnesium sulfate. After filtration, the solvent was evaporated *in vacuo* and recrystallized from acetonitrile. Yield : 71 % as a yellow powder. FT-IR (film), 2951 (C–H), 1662 (C=O), 1597 (C=C), 1473 (C–O) cm^{−1}. ¹H-NMR (300 MHz, CDCl₃, TMS), δ 0.74 (36H, s, C(CH₃)₃), 1.12 (24H, s, C(CH₃)₂), 1.53 (8H, s, C–CH₂–C), 3.25 (4H, d, Ar–CH₂–Ar(*exo*)), 5.11 (4H, d, Ar–CH₂–Ar(*endo*)), 5.65 (8H, s, O–CH₂–CO), 6.79 (8H, d, ArH), 7.29 (8H, t, *m*-PhH), 7.43 (4H, t, *p*-PhH), 7.92 (8H, d, *o*-PhH) (Fig. 2).

Apparatus

Infrared (IR) absorption spectrum of PKTOC was recorded on a FT-IR spectrophotometer (JASCO FT-IR 410). The ¹H NMR spectra was measured by a nuclear magnetic resonance spectrometer (Jeol JNM-GX300).

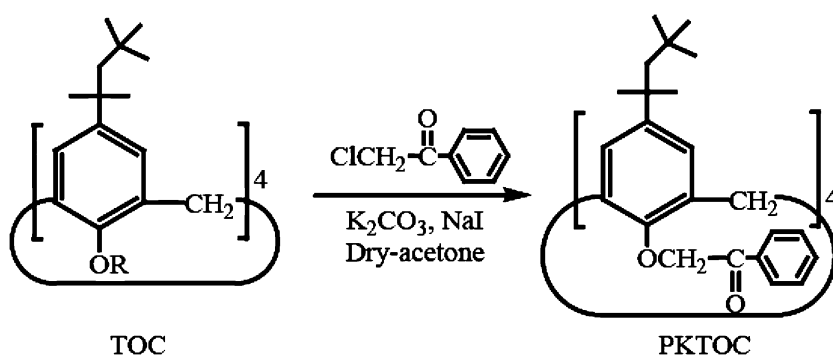
Forward and backward extraction procedure and measurement

Organic solutions were prepared by diluting each *p*-*tert*-octylcalix[4]arene derivative in analytical grade chloroform to the desired concentrations. Aqueous solutions were prepared by dissolving metal salts to the desired concentrations in aqueous nitric acid. Equal volumes (3 cm³) of both phases were mixed and vigorously shaken at 303 K for the desired time, which was sufficient to attain equilibrium. After phase separation, metal concentrations were measured by ICP-AES (Shimadzu, ICPS-8100). The amount of the extracted metal ion was calculated by the following Eq. (1).

$$\%E = \frac{C_i - C_e}{C_i} \times 100, \quad (1)$$

where, C_i and C_e represent initial and equilibrium metal concentrations in the aqueous phase (mol dm^{-3}), respectively.

Fig. 2 Synthetic route of cone conformational *p*-*tert*-octylcalix[4]arene phenyl ketonic derivative



The organic phase obtained after forward extraction was added to newly prepared aqueous solutions containing various stripping reagents for stripping of the loaded metal ions. The mixture was vigorously shaken at 303 K for 72 h, which was sufficient to attain equilibrium.

Study of FT-IR spectrophotometry

Organic solutions were prepared by diluting each *p*-*tert*-octylcalix[4]arene derivative in analytical grade chloroform to the desired concentrations. Aqueous solutions were prepared by dissolving each palladium nitrate amount in nitric acid to the desired acid and metal concentrations. Equal volumes of both phases were mixed and vigorously shaken at 303 K for more than 72 h. After phase separation, the spectra of ligands in the organic phase were measured in order to allow quantitative measurement using a FT-IR spectrophotometer.

Results and discussion

Effect of shaking time on percentage extraction of precious metals in nitric acid media

The effects of the shaking time on the percentage extraction of silver and palladium with PKTOC, together with MKTOC in nitric acid media are shown in Fig. 3a, b.

Generally, because *p*-*tert*-octylcalix[4]arene derivatives are highly hydrophobic, the extraction corresponds to complexation at the interface followed by transport into the bulk organic phase. So, the extraction equilibria are reached very quickly, as expected for ion pairing in the absence of any interfacial resistance to mass transfer. However, the extraction rate towards metal ions exhibited big differences depending on the presence (PKTOC) or absence (MKTOC) of the extended aromatic rings as side arms on the ligands.

Extraction of silver and palladium with PKTOC is sufficiently fast, although both extraction percentages were

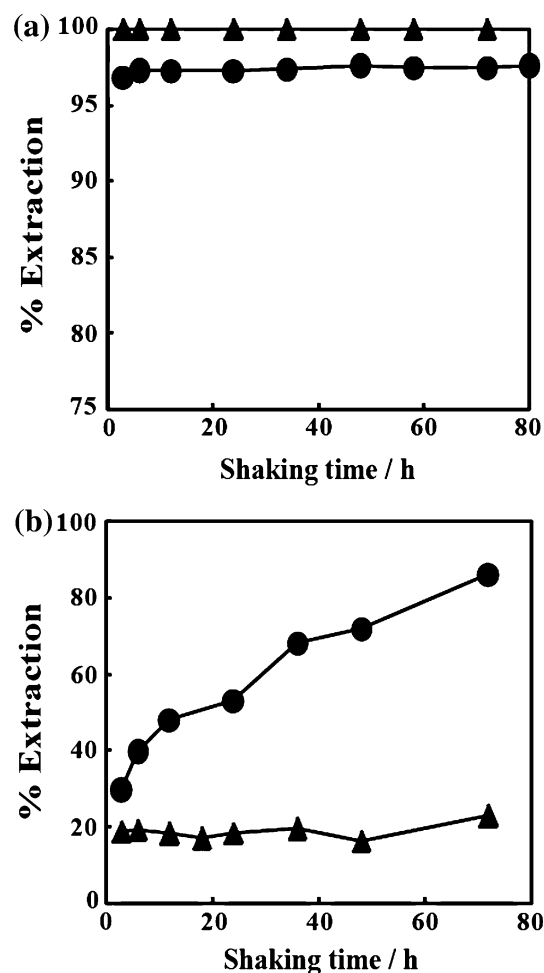


Fig. 3 Effect of shaking time on the extraction percentage of precious metals with **a** PKTOC and **b** MKTOC. [Metals]_i = 0.1 mM, [Ligand] = 5 mM, [HNO₃] = 1.0 M, circle silver(I), triangle palladium(II)

too high and the data were not suitable for determining the time for reaching equilibrium, while the reaching of equilibrium for silver and palladium extraction with MKTOC required more than 72 h. Equilibrium for silver and palladium with PKTOC was reached within 1 h. These results

indicated that two ligands with similar ketonic functionality nevertheless exhibited significant differences in the extraction rate toward silver.

The aromatic rings of PKTOC provide rigidity reflecting their planar nature also incorporating the sp^2 carbonyl groups. Consequently, silver extraction with PKTOC was drastically facilitated. The aromatic rings also may affect the interfacial tension of PKTOC and enhance the extraction rate. However, the apparent silver selectivity for PKTOC disappeared, while it was observed for MKTOC. Nevertheless, the short contact time required of PKTOC is advantageous for analytical as well as scale up separation purposes.

Distribution equilibrium in chloride media

The effects of the HCl concentration on the percentage extraction of precious metals with PKTOC and MKTOC are shown in Fig. 4a, b. For the HCl concentration less than 3 M, silver was precipitated as silver chloride.

Both ketonic type of *p*-tert-octylcalix[4]arene ligands exhibited very poor extraction ability towards all the precious metals in chloride media due to strong competitive complexation with chloride anions; that is, the carbonyl groups at the lower rims of the *p*-tert-octylcalix[4]arene derivatives act as electron-donating groups for cations, consequently the derivatives must compete and remove excess chloride anion(s) from metal cations for neutralization and ion-pair extraction for high extraction efficiency.

Distribution equilibrium in nitric acid media

The effects of the nitric acid concentration on the percentage extraction of precious metals with PKTOC and MKTOC are shown in Fig. 5a, b. High extraction percentages of silver ion with both ligands were observed over the whole nitric acid concentration range, whereas the extraction ability of MKTOC towards the other precious metals was very poor. High silver selectivity can be attributed to the lower number of required anions for neutralization and the size fit between the coordination site and ionic diameter of silver.

The similar ketonic compound, PKTOC, exhibited significantly different extraction behavior compared with MKTOC. Remarkably the PKTOC extracted both palladium and platinum at relatively low nitric acid concentration, while the extraction percentages for platinum drastically decreased with increase of the nitric acid concentration. Although the extraction region for palladium overlapped with that for platinum at low nitric acid concentration, since palladium was more selectively extracted over platinum, especially at high nitric acid concentration, the separation of palladium from platinum using PKTOC was achieved at high nitric acid concentration.

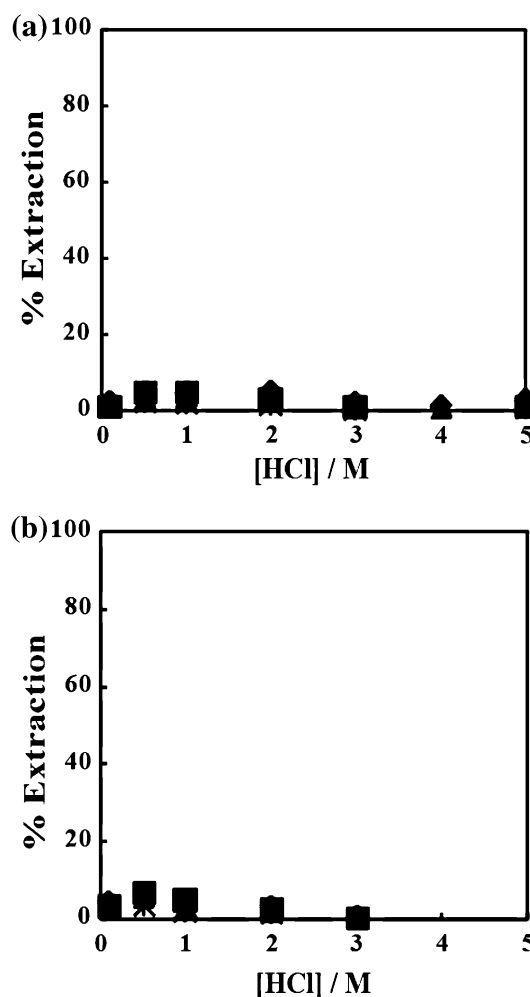


Fig. 4 Effect of HCl concentration on the extraction percentage of precious metals with **a** PKTOC and **b** MKTOC. [Metals]_i = 0.1 mM, [Ligand] = 5 mM, circle silver(I), triangle palladium(II), diamond platinum(IV), square ruthenium(III), asterisk rhodium(III)

The significant difference in extraction behavior between PKTOC and MKTOC incorporating similar ketonic functionality would be attributed to steric hindrance and to the rigidity of the phenyl groups for small metal ions, and the π -electron donating nature of the carbonyl oxygen atoms configured with phenyl groups for soft metal ions. It is notable that a slight structural difference based on the absence or presence of the aromatic ring causes such a significant difference in the extraction behavior towards the present precious metals.

Therefore, it is clear that the structural effect of the coordination site significantly affects the extraction behavior.

Slope analyses

Since palladium was significantly extracted with PKTOC compared with MKTOC over the whole nitric acid concentration range shown in Fig. 5a. In order to determine the

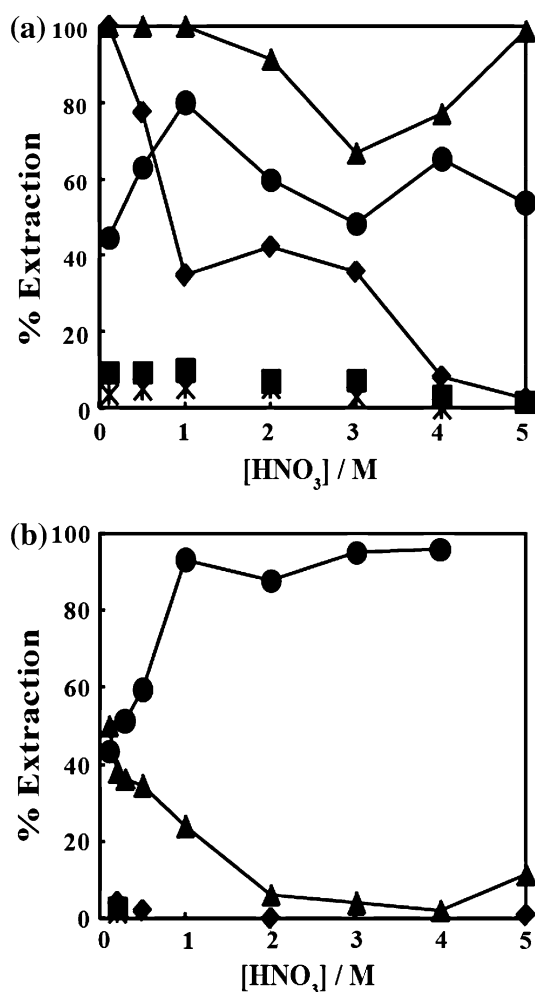


Fig. 5 Effect of nitric acid concentration on the extraction percentage of precious metals with **a** PKTOC and **b** MKTOC. $[\text{Metals}]_i = 0.1$ mM, $[\text{Ligand}] = 5$ mM, circle silver(I), triangle palladium(II), diamond platinum(IV), square ruthenium(III), asterisk rhodium(III)

stoichiometry of palladium extraction with PKTOC and MKTOC and to understand the difference in extraction based on the structural effect, the effect of the ligand concentration on the distribution ratio of palladium with PKTOC and MKTOC was investigated. The results are shown in Fig. 6. The distribution ratio, D is defined as $C_{\text{Pd,org}}/C_{\text{Pd,aq}}$ at equilibrium.

In the case of PKTOC, the plotted points lie on the straight line with a slope of 1 from 2.0 to 6.0 mM ligand concentration, indicating that one molecule of PKTOC participates in the extraction reaction of each palladium ion. Consequently, PKTOC forms 1:1 complex with palladium, and the cation is assumed to be encapsulated in the cavity formed by the carbonyl oxygen atoms.

On the other hand, in the case of MKTOC, the plotted points lie on the straight line with a slope of 2 from 2.0 to 6.0 mM ligand concentration, in accord with palladium being sandwiched by two MKTOC molecules. Consequently, both

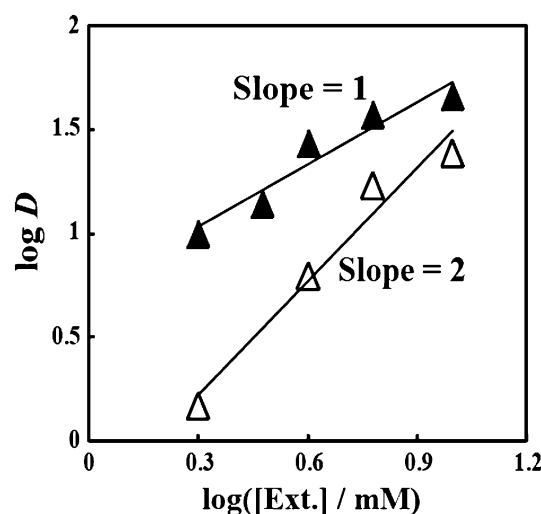


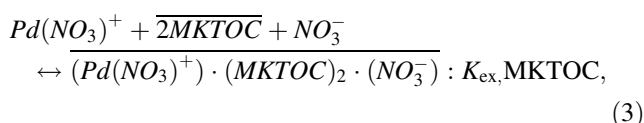
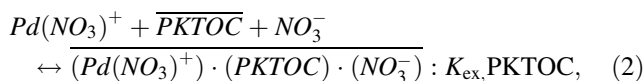
Fig. 6 Effect of ligand concentration on the distribution ratio of palladium ion with PKTOC and MKTOC. $[\text{Pd}^{2+}]_i = 0.1$ mM, $[\text{HNO}_3] = 1.0$ M, Filled triangle PKTOC, Open triangle MKTOC

investigated ligands (PKTOC and MKTOC) form complexes with different stoichiometries at low concentrations of Pd(II). This may reflect the difference in the electron density presented by the different side arms of the respective ligands (PKTOC and MKTOC).

The effects of nitrate concentration on the distribution ratio of palladium with PKTOC and MKTOC are shown in Fig. 7. Both sets of plotted points lie on straight lines with a slope of 1. This suggested that one nitrate was involved in the extraction reaction as a counter anion. That is, it appears that the Pd(II) coordination sphere is saturated on binding to one counterion.

The effects of proton concentration on the distribution ratio of palladium with PKTOC and MKTOC are shown in Fig. 8. For both investigated ligands, the plotted points lie on straight lines with slopes of 0. This result indicated that no change in the extraction mechanism takes place, as concluded from the slope of $\log D$ vs. $\log ([\text{H}^+]/\text{M})$ being 0.

Extraction equilibrium equations for palladium with both PKTOC and MKTOC are proposed to be represented by Eqs. (2) and (3), respectively [22].



where PKTOC and K_{ex} , PKTOC, MKTOC and K_{ex} , MKTOC denote the ligand and the extraction equilibrium constant, respectively. The extraction constants are defined as shown in Eqs. (4) and (6), respectively.

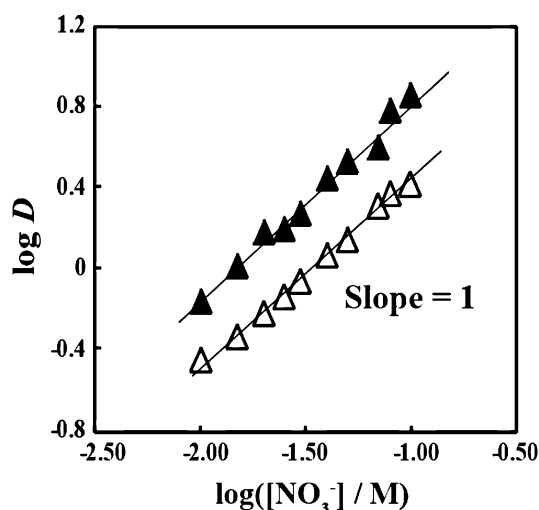


Fig. 7 Effect of nitrate concentration on the distribution ratio of palladium with PKTOC and MKTOC. $[Pd^{2+}]_i = 0.1$ mM, $[Ligand] = 5$ mM, $[H^+] = 1.0$ M, $[NO_3^-] = 0.1$ – 0.9 M, $[ClO_4^-] = 0.9$ – 0.1 M, Filled triangle PKTOC, Open triangle MKTOC

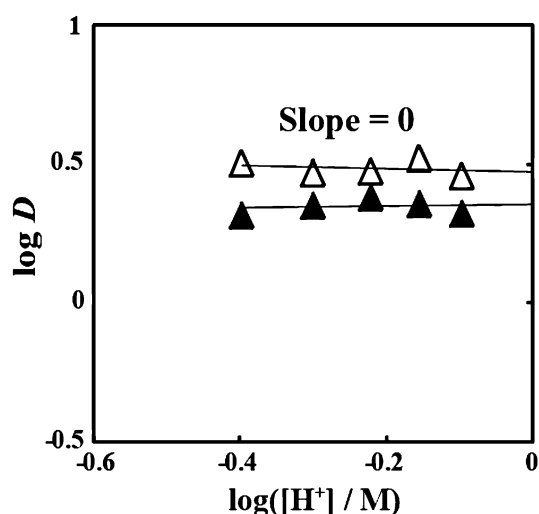


Fig. 8 Effect of proton concentration on the distribution ratio of palladium with PKTOC and MKTOC. $[Pd^{2+}]_i = 0.1$ mM, $[Ligand] = 5$ mM, $[NO_3^-] = 1.0$ M, $[H^+] = 0.1$ – 0.9 M, $[Li^+] = 0.9$ – 0.1 M, Open triangle PKTOC, Open triangle MKTOC

$$K_{ex,PKTOC} = \frac{[(Pd(NO_3)^+) \cdot (PKTOC) \cdot (NO_3^-)]}{[Pd(NO_3)^+] \cdot [PKTOC] \cdot [NO_3^-]}, \quad (4)$$

$$D_{PKTOC} = \frac{[(Pd(NO_3)^+) \cdot (PKTOC) \cdot (NO_3^-)]}{[Pd(NO_3)^+]}, \quad (5)$$

$$K_{ex,MKTOC} = \frac{[(Pd(NO_3)^+) \cdot (MKTOC)_2 \cdot (NO_3^-)]}{[Pd(NO_3)^+] \cdot [MKTOC]^2 \cdot [NO_3^-]}, \quad (6)$$

$$D_{MKTOC} = \frac{[(Pd(NO_3)^+) \cdot (MKTOC)_2 \cdot (NO_3^-)]}{[Pd(NO_3)^+]}. \quad (7)$$

In order to compare the two ligands (PKTOC and MKTOC) with different concentrations of ligands, K_{ex} values were estimated.

$$D_{PKTOC} = K_{ex,PKTOC} [PKTOC] [NO_3^-], \quad (8)$$

$$\log D_{PKTOC} = \log K_{ex,PKTOC} + \log [PKTOC] + \log [NO_3^-], \quad (9)$$

$$D_{MKTOC} = K_{ex,MKTOC} [MKTOC]^2 [NO_3^-], \quad (10)$$

$$\log D_{MKTOC} = \log K_{ex,MKTOC} + 2 \log [MKTOC] + \log [NO_3^-]. \quad (11)$$

From the linearized equation, extraction equilibrium constants for the PKTOC and MKTOC for palladium extraction were $K_{ex, PKTOC} = 1.38 \times 10^4 \text{ mol}^{-3} \text{ dm}^9$ and $K_{ex, MKTOC} = 5.95 \times 10^3 \text{ mol}^{-3} \text{ dm}^9$, respectively.

Study of FT-IR spectroscopy

To probe the coordination site of PKTOC for the extraction of palladium, a FT-IR spectrophotometric study was performed. The FT-IR spectra of the PKTOC before and after palladium loading in nitric acid media are shown in Fig. 9. The absorption peak of the carbonyl group was observed at $1,703 \text{ cm}^{-1}$ after loading, different from the free carbonyl peaks at $1,600$ and $1,662 \text{ cm}^{-1}$. A strong band for aryl-C stretch was present at 772 cm^{-1} , different from the free aryl-C peak at 511 cm^{-1} . This result indicates that the carbonyl oxygen atoms of PKTOC are directly coordinated to the metal ion. This may be attributed to the high electron

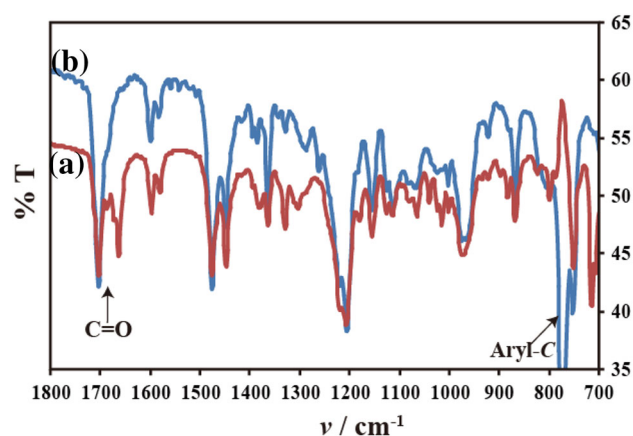


Fig. 9 FT-IR spectra of the PKTOC **a** before and **b** after Pd(II) loading. $[Pd^{2+}]_i = 0.1$ mM, $[HNO_3] = 0.1$ M, $[PKTOC] = 5$ mM

Table 1 Stripping percentages of silver and palladium from the metal loading PKTOC

Metal ions	% Extraction	Back extraction reagent	% Back extraction
Pd(II)	98.5	0.1 M NH ₄ SCN	66.9
		1 M NH ₄ SCN	92.4
		0.1 M thiourea	92.7
		1 M thiourea	95.6
Ag(I)	92.7	0.1 M NH ₄ SCN	8.9
		1 M NH ₄ SCN	62.7
		0.1 M thiourea	96.5
		1 M thiourea	89.3

density in the phenyl group-containing side arms of PKTOC.

On the other hands, the FT-IR spectra of the MKTOC before and after palladium loading in nitric acid media was not appreciably changed in the carbonyl stretching region. This means that the carbonyl oxygen atoms of MKTOC with their rigid methyl group-containing side arms was not directly coordinated to palladium. This may reflect the rigid nature of the methyl-containing side arms in MKTOC.

Stripping of precious metals

The degree of stripping of the respective loaded precious metal ions by PKTOC was investigated employing various stripping reagents. The results are summarized in Table 1. Silver and palladium were quantitatively stripped with thiourea. In the case of palladium, a high stripping percentage was exhibited with ammonium thiocyanate compared with the silver case. The separation of silver and palladium can also be achieved: by first stripping the palladium with 0.1 M ammonium thiocyanate, then silver with the thiourea. Since the stripping percentages for silver and palladium on PKTOC with particular stripping reagents were higher than those on MKTOC, it is concluded that PKTOC coordinates more strongly to silver than palladium under the conditions employed.

Conclusions

The ketonic derivatives of *p*-*tert*-octylcalix[4]arene, PKTOC and MKTOC, were prepared to investigate their extraction behavior towards precious metals. This work showed that PKTOC more strongly extracted silver, palladium and platinum relative to MKTOC in nitric acid media. Specially, the extractability of PKTOC for palladium and platinum was superior to that of MKTOC at low nitric acid concentration.

Differences in the ligand side-arm structure involving the absence or presence of aromatic rings caused significant differences in the extraction behavior for palladium and platinum. Determination of the stoichiometry for PKTOC and palladium under different extraction conditions has been discussed. From the results of the slope analysis, PKTOC formed 1:1 complexes with palladium. The coordination site of PKTOC for palladium was determined to be the carbonyl oxygen atoms as indicated by the FT-IR spectra.

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