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Solvent Extraction of Transition Metal Cations by Calixarene-Based Cyclic Ligands

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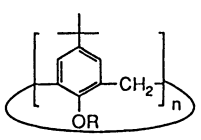
Calix[*n*]arenes (*n*=4 and 6) bearing carboxyl groups (**1**$_n$), hydroxamate groups (**2**$_n$), and dimethylamino groups (**3**$_n$) on the lower rim and their monomeric analogs (**1**$_1$, **2**$_1$, and **3**$_1$) were synthesized to estimate selective extraction of transition metal cations from the aqueous phase to the organic (chloroform) phase. **1**$_4$ and **1**$_6$ showed the selectivity toward Fe^{3+}, Cu^{2+}, Zn^{2+}, and Pd^{2+}. In particular, **1**$_6$ showed the unusually high extractability toward Fe^{3+}. **2**$_4$ and **2**$_6$ showed the selectivity toward Fe^{3+}, Cu^{2+}, and Pd^{2+}, but only Fe^{3+} was extracted to a significant extent at pH 2.2, the order of the extractability being **2**$_6$>**2**$_4$>**2**$_1$. **3**$_4$ and **3**$_6$ showed the selectivity toward Pd^{2+} and Pt^{4+}. The detailed examination of the extraction mechanism established that the ion-pair extraction mechanism is operative in Pt^{4+} (i.e., extracted as $[PtCl_6]^{2-}$) whereas both the ion-pair extraction mechanism and the chelate-complex extraction mechanism are operative in Pd^{2+} (i.e., extracted as $[PdCl_4]^{2-}$ in the ion-pair extraction mechanism). The results indicate that the ligand groups circularly arranged on the lower rim of the calixarene cavity form novel binding sites for transition metal cations.

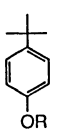
Calix[*n*]arenes are cyclic oligomers in which *n* moles of phenol units are linked by *n* moles of methylene bridges. The cyclic structure suggests the potential use of calix[*n*]arenes as specific receptors for metal ions. In contrast to a number of reports on the binding of alkali metal ions, reports on the binding of transition metal ions have still been limited.[1] Yoshida et al.[2] found that *p*-*t*-butylcalix[6]arene can extract Cu^{2+} from the ammonia-alkaline solution to the organic solvent. Gutsche and Nam[3] introduced dimethylamino groups onto the upper rim (*p*-positions of calix[4]arene): this compound could bind Cu^{2+} and Ni^{2+}. Through the molecular design of calixarene-based uranophiles, however, we learned that functional groups introduced onto the lower rim (i.e., close OH side) can act cooperatively whereas those introduced onto the upper rim (i.e., open *p*-position side) act rather independently.[4-6] The results promoted us to synthesize calix[*n*]arenes bearing ligand groups for transition metal ions onto the lower rim. We thus introduced hydroxamate and dimethylamino groups onto the lower rim of *p*-*t*-butylcalix[*n*]arenes (*n*=4 and 6) and compared the extraction ability with *p*-*t*-butylcalix[*n*]arenes (*n*=4 and 6) bearing carboxyl groups.

Experimental

Compounds **2**$_n$ were synthesized from **1**$_n$ by the reaction of the acid chlorides and *O*-benzylhydroxylamine followed by debenzylation with a catalytic hydrogenation method. Compounds **3**$_n$ were synthesized by the reaction of the acid chlorides and *N,N*-dimethylethylenediamine. The products were identified on the basis of IR and NMR spectral evidence and elemental analyses. In two-phase solvent extraction, the aqueous phase (containing 1.06×10^{-4} M of metal chlorides) was adjusted either to pH 2.2 (0.01 M[#] nitrate buffer, μ=0.1 with KCl) or to pH 5.4 (0.01 M acetate buffer, μ=0.1 with KCl) whereas the organic phase is chloroform (5 cm^3) containing 5.30×10^{-4} M of **1**$_n$, **2**$_n$, or **3**$_n$ (3.18×10^{-3} M for **1**$_1$, **2**$_1$, or **3**$_1$). The extraction was carried out at 30 °C for 12 h. The concentration of metal ions extracted into the organic phase was calculated from the analysis of metal ions remaining in the aqueous phase using atomic absorption spectrometry. The results are shown in Figs. 1 and 2.



1$_n$: R = CH_2COOH
2$_n$: R = $CH_2CONHOH$
3$_n$: R = $CH_2CONH(CH_2)_2NMe_2$



1$_1$: R = CH_2COOH
2$_1$: R = $CH_2CONHOH$
3$_1$: R = $CH_2CONH(CH_2)_2NMe_2$

Materials. The syntheses of **1**$_n$ and **2**$_n$ were described previously.[5,7]

5,11,17,23-Tetra-*t*-butyl-25,26,27,28-tetrakis-[*N*-(2-dimethylaminoethyl)aminocarbonylmethoxy]calix[4]arene(3$_4$). To a THF solution (10 cm^3) containing *N,N*-dimethylethylenediamine (3.00 g, 34.0 mmol) and triethylamine (6.89 g, 68.0 mmol) was added a THF solution (30 cm^3) containing 5,11,17,23-tetra-*t*-butyl-25,26,27,28-tetrakis(chlorocarbonylmethoxy)calix[4]arene[7] (1.62 g, 1.70 mmol). The solution was stirred at 35 °C for 30 h. The solution was filtered to remove precipitated hydrochloride salts, the filtrate being concentrated in vacuo. The residue was dissolved in chloroform (300 cm^3) and washed with water (100 cm^3×2) and aqueous 3% NaCl solution. The organic layer was separated and dried over anhydrous $MgSO_4$. The solution was concentrated to dryness, the residue being recrystallized from petroleum ether; white powder, mp 211—212 °C, yield 85%; IR (KBr) ν_{NH} 3300 cm^{-1}, $\nu_{C=O}$ 1650 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ=1.08 (9H, s, *t*-Bu), 2.24 (6H, s, NCH_3), 2.49 and 3.46 (2H each, t and t×d (respectively), NCH_2), 3.23 and 4.51 (1H each, d each, $ArCH_2Ar$), 4.53 (2H, s, OCH_2), 6.77 (2H, s, ArH), 7.77 (1H, t (broad), NH). Found: C, 70.34; H, 8.95; N, 9.67%. Calcd for $(C_{17}H_{26}N_2O_2)_4$: C, 70.31; H, 9.02; N, 9.65%.

[#] 1 M=1 mol dm^{-3}.

5,11,17,23,29,35-Hexa-*t*-butyl-37,38,39,40,41,42-hexakis[*N*-(2-dimethylaminoethyl)aminocarbonylmethoxy]calix[6]arene (3_6). This compound was synthesized from 5,11,17,23,29,35-hexa-*t*-butyl-37,38,39,40,41,42-hexakis-(chlorocarbonylmethoxy)calix[6]arene[7] in a manner similar to that described for 3_4 and recrystallized from petroleum ether and dichloromethane; white powder, mp 149—152 °C, yield 69%; IR (KBr) ν_{NH} 3280 cm^{-1}, $\nu_{C=O}$ 1660 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C) δ=0.74—1.41 (9H, m, *t*-Bu), 1.95—2.18 (6H, m, NCH_3), 2.35—2.70 (2H, m, $\underline{CH_2}NMe_2$), 3.05—3.60 (4H, m, $ArCH_2Ar$ and $\underline{CH_2}NH$), 6.61—7.36 (2H, m, ArH), 7.53 (1H, s(broad), NH). Found: C, 69.25; H, 9.02; N, 9.19%. Calcd for $(C_{17}H_{26}N_2O_2)\cdot HCl$: C, 68.87; H, 8.88; N, 9.45%.

1-*t*-Butyl-4-[*N*-(2-dimethylaminoethyl)aminocarbonylmethoxybenzene (3_1). This compound was also prepared from 1-*t*-butyl-4-(chlorocarbonylmethoxy)benzene in a manner similar to that described for the above compounds and purified by column chromatography (silica gel, chloroform–hexane 1 : 1 v/v); colorless oil, yield 87%; IR (Neat) ν_{NH} 3320 cm^{-1}, $\nu_{C=O}$ 1670 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$ 25 °C) δ=1.29 (9H, s, *t*-Bu), 2.20 (6H, s, NCH_3), 2.41 and 3.39 (2H each, t and t×d (respectively), NCH_2), 4.47 (2H, s, OCH_2), 6.66 and 7.31 (2H each, d each, ArH), 7.09 (1H, t (broad), NH). Found: C, 68.94; H, 9.50; N, 9.93%. Calcd for $C_{16}H_{26}N_2O_2$: C, 69.03; H, 9.41; N, 10.06%.

Solvent Extraction. Inorganic salts used for solvent extraction are all special grade reagents: $Fe(NO_3)_3\cdot 9H_2O$ (99.9%) from Wako Pure Chemical Ind.) for Fe^{3+}, K_2PtCl_6 from Kanto Kagaku for Pt^{4+}. K_2PdCl_4 was prepared from $PdCl_2$ (Kishida Kagaku) and KCl. A chloroform solution (5 cm^3) containing $\mathbf{1}_n$, $\mathbf{2}_n$, or $\mathbf{3}_n$ (5.30×10^{-4} M for n=4 and 6, 3.18×10^{-3} M for n=1) and an aqueous solution (25 cm^3) containing metal salt (1.06×10^{-4} M) were placed in a flask. The aqueous solution was buffered to pH 2.2 (0.01 M $NaNO_3$–HNO_3, μ=0.1 with KCl) or to pH 5.4 (0.01 M CH_3COONa–CH_3COOH, μ=0.1 with KCl). The mixture was shaken for 12 h at 30 °C. The extractability was not affected by further shaking, indicating that the equilibrium has been attained within 12 h. The aqueous phase was separated and subjected to the analysis by atomic absorption spectrometry. The extractability (Ex%) was determined from the decrease in the metal concentration in the aqueous phase: $Ex\% = \{([Metal]_{blank} - [Metal]_{water})/[Metal]_{blank}\}\times 100$ where $[Metal]_{blank}$ and $[Metal]_{water}$ denote the metal concentrations in the aqueous phase after extraction with pure chloroform and with the chloroform solution containing extractants, respectively, and $[Metal]_{og}$ denotes the metal concentration extracted into the organic phase.

Results and Discussion

Firstly, we determined the Ex% of metal nitrates at pH 2.2 and pH 5.4 (Figs. 1 and 2). At pH 5.4 $\mathbf{1}_6$ extracted more than 50% of Fe^{3+}, Cu^{2+}, Zn^{2+}, and Pd^{2+}. At pH 2.2, extraction of metal ions was extremely suppressed. However, Fe^{3+} was still extracted even at pH 2.2 by $\mathbf{1}_6$ among $\mathbf{1}_n$ and by $\mathbf{2}_1$, $\mathbf{2}_4$, and $\mathbf{2}_6$ among $\mathbf{2}_n$ but not by $\mathbf{3}_n$. The dimethylamino group in $\mathbf{3}_n$ is mostly protonated at pH 2.2 (vide post), so that $\mathbf{3}_n$ cannot act as extractants for Fe^{3+} at this pH region. It is well-known that hydroxamic acids are useful as an analytical reagent for Fe^{3+} because of their high Fe^{3+} affinity.[8] It is not surprising, therefore, that $\mathbf{2}_n$ can extract Fe^{3+} even at pH 2.2. The pK_a values for hydroxamic acids are estimated to be 8—9 in water. Thus, the extraction ability at pH 2.2 indicates that the dissociation of the hydroxamic groups in $\mathbf{2}_n$ is remark-

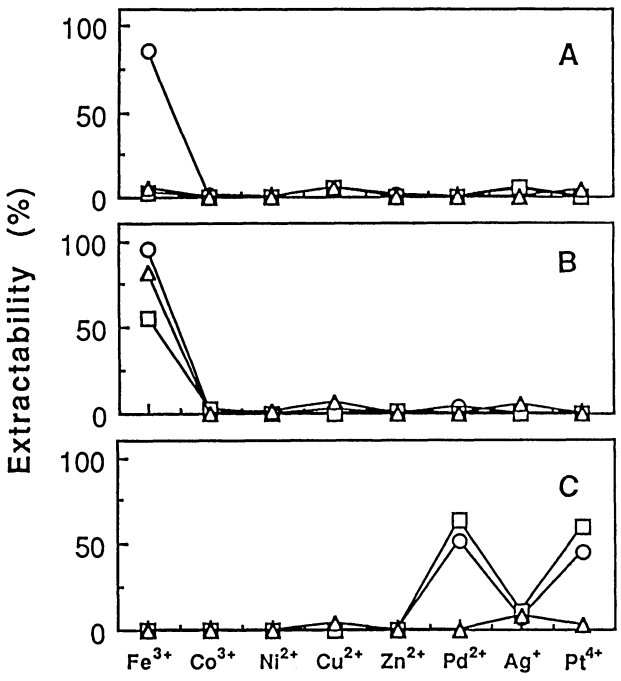


Fig. 1. Extraction of metal nitrates from an aqueous solution (pH 2.2) to a chloroform solution at 30°C; (A) $\mathbf{1}_n$, (B) $\mathbf{2}_n$, (C) $\mathbf{3}_n$, ○ n=6, □ n=4, △ n=1.

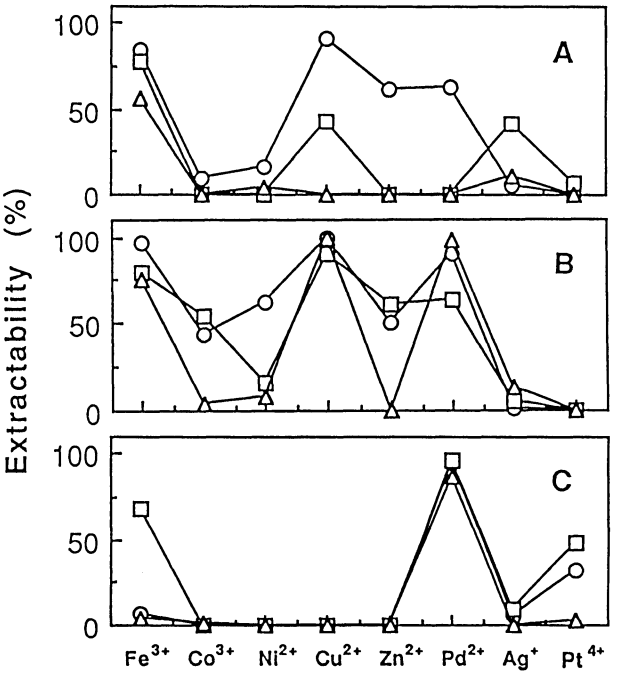


Fig. 2. Extraction of metal nitrates from an aqueous solution (pH 5.4) to an chloroform solution at 30 °C; (A) $\mathbf{1}_n$, (B) $\mathbf{2}_n$, (C) $\mathbf{3}_n$, ○ n=6, □ n=4, △ n=1.

ably facilitated (by about 6—7 pK units) through the binding to Fe^{3+}. When an aqueous solution (10 cm^3, not buffered but adjusted to pH 2.20 with HNO_3) containing Fe^{3+} (1.35×10^{-3} M) was shaked with a chloroform solution (5 cm^3) containing $\mathbf{2}_6$ (2.68×10^{-3} M), the pH of the aqueous phase was lowered to 2.08±0.01.## Since such a pH change was not observed upon shaking with a pure chloroform solution, the result indicates that protons are released from the organic phase to the aqueous phase upon metal extraction. We also confirmed that upon extraction of Fe^{3+} with $\mathbf{2}_n$ the yellow color, characteristic of Fe^{3+}-hydroxamate complexes, first appears at the interface followed by diffusion into the organic phase.

It is surprising, on the other hand, that only $\mathbf{1}_6$ can extract Fe^{3+} among $\mathbf{1}_n$. The loss of the Fe^{3+} affinity in $\mathbf{1}_1$ and $\mathbf{1}_4$ is explained by the fact that the carboxyl group is classified (compared with the hydroxamate group) to a poor ligand for Fe^{3+}. The X-ray crystallographic studies of metal·calix[4]arene complexes (e.g., metal $=Cu^{1+}$, Nb^{5+}, Ti^{4+}, etc.) show that calix[4]arenes cannot form 1:1 metal/calix[4]arene complexes but rather form metal-bridged cluster-type complexes.[9-11] This suggests that the basic skeleton of calix[4]arene is too rigid for carboxyl groups to adopt a unimolecular octahedral geometry required by Fe^{3+}. The basic skeleton of calix[6]arene is more flexible. Examination of a CPK molecular model of $\mathbf{1}_6$ reveals that the six carboxyl groups are allowed to adopt a unimolecular octahedral geometry required by Fe^{3+}. This explains why $\mathbf{1}_6$ can extract Fe^{3+} even at pH 2.2.

In order to obtain further insights into the extraction mechanism, we examined the pH-dependence of Ex%. Figure 3 shows plots of Ex% for Ni^{2+} versus pH. From these data, one can make plots of log D (distribution ratio=[metal] in the organic phase/[metal] in the aqueous phase) versus pH as shown in Fig. 4: that is, for an extraction equilibrium $M^{n+}_{aq}=(LH_m)_{org}$ $(MLH_{m-n})_{org}+nH^+_{aq}$ (where aq and org denote the species in the aqueous and the organic phase),

$$D=[MLH_{m-n})_{org}/[M^{n+}]_{aq} \quad (1)$$

The extraction equilibrium constant (K_{ex}) is given by Eq. 2. Thus, Eq. 1 is re-written as in Eq. 3.

$$K_{ex}=[MLH_{m-n})_{org}[H^+]^n_{aq}/[M^{n+}]_{aq}[LH_m]_{org} \quad (2)$$

$$\log D=n\cdot pH+\log K_{ex}+\log[LH_m]_{org} \quad (3)$$

Eq. 3 indicates that the slope n for the log D versus pH plot corresponds to the number of protons released upon extraction. The plot for $\mathbf{1}_6$ results in a slope of unity whereas that for $\mathbf{2}_6$ results in a slope of 1.8. The

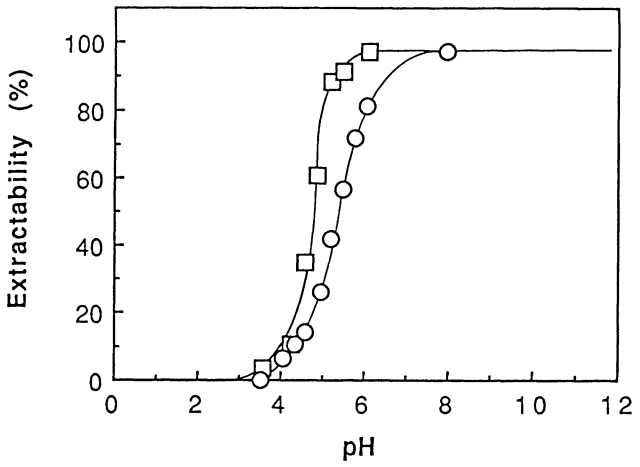


Fig. 3. Extractability of Ni^{2+} as a function of pH in the aqueous phase; ○ $\mathbf{1}_6$, □ $\mathbf{2}_6$.

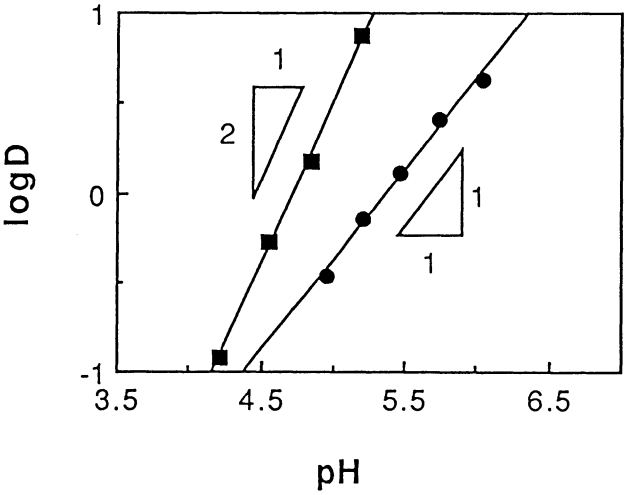


Fig. 4. Log D vs. pH; ● $\mathbf{1}_6$, ■ $\mathbf{2}_6$.

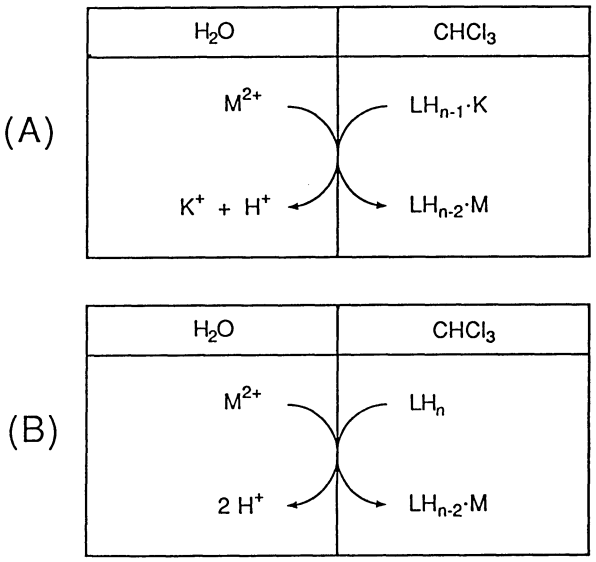


Fig. 5. Extraction mechanisms proposed for $\mathbf{1}_n$ (A) and $\mathbf{2}_n$ (B).

Provided that dissociation of hydroxamic acid groups and complexation of Fe^{3+} occurs stoichiometrically, we can expect the final pH of the aqueous phase to be lowered to 1.99. Thus, pH 2.08 is higher than this value. The discrepancy is ascribed to partial aquotization of Fe^{3+} ion.

results indicate that in two-phase solvent extraction with $\mathbf{1}_6$ the dissociation of one proton (i.e., an exchange between Ni^{2+} and K^+ plus H^+) takes place at the water–chloroform interface whereas in two-phase solvent extraction with $\mathbf{2}_6$ the dissociation of two protons (i.e., an exchange between Ni^{2+} and $2H^+$) takes place at the water–chloroform interface. The extraction processes are shown as in Fig. 5. In order to ascertain that the K^+ salt of $\mathbf{1}_n$ really exists in the chloroform phase, we shaked an aqueous solution (25 cm^3) containing 0.01 M CH_3COOH–CH_3COOK buffer (pH 4.1) and a chloroform solution (5 cm_3) containing 5.30×10^{-4} M) of $\mathbf{1}_6$. After 12 h at 30 °C the chloroform phase was separated and extracted with 0.1 M HCl solution. The atomic absorption analysis of this solution established that 76% of $\mathbf{1}_6$ is dissociated as the K^+ salt: that is, $LH_{5.24}K_{0.76}$ in Fig. 5. The difference in the extraction mechamism is accounted for by the difference in the pK_a values between the carboxyl group and hydroxamate group.

Examination of Figs. 1C and 2C proves that $\mathbf{3}_4$ and $\mathbf{3}_6$ serve as selective extractants for Pd^{2+} and Pt^{4+}. We notice a peculiar behavior, however; on going from pH 5.4 to pH 2.2 the Ex% for Pd^{2+} decreases whereas that for Pt^{4+} increases. It is known that Pd^{2+} and Pt^{4+} form stable chloride complex salts $[PdCl_4]^{2-}$ and $[PtCl_6]^{2-}$, respectively, which can be extracted by cationic extractants through the formation of ion pairs.[12] If this is the case in $\mathbf{3}_n$, the Ex% can be increased at lower pH region. The literatures on the distribution of the chloride complex salts[12–14] tell us that the major species under the extraction conditions (μ=0.1 with KCl) are $[PdCl_4]^{2-}$ and $[PtCl_6]^{2-}$. This means that one has to take two different extraction mechanisms into account, ion-pair extraction and chelate-complex extraction. To distinguish between these two mechanisms, we first estimated the proton dissociation of $\mathbf{3}_n$ at the water–chloroform interface. The aqueous solution (5 cm^3, 0.01 M buffer, μ=0.1 with KCl) containing lithium picrate (6.02×10^{-4} M) was shaked with the chloroform solution (5 cm^3) containing $\mathbf{3}_n$ ($6.0\times10^{-4}/n$ M) at 30 °C for 30 min. The concentration of picrate ion extracted into the organic phase was estimated from the absorption maximum in the aqueous phase (350 nm). The Ex% was estimated by $(A_{blank}-A)/A_{blank}\times100$ where A_{blank} and A denote the absorbance in the absence of and the presence of $\mathbf{3}_n$. The number of the protonated dimethylamino groups can be determined spectrophotometrically from the absorbance of picrate ions extracted into the organic phase as a counteranion of the protonated dimethylamino group. The results are illustrated in Fig. 6. It is seen from this figure that the dimethylamino group in $\mathbf{3}_1$ is totally protonated at acidic pH region (pH<4) whereas three of the four and four of the six dimethylamino groups are protonated in $\mathbf{3}_4$ and $\mathbf{3}_6$ respectively. The similar incomplete protonation is frequently seen for azamacrocycles; that is, further protonation of protonated azamacrocycles is suppressed because of electrostatic repulsion between likely charges.[15,16] The results observed for $\mathbf{3}_4$ and $\mathbf{3}_6$ can be explained on the same basis. Now, Fig. 6 shows that the protonated dimethylamino group disappears at

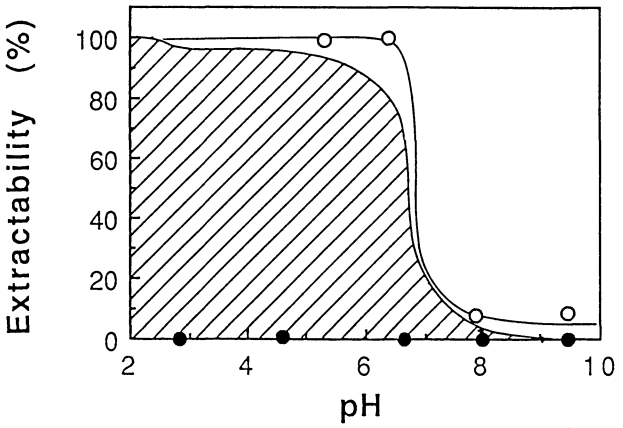


Fig. 7. Extraction of Pd^{2+} (○) and Pt^{4+} (●) by $\mathbf{3}_1$. The shadowed area denotes Ex% for picrate ion.

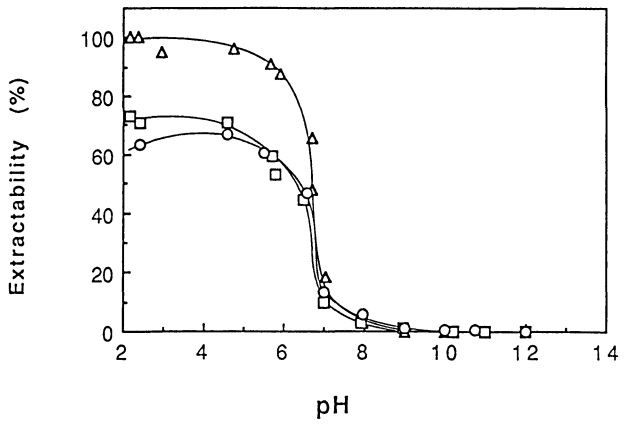


Fig. 6. Extractability of picrate ion as a function of pH in the aqueous phase; ○ $\mathbf{3}_6$, □ $\mathbf{3}_4$, △ $\mathbf{3}_1$.

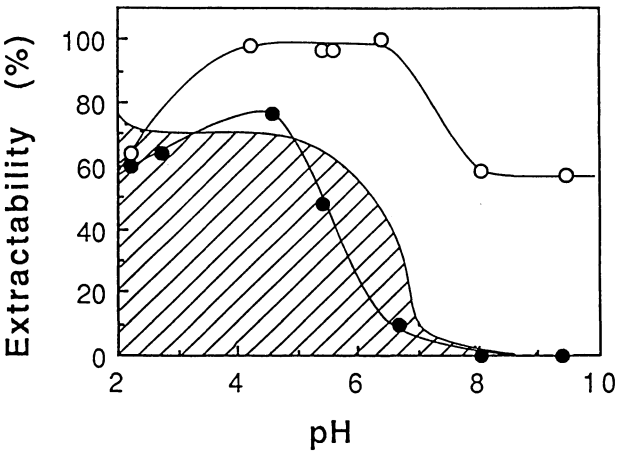


Fig. 8. Extraction of Pd^{2+} (○) and Pt^{4+} (●) by $\mathbf{3}_4$. The shadowed area denotes Ex% for pictrate ion.

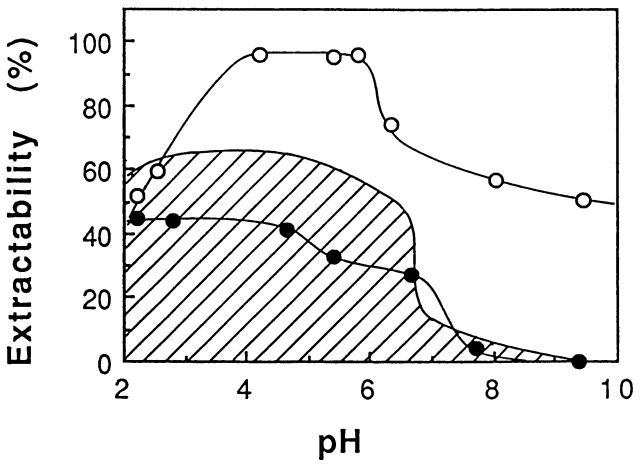


Fig. 9. Extraction of Pd^{2+} (○) and Pt^{4+} (●) by $\mathbf{3}_6$. The shadowed area denoted Ex% for picrate ion.

around pH 8. If the significant extraction of Pd^{2+} and Pt^{4+} takes place above pH 8, it follows that the extraction is due to the formation of the chelate complex. Figure 7 shows the extraction of Pd^{2+} and Pt^{4+} with $\mathbf{3}_1$. Pt^{4+} was not extracted at all pH region whereas Pd^{2+} was extracted only at acidic pH region and the pH-dependence of Ex% is similar to that of the protonation (shadowed area). This indicates that Pd^{2+} is extracted through the formation of an ion pair: judging from the "neutrality" of extracted species, we consider the ion pair to be $(\mathbf{3}_1^+)_2 \cdot [PdCl_4]^{2-}$. Figures 8 and 9 show the extraction of Pd^{2+} and Pt^{4+} with $\mathbf{3}_4$ and $\mathbf{3}_6$ respectively. Although Pt^{4+} is significantly extracted at acidic pH region, the coincidence between Ex% and protonation (shadowed area) suggests that the extraction is ascribed to the formation of an ion pair, $\mathbf{3}_6^{4+} \cdot [PtCl_6]^{2-}$. The finding provides an important fact about ion-pair extraction: that is, tricationic $\mathbf{3}_4$ and tetracationic $\mathbf{3}_6$ are superior to monocationic $\mathbf{3}_1$ as an extractant for $[PtCl_6]^{2-}$. On the other hand, Pd^{2+} was extracted even at pH>8 although Ex% becomes somewhat lower than that at pH<8. This supports the view that Pd^{2+} is extracted according to two different mechanisms; ion pair extraction mainly operating at acidic pH region and chelate-complex extraction mainly operating at basic pH region.

In conclusion, the present paper demonstrated that the ligand groups circularly arranged on the lower rim of the calixarene cavity construct novel "cyclic" metal receptors for selective extraction of transition metal cations. The results suggest that the fine tuning in molecular design can be done by using functional groups arranged on the lower rim (closed side of the calixarene cavity) rather than by using those arranged on the upper rim (open side of the calixarene cavity).

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