Metal-Ion Extractability of Sulfur-Bridged Oligomers of Phenol; Distinct Effect of the Number of Sulfur Bridges Rather Than the Cyclic/Acyclic Form[1]

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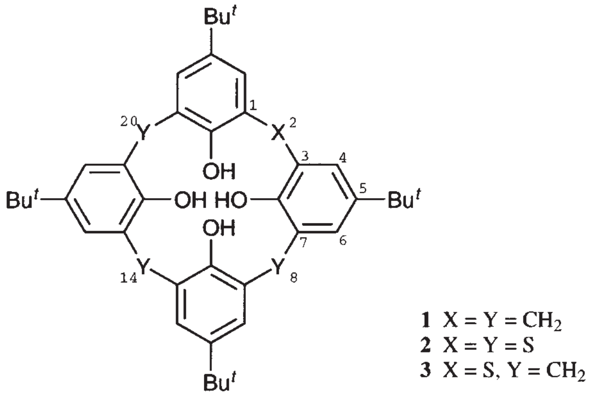
The solvent-extraction behavior of 2,8,14,20-tetrathiacalix[4]arene **2** was compared with those of 2-monothiacalix[4]arene **3** as well as linear tetramer (**4**) and dimer (**5**) of *p-tert*-butylphenol linked by sulfide bonds at the *ortho* positions in order to clarify the effect of the cyclic and acyclic structure and the number of sulfide bonds. The linear tetramer **4** showed almost the same extraction behavior as that of the cyclic counterpart **2**, showing the dependence on the pH for the extraction of Co(II), Ni(II), Cu(II), and Zn(II) ions. On the other hand, monothiacalix[4]arene **3** and acyclic dimer **5** showed far inferior extractability as compared to the former two, suggesting that the number of sulfide linkages, rather than the cyclic/acyclic structure, is predominant to determine the extractability. An equilibrium study on the extraction behavior of open-chain **4** (H_4L) toward Co(II), Cu(II), and Zn(II) ions revealed that the composition of the extracted species can be written as $[M_i(H_2L)_i]$ (*i*: integer), as was the case obtained by cyclic **2**. Furthermore, the extraction constants of **4** for those metal ions were almost the same as those obtained by **2**. The similarity of the extraction behavior between **2** and **4** suggests that the acyclic tetramer **4** may act as a pseudo-thiacalix[4]arene to have the same complexation manner as cyclic **2** by the O^-,S,O^--donor set, in which the presence of a phenol unit flanked by sulfide bonds at the both *ortho* positions is essential. In other words, the effect of the bridging sulfide in the phenol oligomers may be reasonably explained by the electron-withdrawing effect of the sulfide moiety to provide the phenol unit with a higher acidity to form $[M_2(H_2L)_2]$-type complexes having a double-cone structure stabilized by two sets of O^-,S,O^--ligated metal bridges.

It has been a common understanding to modify calix[4]arenes (e.g. **1**, Scheme 1) at the upper and lower rims in a stereo- and regioselective fashion for applying them to selective extractants for specific metal ions.[2] Otherwise, a replacement of the bridging methylene of the calix scaffold with heteroatoms had been highly intriguing, but quite challenging in calixarene chemistry due to synthetic difficulty.[3] In this context, it should be mentioned that Sone and his coworkers first synthesized 5,11,17,23-tetra-*p-tert*-butyl-2,8,14,20-tetrathiacalix[4]arene-25,26,27,28-tetrol (**2**) via stepwise joining of the phenol unit by sulfide bridges, followed by the final cyclization of a linear tetramer.[4] Subsequently, a facile one-step synthesis of **2** was reported from this group by simply heating a mixture of *p-tert*-butylphenol and elemental sulfur in the presence of a base.[5] Since then, it has been recognized that the bridging sulfur can provide a binding site to metal ions, opening an alternative approach to build calixarene-based ligands without relying on additional ligating substituents.[6] So far, native tetrathiacalix[4]arenes, including **2**, have been revealed to have high extractability toward transition metal ions categorized into Pearson's soft to intermediate acids.[7,8] This sharply contrasts with the fact that the conventional *p*-alkylcalix[4]arenes per se do not have an extraction ability,[7–9] implying the vital role of the bridging sulfur of **2** in binding to metal ions.



Scheme 1. Calix[4]arene (**1**) and the analogues with sulfur bridge(s) (**2**, **3**). Small numbers indicate the numbering system of calix-ring.

Recently, an X-ray structural analysis of Zn(II) complexes of tetrathiacalix[4]arene **2** has revealed the coordination manner via ligation of the bridging sulfur with cooperative binding of the adjacent phenolic oxygens (Scheme 2).[10a,b] Notably, the same coordination manner was found in the Co(II),[10b] Cu(II),[10c] Hg(II),[10e] and Nd(III)[10f] complexes. The universality of the coordination manner of **2** by the O^-,S,O^- donor set,[11] in turn, poses questions concerning the design of an extractant consist-

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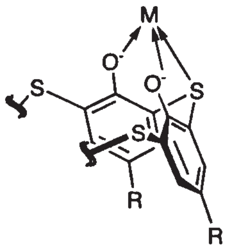
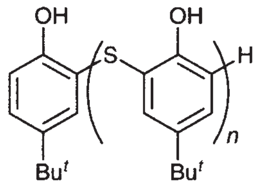


Scheme 2. Coordination manner of tetrathiacalix[4]arene. For clarity, part of tetrathiacalix[4]arene is drawn.



4 *n* = 3
5 *n* = 1

Scheme 3. Linear tetramer (**4**) and dimer (**5**) of phenol linked by sulfide(s).

ing of phenol units and sulfur bridges. Is one bridging sulfur enough to provide a calix[4]arene with extractability? Is it necessary to be cyclic? These questions prompted us to study the extraction behavior of 5,11,17,23-tetra-*p*-*tert*-butyl-2-monothiacalix[4]arene-25,26,27,28-tetrol (**3**), an open-chain tetramer (**4**, Scheme 3), and a simple dimer (**5**) toward transition metal ions, as compared with that of tetrathiacalix[4]arene (**2**). Here, we show the distinct effect of the number of sulfide bonds, more specifically, the presence of the phenol unit flanked by two sulfides at both *ortho* positions, rather than a cyclic/acyclic arrangement.[12]

Results and Discussion

pH Dependence of the *E*%. The pH dependence of the extraction ability of the phenol oligomers **2**–**5** toward Co(II), Ni(II), Cu(II), Zn(II), and Mg(II) was studied in terms of percent extraction, *E*%, defined by Eq. 1, where $[\mathrm{Metal}]_{\mathrm{org}}$ is the concentration of metal ions extracted into the organic phase and estimated by Eq. 2:

$$E\% = [\mathrm{Metal}]_{\mathrm{org}}/[\mathrm{Metal}]_{\mathrm{aq,init}} \times 100\%, \qquad (1)$$

$$[\mathrm{Metal}]_{\mathrm{org}} = [\mathrm{Metal}]_{\mathrm{aq,init}} - [\mathrm{Metal}]_{\mathrm{aq}}. \qquad (2)$$

Here, $[\mathrm{Metal}]_{\mathrm{aq,init}}$ and $[\mathrm{Metal}]_{\mathrm{aq}}$ denote the concentration of metal ions in the aqueous phase at $t = 0$ and 24 h, respectively. Equilibrium was attained within 24 h unless otherwise noted.

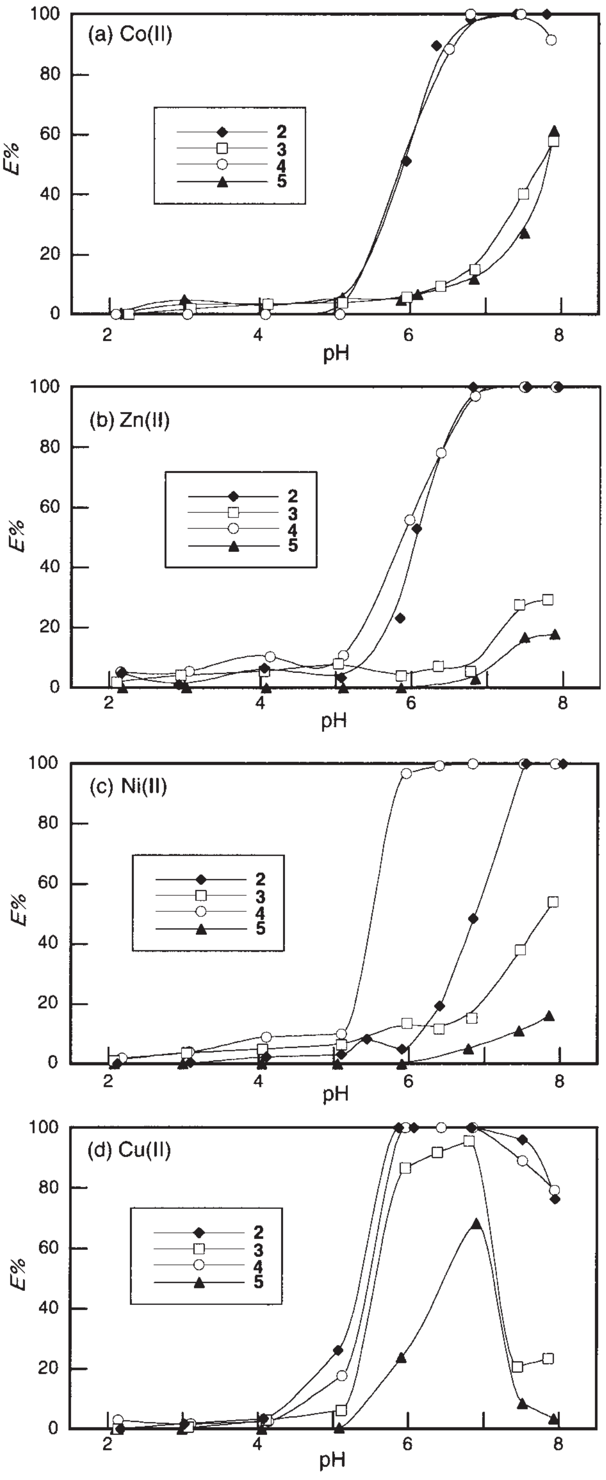


Fig. 1. The pH dependence of *E*% for (a) Co(II), (b) Zn(II), (c) Ni(II), and (d) Cu(II). Aq. (10 cm^3): 1.0×10^{-4} M metal ion, 0.05 M buffer, Org. (10 cm^3): 5.0×10^{-4} M tetrathiacalix[4]arene **2**, monothiacalix[4]arene **3**, or linear tetramer **4**, or 10×10^{-3} M dimer **5**. Temperature: ca. 20 °C.

It can be seen from Fig. 1a that tetrathiacalix[4]arene **2** quantitatively extracted Co(II) from the aqueous phase into organic phase above pH 6.9, which is consistent with the previously reported result.[7] Notably, the linear tetramer **4** extracted Co(II) ion to the same extent as did **2**, suggesting that the ligand structure, whether it is cyclic or acyclic, is not the predominant factor to determine the thermodynamic stability of the Co(II) complexes. Also noted is the much lower extraction ability of monothiacalix[4]arene **3** and dimer **5**; less than 20% of the Co(II) ion was extracted at pH 6.9. A comparison of the extractability of monothia **3** with that of tetrathia **2** clearly shows that the number of O$^-$,S,O$^-$ coordination units plays a critical role in the extraction (vide infra). For dimer **5**, since it is a tridentate ligand, the Co(II) center in a 1:1 complex still has three coordinated waters, which should reduce the distribution of the complex into the organic phase. In the extraction of Zn(II) (Fig. 1b), ligands **2** and **4**, and **3** and **5** behave similarly as in the case of extraction of Co(II).

In the case of Ni(II) (Fig. 1c), the cyclic tetramer **2** and the acyclic tetramer **4** behaved in different fashions in a weakly acidic pH region; the liner tetramer **4** had a higher extractability than tetrathiacalix[4]arene **2**. Considering the previous result that the extraction of Ni(II) with tetrathiacalix[4]arene **2** proceeded very slowly in a weakly acidic region,[7,13] the *E*% values of this pH region, shown in Fig. 1c, seem not to have reached the equilibrium values. On the contrary, extraction with the linear tetramer **4** proceeded smoothly to attain equilibrium within 24 h to have larger *E*% values. This is compatible with the common observation in the reaction kinetics of polydentate ligands, where open-chain ligands generally form metal complexes faster than the corresponding macrocyclic counterparts.[14]

In the case of Cu(II) (Fig. 1d), not only the liner tetramer **4** but also monothiacalix[4]arene **3** had similar half extraction pH ($pH_{1/2}$) values[15] to that of tetrathia **2**: $pH_{1/2} = 5.3$ for **2**, 5.6 for **3**, and 5.5 for **4**. In a weakly acidic pH region, these sulfur bridged ligands **2**–**4** had a higher affinity to the Cu(II) ion rather than proton presumably because of the high stability of the Cu(II)–S bond due to back donation from the Cu(II) center to the sulfur. This was also suggested by the higher *E*% of the dimer **5** toward the Cu(II) ion than that toward the Co(II) ion.[16] Consequently, one O^-,S,O^- unit was sufficient for the sulfur-bridged phenol ligands to extract Cu(II) ion in a weakly acidic region. At neutral to slightly basic pH, however, the *E*% of the monothiacalix **3** and dimer **5** decreased sharply, while tetrathia **2** and the linear tetramer **4** still retained the high *E*% values. Thus, the Cu(II) complex of **3** and **5** seemed to be readily decomposed by a replaement of the OH^- ion.

Next, the extraction of Mg(II) was investigated in a similar fashion with the above metal ions, but it was shown that Mg(II) was not extracted by either ligand ($E\% \leq 10\%$) in the pH region 4–10 (data not shown[17]). Thus, irrespective of the cyclic/acyclic form and the number of the coordination units, the sulfur-bridged oligomers of phenol did not have any affinity toward hard Mg(II) ion, due to a dislike of the bridging sulfur to Mg(II) as suggested by the hard and soft acids and bases (HSAB) rule.[8,18]

Extraction Mechanism of Acyclic Tetramer 4. Unexpectedly, the linear tetramer **4** exhibited a comparable extractability to that of thiacalix[4]arene **2**, which led us to pursue a quantitative study of the extraction mechanism and the equilibrium extraction constants. The general extraction reaction by a linear tetramer is described as

$$\begin{aligned} &M^{2+} + mH_4L_{org} + (n-2)C^+ \\ &\quad \rightleftharpoons C_{n-2}[MH_{4m-n}L_m]_{org} + nH^+, \end{aligned} \tag{3}$$

where M^{2+}, H_4L, C^+, $[MH_{4m-n}L_m]$, and $C_{n-2}[MH_{4m-n}L_m]$ denote the metal ion, the tetramer **4** having four dissociable protons, the counter cation, the metal complex, and the ion-associate to be extracted, respectively. The subscript org means species in the organic phase. The thermodynamic extraction constant (K_{ex}) is given by

$$K_{ex} = \frac{a_{C_{n-2}[MH_{4m-n}L_m],org} \cdot a_{H^+}^{n}}{a_{M^{2+}} \cdot a_{H_4L,org}^{m} \cdot a_{C^+}^{n-2}}, \tag{4}$$

where *a* denotes the activity for each species. The distribution ratio (*D*), defined by Eq. 5, is employed to determine the degree of distribution of the extracted metal species, $C_{n-2}[MH_{4m-n}L_m]$, in the organic phase against M^{2+} remaining in the aqueous phase,

$$D = a_{C_{n-2}[MH_{4m-n}L_m],org}/a_{M^{2+}}. \tag{5}$$

The combination of Eqs. 4 and 5 gives

$$\begin{aligned} \log D = {} & \log K_{ex} + m \log a_{H_4L,org} \\ & + n\text{pH} + (n-2)\log a_{C^+}. \end{aligned} \tag{6}$$

The dependence of $\log D$ on $\log a_{H_4L,org}$ or the pH gives *m* or *n*, respectively, where the other variables are kept constant.

The $\log D$ vs $\log a_{H_4L,org}$ plots are fitted by Eq. 6 to reveal that the slope *m* is unity (Fig. 2a), meaning that the ligand/

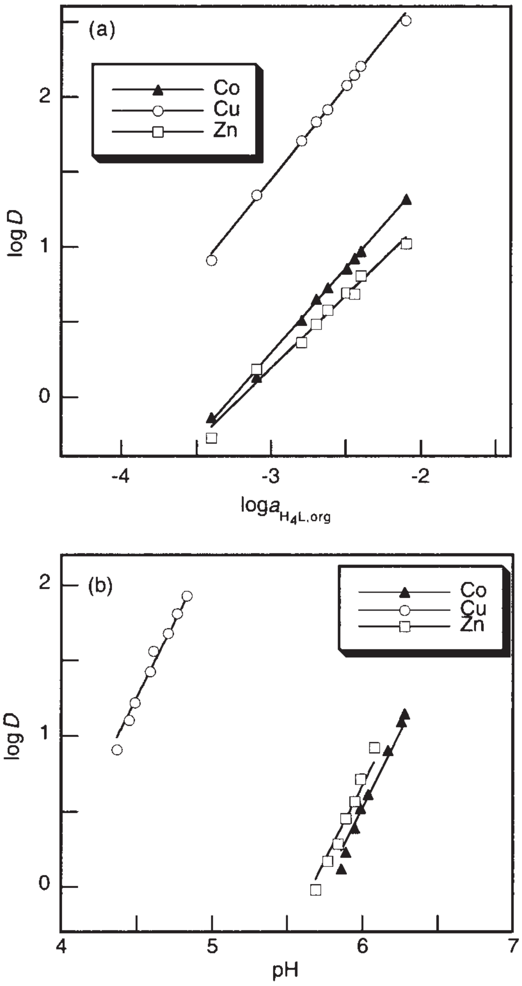


Fig. 2. The dependence of $\log D$ on (a) $\log a_{H_4L,org}$ and (b) pH. (a) Aq. (10 cm^3): 1.0×10^{-4} M metal chloride, 0.01 M pyridine, 0.05 M buffer, pH 6.00 for Co(II), pH 4.87 for Cu(II), pH 5.91 for Zn(II), Org. (10 cm^3): (0.4–8.0) $\times 10^{-3}$ M linear tetramer **4**. The slopes (*m*) obtained were 1.1_4 (Co(II)), 1.2_4 (Cu(II)), and 0.9_7 (Zn(II)). (b) Aq.: 1.0×10^{-4} M metal ion, 0.01 M pyridine, 0.05 M buffer. For Co(II) extraction, L-ascorbic acid was added to avoid oxidation of Co(II). Org.: 2.0×10^{-3} M linear tetramer **4**. The slopes (*m*) obtained were 2.3_7 (Co(II)), 2.2_0 (Cu(II)), and 2.4_3 (Zn(II)). Temperature: ca. 20 °C.

M(II) ratio in the extracted species was one. For Cu(II), the m value is somewhat larger than 1, suggesting the partial formation of a self-adduct or a 1:2 complex. On the other hand, $\log D$ vs pH plots gave good linear fittings with a slope n of nearly 2 (Fig. 2b), meaning that two protons were released upon the extraction of one M(II) ion into the organic phase. Strictly, the n value is 10–20% larger than 2, suggesting that a minor component of the extracted species released three protons to have one negative charge (such as $[MHL]^-$), which was neutralized with a counter ion C^+, such as pyridinium or ammonium cations, to be extracted. On the whole, the extraction equations (Eqs. 3, 4, and 6) are rewritten by introducing $m = 1$ and $n = 2$ to give

$$M^{2+} + H_4L_{org} \rightleftharpoons [MH_2L]_{org} + 2H^+, \tag{7}$$

$$K_{ex} = \frac{a_{[MH_2L],org} \cdot a^2_{H^+}}{a_{M^{2+}} \cdot a_{H_4L,org}}, \tag{8}$$

$$\log D = \log K_{ex} + \log a_{H_4L,org} + 2\mathrm{pH}. \tag{9}$$

Thus, the extracted species is eventually described as $[MH_2L]$. It should be noted that the above-mentioned slope analysis provides only the ligand-to-metal ratio in the extracted complex, not the actual number of metal ions and ligands. Thus, the extracted species may be $[M_i(H_2L)_i]$ ($i \geq 2$) rather than a monometalic complex, $[MH_2L]$ (vide infra). An equilibrium study revealed that tetrathiacalix[4]arene **2** releases two protons to bind to one M(II) ion for extraction (M(II) = Co(II), Cu(II), and Zn(II)).[7] It is interesting that linear **4** shows the same extraction manner (Eq. 7).

Table 1 lists the estimated K_{ex} values by fitting the plots in Fig. 2a with Eq. 9. Notably, Cu(II) ion has a higher K_{ex} value by more than three orders of ten than do Co(II) and Zn(II), which may be ascribed to the high affinity of Cu(II) to sulfide (vide supra). More interestingly, each K_{ex} value of linear **4** is roughly the same as that obtained by tetrathiacalix[4]arene **2**,[7] which agrees well with the fact that the *E*% of the cyclic and acyclic tetramers shows a quite similar pH dependence (Fig. 1). Then, what causes the similarity of the K_{ex} values between **2** and **4**?

The extraction constant (K_{ex}) is divided into equilibrium constants, such as partition coefficients of the ligand and the complex into the organic phase (K_{D,H_4L} and $K_{D,[MH_2L]}$, respectively), first and second acid dissociation constants (K_{a1}, K_{a2}) of H_4L, and the stability constant of the complex ($K_{[MH_2L]}$) as shown in

$$K_{ex} = K^{-1}_{D,H_4L} \cdot K_{D,[MH_2L]} \cdot K_{a1} \cdot K_{a2} \cdot K_{[MH_2L]}. \tag{10}$$

Table 1. The Extraction Constant of Metal Ions by Acyclic and Cyclic Tetramer of Sulfur-Bridged Phenols Obtained by Slope Analysis

Ligand	log (K_{ex}/M)		
	Co(II)	Cu(II)	Zn(II)
Linear tetramer **4**	$-8.7_8 \pm 0.0_2$	$-5.0_5 \pm 0.0_2$	$-8.6_3 \pm 0.0_2$
Cyclic tetramer **2**[a)]	$-8.5_8 \pm 0.0_3$	$-5.9_5 \pm 0.0_2$[b)]	$-8.8_6 \pm 0.0_2$

a) See Ref. 7. b) The K_{ex} value was re-evaluated by considering the complexation of Cu(II) with succinic acid added as pH buffer. For the routine, see Ref. 7.

As a consequence of regular solution theory,[19,20] we obtain

$$K_{D,H_4L} \approx K_{D,[MH_2L]}. \tag{11}$$

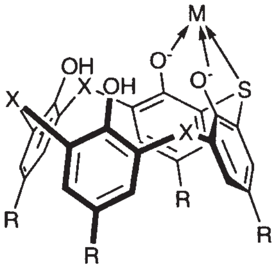
Thus, K_{ex} is approximated by

$$K_{ex} \approx K_{a1} \cdot K_{a2} \cdot K_{[MH_2L]}. \tag{12}$$

It is reported that the linear tetramer of phenol linked by CH_2 bridges, known as pesudo-calix[4]arene,[21] adopts a cone conformation in solution by forming a circular array of the OH···O hydrogen bonding, which is as strong as that in calix[4]arene.[22] In analogy to the methylene-bridged tetramers, it is reasonable to assume that the sulfur-bridged linear tetramer **4** also adopts a cone conformation by a circular array of hydrogen bonding similar to tetrathiacalix[4]arene **2** in a chloroform solution.[4b,23] Considering the similar environment of the phenolic OH groups of **2** and **4**, both having at least two sets of phenol units flanked by two sulfide substituents at both *ortho* positions, the K_{a1} and K_{a2} of the linear tetramer **4** may not differ very much from those of cyclic **2**. Therefore, the similarity in the K_{ex} values between **2** and **4** suggests the similarity in $K_{[MH_2L]}$, the formation constant of the complex $[MH_2L]$ and then the coordination manner as well as the three-dimensional structure. Thus, as long as linear tetramer **4** behaves as a pseudo-thiacalix[4]arene, it may be expected that the complexation ability toward M(II) is almost the same as that of **2** to have analogous extraction mechanisms and similar K_{ex} values.

Factors Determining the Extractability of the Phenol Oligomers. A comparison of the extraction behavior of the four kinds of phenol oligomers (**2**–**4**) unambiguously shows the predominant role of the number of bridging sulfurs, more specifically the presence of the phenol units flanked by sulfides at both *ortho* positions, rather than the cyclic/acyclic structure. In particular, the different extractability between tetrathiacalix[4]arene **2** and monothiacalix[4]arene **3** clearly indicates the crucial role of the number of sulfur bridges, which can be understood as follows.

If the extracted species of tetrathiacalix[4]arene **2** is a 1:1 complex, $[MH_2L]$, in which one O^-,S,O^- unit coordinates to M(II), a reason must be found why monothiacalix[4]arene **3** cannot afford the corresponding complex of the O^-,S,O^--ligated structure (Scheme 4). One plausible reason for the difference in their extractability can be ascribed to the effects of the bridging sulfur on the acidity of the phenolic OH of tetra- and mono-thiacalix[4]arenes. Recently, our study on the acid–

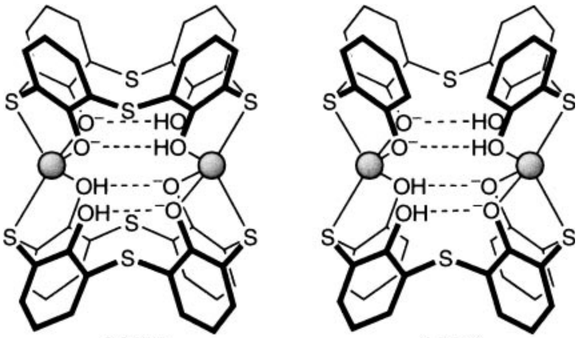


Scheme 4. Possible coordination structure of the 1:1 metal complex of tetrathiacalix[4]arene **2** (X = S) and monothiacalix[4]arene **3** (X = CH_2) (R = Bu^t). Water molecules should occupy the three remaining coordination sites of M (not drawn).

base properties of water-soluble tetrasulfonates of calix[4]arene and tetrathiacalix[4]arene has revealed that the K_{a1} and K_{a2} of tetrathiacalix[4]arene are greater by one and three orders of ten, respectively, than those of calix[4]arene due to the electron withdrawing-nature of the sulfide subsitutents.[24] Based on the linear free-energy relationship,[25] it is quite reasonable to assume that the acid-dissociation constants of tetrathiacalix[4]arene **2** should be much larger to promote deprotonation and, thus, extraction at a lower pH region (see Eq. 12), while the acidity of monothia **3** is too weak to have any appreciable extractability at a lower pH. Furthermore, the 1:1 complex depicted in Scheme 4, even if formed, should fill their coordination sites with water, which would also retard the distribution of the complex into the organic phase. In accordance with these lines, sulfur-bridged dimer **5** showed quite similar extraction behavior to calix[4]arene (**3**), although the latter may have some advantage in extracting metal ions into organic phase due to the more hydrophobic nature of the molecule (Fig. 1c, d).

On the other hand, X-ray crystallography has revealed a double-cone structure for various metal complexes of tetrathiacalix[4]arene **2**,[10] which suggests another possibility that the extracted species may be 2:2 complexes $[M_2(H_2L)_2]$ having a similar double-cone structure (Scheme 5, **2**–M(II)). In the proposed complexes, two dianions H_2L^{2-} are bound to each other via coordination to two M(II) ions using each O^-,S,O^- donor set.[26] The remaining protons on the two phenolic oxygens may be stabilized by hydrogen bonding to the neighboring O^-, which coordinates to M(II). The same complex structure can be drawn for the open-chain **4** by simply removing one sulfide bridge –S– from each calix-cone of **2**–M(II) (Scheme 5, **4**–M(II)), substantiating the common extraction mechanism and similarity of the extractability between cyclic tetramer **2** and acyclic one **4**. In addition, it is trivial that monothiacalix[4]arene **3** cannot afford the double-cone 2:2 complex structure depicted in Scheme 5.[27]

In conclusion, we have shown here that tetrathiacalix[4]arene **2** and its open-chain counterpart **4**, and monothiacalix[4]arene **3** and sulfur-bridged dimer **5** exhibit quite similar extraction behaviors to each other for several transition metal ions. The high extractability of the former two could be ascribed to the O^-,S,O^- coordination unit, in which at least one of the relevant phenol units is flanked by two sulfide bonds at both *ortho* positions to provide a higher coordination ability by an increased acidity. The possibility of the formation of 2:2 complexes from the former ligands, **2** and **4**, is also suggested for the extraction as compared with the poor extractability of the latter two, **3** and **5**.



2-M(II) **4**-M(II)

Scheme 5. Schematic view of the possible coordination structure of the extracted species $[M_2(H_2L)_2]$ of tetrathiacalix[4]arene **2** and the linear tetramer **4** (right). For clarity, *p-tert*-butyl groups are omitted, and benzene rings are depicted without π-bondings.

Experimental

Materials. Samples of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrahydroxy-2,8,14,20-tetrathiapentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]-octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene (**2**),[5] 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrahydroxy-2-thiapentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene (**3**),[4] 2-[3-[3-(5-*tert*-butyl-2-hydroxyphenylthio)-5-*tert*-butyl-2-hydroxyphenylthio]-5-*tert*-butyl-2-hydroxyphenylthio]-4-*tert*-butylphenol (**4**),[28] and linear 2,2′-thiobis[4-*tert*-butylphenol] (**5**)[28] were synthesized as reported previously. Standard solutions (0.01 M) of Mg(II), Co(II), Ni(II), Cu(II), and Zn(II) were prepared by dissolving the chlorides into 0.01 M HCl solution. The accurate concentration was checked by the accepted chelatometry.[29] The pH of the aqueous phase was adjusted with buffers: HNO_3–NH_3 (for pH 2.0), glycine–HNO_3 (2.5–3.5), succinic acid–NH_3 (4.0–5.0), MES–NH_3 (5.5–6.0), PIPES–NH_3 (6.5–7.0), Tris–HNO_3 (7.5–8.5), and CHES–NH_3 (9.0–10.0).

Solvent Extraction. The typical procedure for the extraction study was as follows. To a 30-cm^3 vial tube were pipetted an aqueous solution (10 cm^3) containing metal ion as well as a pH buffer and a solution of a ligand in chloroform (10 cm^3), and then shaken at 300 strokes/min for 24 hr at room temperature (ca. 20 °C). For the detailed initial compositions of both phases, see the captions of the figures. After phase separation by centrifugation, the total concentration of the metal species remaining in the aqueous phase, $[\mathrm{Metal}]_{aq}$, was measured by a Seiko SPS 1200A ICP-AES spectrometer. For a pH measurement of the aqueous phase, a Horiba D-14 pH meter with an S8720 electrode was used. For estimating $a_{C_{n-2}[MH_{4m-n}L_m],org}$ and $a_{M^{2+}}$, a previously reported routine was employed.[7]

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27 cf. It may be expected that 2,14-dithiacalix[4]arene (**6**) should have extractability via forming 2:2 double-cone structure similar to Scheme 5. In fact, it has been observed that **6** extracted transition metal ions, although the extractability was somewhat lower than that of tetrathia **2**. N. Kon, N. Iki, Y. Yamane, S. Shirasaki, and S. Miyano, in preparation.

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