Sulfur-bridged Oligo(benzoic acid)s as a Novel Family of Metal Extractants

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Sulfur-bridged phenol dimer and tetramer were converted into corresponding oligo(benzoic acid)s, which have high complexation ability toward lanthanide ions as revealed by solvent extraction study.

Many studies have been conducted on chelating ligands especially in the field of solvent extraction of metal ions for the purpose of separation, concentration, and recovery of the metals because of increasing demand for use as functional materials.[1]

In a solvent extraction experiment,[2] it has been observed that thiacalix[4]arene **1** and its oxidized derivatives **2** and **3** (Chart 1) exhibit high extractability toward metal ions, which is attributed to the coordination of the sulfur functions to a metal center in cooperation with phenoxy oxygens, as revealed by X-ray structural analysis.[3] Furthermore, the extraction selectivity of metal ions can be controlled by the oxidation state of the bridging sulfur. From the view point of application of **1**–**3** as extractants, however, the following disadvantages were noted: (1) they can extract metal ions only in a relatively high pH region and (2) their extraction rate is low.[2a] We assumed that the direct replacement of the hydroxy groups of **1**–**3** with carboxy groups would yield a new extractant that can rapidly extract various metal ions even in a low pH region owing to the high acidity and high affinity of carboxy groups toward metal ions. However, the direct replacement of the hydroxy groups with other functional groups by conventional C–O bond cleavage of aryl triflates or other esters using transition-metal catalysts is rather difficult, particularly in the case of calixarenes with small ring size because of the steric hindrance caused by the sterically crowded cyclic structure.[4]

On the other hand, we recently reported that a linear tetramer $\mathbf{4_4}$ ($n = 4$) exhibits high extractability toward soft metal ions that is almost equal to that of **1**.[5] Furthermore, it was expected that the replacement of hydroxy groups of $\mathbf{4_4}$ should be possible owing to the reduced steric hindrance compared to that of **1**. In fact, we have already reported the preparation of the P–S–P ligand $\mathbf{5_2}$ from the phenol dimer $\mathbf{4_2}$ ($n = 2$) and its unique coordination modes to the palladium(II) ion that were caused by the cooperative coordination of phosphorous and sulfur atoms to the metal center.[6] Therefore, as new ligands, we designed a sulfur-bridged benzoic acid tetramer $\mathbf{6_4}$, in which the hydroxy groups of $\mathbf{4_4}$ are directly replaced with carboxy groups, and its oxidized derivative $\mathbf{7_4}$. Herein, we report the synthesis of sulfur-bridged oligo(benzoic acid)s $\mathbf{6_2}$, $\mathbf{6_4}$, and $\mathbf{7_4}$ and the investigation of their coordination ability toward metal ions by a solvent extraction study.

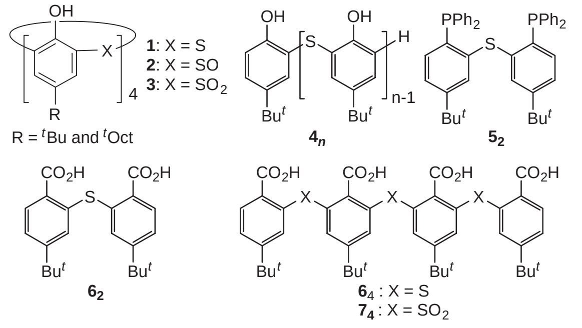

Chart 1.

The sulfur-bridged benzoic acid dimer $\mathbf{6_2}$ and tetramer $\mathbf{6_4}$ were prepared from the phenol dimer $\mathbf{4_2}$ and tetramer $\mathbf{4_4}$,[7] respectively, via the palladium-catalyzed carboxylation of the corresponding triflate followed by hydrolysis.[8,9] Furthermore, the oxidation of $\mathbf{6_4}$ by $NaBO_3$ yielded the corresponding sulfonyl compound $\mathbf{7_4}$.[9]

Fortunately, a single crystal of $\mathbf{7_4}$ that was suitable for an X-ray structural study was obtained by the vapor diffusion of hexane to a CH_2ClCH_2Cl solution of $\mathbf{7_4}$ (Figure 1).[9] It should be noted that $\mathbf{7_4}$ exhibits a pseudocyclic structure, in which two carboxy groups of the terminal benzoic acid form intramolecular hydrogen bondings, as indicated by the geometry and the interatomic distance between O1–O8 (2.630 Å) and O2–O7 (2.678 Å), respectively. Furthermore, two carboxy groups of the inner benzoic acids form intermolecular hydrogen bondings with the sulfonyl oxygen of a neighboring molecule to form a 3-D network structure (Figure S5).[10]

A solvent extraction study was performed to evaluate the coordination ability of oligo(benzoic acid)s toward metal ions.[9] To a 30-cm^3 vial tube were pipetted an aqueous solution (10 cm^3) containing metal ion ($[\mathrm{Metal}]_{\mathrm{aq,init}} = 1.0 \times 10^{-4}$ M), Me_4NCl (0.1 M) as well as a pH buffer (0.05 M) and a 10 cm^3 of 4-methyl-2-pentanone or $CHCl_3$ solution ($[\mathbf{6_4}$ and $\mathbf{7_4}] = 5.0 \times 10^{-4}$ M, $[\mathbf{6_2}] = 1.0 \times 10^{-3}$ M) and then shaken at 300 strokes/min for 1 h at ambient temperature (ca. 20 °C). The percent extraction, $E\%$, values of various metal ions by $\mathbf{6_2}$, $\mathbf{6_4}$, and $\mathbf{7_4}$ were calculated by the following equation.

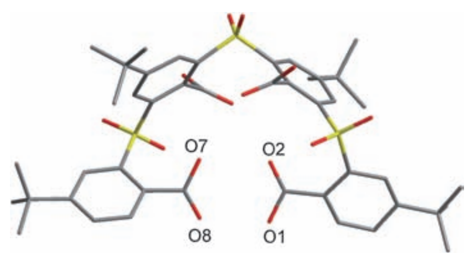

Figure 1. X-ray structure of compound $\mathbf{7_4}$. Hydrogen atoms and solvents are omitted for clarity.

Table 1. The *E%* values of metal ions by $\mathbf{6_2}$, $\mathbf{6_4}$, and $\mathbf{7_4}$[a]

Metal	pH[b]	Ligands		
		$\mathbf{6_2}$	$\mathbf{6_4}$	$\mathbf{7_4}$
Ag^+	6.0	10	16	5
Cu^{2+}	7.0	51	89	76
Ni^{2+}	8.0	16	12	0
Mg^{2+}	10.0	0	0	37
Ho^{3+}	5.0	5	5	34
	5.5	5	17	86
	6.0	34	80	88
	7.0	99	99	100
	3.0[c]	—[d]	—[d]	99

[a] 4-Methyl-2-pentanone was used as organic phase. [b] pH values before extraction. [c] $CHCl_3$ was used as organic phase. [d] Not examined owing to low solubility of $\mathbf{6_2}$ and $\mathbf{6_4}$ in $CHCl_3$.

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

where $[\mathrm{Metal}]_{\mathrm{aq}}$ are the concentrations of the metal ions in an aqueous phase after extraction.

Table 1 lists the *E%* values of the metal ions at a representative pH. Contrary to expectations, oligo(benzoic acid)s $\mathbf{6_2}$, $\mathbf{6_4}$, and $\mathbf{7_4}$ exhibited a moderate *E%* value for only Cu^{2+} among soft to intermediate metal ions (Ag^+, Cu^{2+}, and Ni^{2+}).[11] These results indicate that the extractability of oligo(benzoic acid)s $\mathbf{6_2}$, $\mathbf{6_4}$, and $\mathbf{7_4}$ toward soft to intermediate metal ions is lower than that of **1** and $\mathbf{4_4}$. It has been already revealed that the high complexation ability of **1** and $\mathbf{4_4}$ toward soft to intermediate metal ions results from the ligation of the bridging sulfur as a soft doner with the cooperative binding of the adjacent phenolic oxygens, as shown in Figure S1. On the contrary, it is assumed that the cooperative coordination of the carbonyl oxygen and the bridging sulfur of oligo(benzoic acid)s toward the metal center may be difficult because of the long distance between the two atoms, causing their low extractability toward soft to intermediate metal ions.

On the other hand, Mg^{2+}, categorized as a hard metal ion, could be extracted only by $\mathbf{7_4}$. We noted an important feature of oligo(benzoic acid)s in that they exhibited high extractability toward lanthanide ions, e.g., Ho^{3+}, which were hardly extracted by **1**.[2b] Furthermore, pH values, above which $\mathbf{6_2}$, $\mathbf{6_4}$, and $\mathbf{7_4}$ exhibited high extractabilies, at pH values above 7.0, 6.0, and 5.5, respectively. The mechanism of this extraction was suggested to be chelate extraction via the release of the protons of carboxy groups owing to the dependence of *E%* on the aqueous pH. In chelate extraction, extraction at a lower pH implies high extractability. Therefore, the extractability of oligo(benzoic acid)s toward lanthanide metal ions follows the order $\mathbf{7_4} > \mathbf{6_4} > \mathbf{6_2}$, indicating that the number of benzoic acid molecules and the oxidation state of the bridging sulfur play a critical role in the extraction. The improvement in the extractability toward lanthanide ions due to oxidation of the bridging sulfur of $\mathbf{6_4}$ is probably attributable to the increase in the acidity of benzoic acid due to the electron-withdrawing effect of the sulfonyl function and/or the coordination of the sulfonyl oxygen to the metal center as a hard donor as shown in Figure S1.[10] It should be noted that Ho^{3+} could be quantitatively extracted by $\mathbf{7_4}$ even at pH 3.0, when $CHCl_3$ was used as organic phase (Table 1 and Figure S4). This indicates that $\mathbf{7_4}$ has a higher extractability toward lanthanide ions than that of sulfonylcalix[4]arene **3**, which has a high affinity toward hard metal ions. Furthermore, the time profile of *E%* was studied (Figure S2).[10] The extraction of Ho^{3+} by $\mathbf{6_4}$ and $\mathbf{7_4}$ attains equilibrium within 5 min, indicating that these benzoic acid tetramers can achieve efficient extraction within a short time. On the other hand, the extractabilities of $\mathbf{6_4}$ and $\mathbf{7_4}$ toward other lanthanide ions were examined (Figures S3 and S4),[10] and the pH dependence of *E%* toward several lanthanide ions was observed to be similar, indicating that it is difficult to separate lanthanide ions according to their ion size by using $\mathbf{6_4}$ and $\mathbf{7_4}$ at this stage.

In conclusion, sulfur-bridged oligo(benzoic acid)s were easily prepared from their corresponding phenol dimer and tetramer. X-ray crystallography revealed that $\mathbf{7_4}$ exhibits an interesting pseudocyclic structure stabilized by the intramoleculer hydorogen bonding of carboxy groups. The solvent extraction study revealed that the synthesized oligomers could act as efficient extractants for lanthanide ions.

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9 Detailed synthetic methods, spectral data, conditions of solvent extraction, and crystallographic data of the compounds reported in this manuscript have been deposited in Supporting Information.[10] Crystallographic data have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-704755. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

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