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'Thiacalix[4]aniline' as a highly specific extractant for Au(III) and Pd(II) ions†

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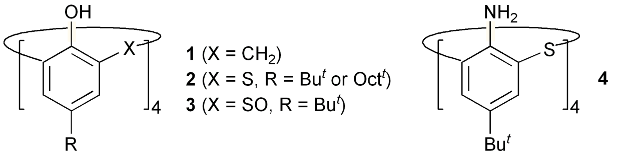
Thiacalix[4]aniline (4), a cyclic tetramer of *p-tert*-butylaniline bridged with four sulfides, extracted Au(III) and Pd(II) ions specifically from acidic solutions among 41 metal ions including soft metal ions such as Hg(II), Cd(II), Zn(II), Pb(II), and Cu(II).

In spite of the poor complexing ability of calix[4]arenes (**1**, Scheme 1) *per se* towards metal ions, this class of macrocycles is now a versatile molecular platform from which to derive selective extractants for separation of precious, environmentally hazardous, or radioactive metal ions.[1] The cyclic tetramers of phenols **1** owe their versatility mostly to the ease in the etherification at the hydroxy functions with ligating pendant groups in a conformationally selective manner to provide the desired extraction ability for specific metal ions. For instance, *p-tert*-butylcalix[4]arene was successfully modified with thioether or amide functions in cone conformations to provide selective extractants for the Au(III) ion.[2] In contrast to this conventional strategy, we have proposed an alternative method to design calix-based ligands by use of the coordination ability of the bridging group of thiacalix[4]arene **2**, in which four methylene groups of **1** are replaced by sulfides.[3,4] Consequently, selective extraction of Pearson's soft to intermediate metal ions by thiacalix[4]arene **2** was readily achieved by cooperative donation of the sulfur moiety and two adjacent phenoxide oxygens.[5] Moreover, the metal ion selectivity was advantageously tunable to include hard ones by oxidation of the sulfur bridges to SO (**3**) and SO_2.[4]

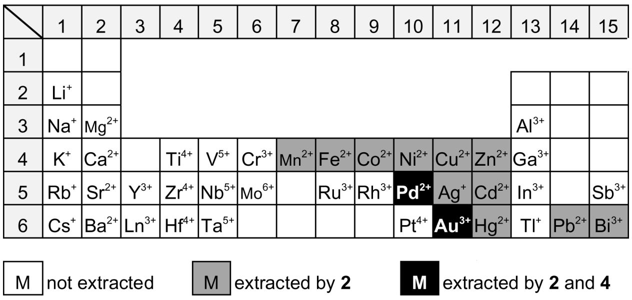
As a part of our continuing efforts to exploit the latent functionality of the sulfur-bridged calix system, we have recently applied the chelation-assisted nucleophilic aromatic substitution protocol to a tetramethoxy derivative of sulfinylcalix[4]arene **3** to obtain, after reduction of the SO function to S, 'thiacalix[4]aniline **4**' comprising four anilines joined by sulfide linkages.[6] It should be noted here that the methylene-bridged counterparts of **4**, in which the arene units are comprised of only aniline nuclei, are unknown. It may be easily expected that the new calix member **4** would bring about inherent functions relying on aniline chemistry to the calix-class host family (*e.g.* **1**–**3**), which so far has been restricted to phenol chemistry. As a first example of the characteristic features of **4**, here we report the unexpectedly high specificity to extract Au(III) and Pd(II) ions.



Scheme 1 Calix[4]arene (**1**), thiacalix[4]arene (**2**), sulfinylcalix[4]arene (**3**), and thiacalix[4]aniline (**4**). Oct^t = 1,1,3,3-tetramethylbutyl group.

The metal-ligating ability of thiacalix[4]aniline **4** was investigated by solvent extraction toward almost all commercially available metal ions except radioactive ones.[7] The pH of the aqueous phase was varied in the range where metal hydroxides did not form. The results are summarized in a Periodic Table (Fig. 1) together with the extractability of tetrahydroxy derivatives **2**. The metals were defined to be extracted when the percent extraction, *E*%, was greater than 30%. As we have reported, thiacalix[4]arenes **2** could selectively extract soft to intermediate metal ions (Fig. 1) *via* coordination of the bridging sulfur as well as of the two flanking phenolates.[5] In contrast, it is surprising to find that thiacalix[4]aniline **4** extracted only two metal ions, Au(III) and Pd(II), classified as the softest among metal ions. This may suggest that in addition to the bridging sulfur, the nitrogen atom of an amino group, having softer characteristics than phenolate oxygen, preferentially coordinated to these soft metal ions. Table 1 shows the pH dependence of the *E*% for Au(III) and Pd(II) by **4**. As can be seen, Au(III) and Pd(II) ions were almost quantitatively extracted below pH 4.1. By contrast, *E*% values decreased above this pH, suggesting that hydroxy ion became able to compete with **4** for coordination to those metal ions.

It is well known that Au(III) and Pd(II) have high affinity toward chloride ion, which sometimes interferes in the extraction of those metal ions. Therefore, caution should be paid in choosing the acid for adjusting pH of the media. Then, the above-mentioned screening experiment was carried out in nitrate media. In addition, H_2SO_4 and HCl were examined to adjust the pH (Table 2).[8] Notably, the *E*% for Au(III) ion was high at low pH region regardless of the acid species, indicating



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1															
2	Li^+														
3	Na^+	Mg^{2+}											Al^{3+}		
4	K^+	Ca^{2+}		Ti^{4+}	V^{5+}	Cr^{3+}	▨ Mn^{2+}	▨ Fe^{2+}	▨ Co^{2+}	▨ Ni^{2+}	▨ Cu^{2+}	▨ Zn^{2+}	Ga^{3+}		
5	Rb^+	Sr^{2+}	Y^{3+}	Zr^{4+}	Nb^{5+}	Mo^{6+}		Ru^{3+}	Rh^{3+}	■ Pd^{2+}	▨ Ag^+	▨ Cd^{2+}	In^{3+}		Sb^{3+}
6	Cs^+	Ba^{2+}	Ln^{3+}	Hf^{4+}	Ta^{5+}					Pt^{4+}	■ Au^{3+}	▨ Hg^{2+}	Tl^+	▨ Pb^{2+}	▨ Bi^{3+}

☐ M not extracted ▨ M extracted by **2** ■ M extracted by **2** and **4**

Fig. 1 Periodic table of the extracted (*E*% > 30%) metal ions by thiacalix[4]arene **2** and thiacalix[4]aniline **4**. Ln = Pr and Eu.

Table 1 The *E*% values of Au(III) and Pd(II) ions by thiacalix[4]aniline **4**

Au(III) ion						
pH	2.2	3.1	4.1	5.0	5.9	7.0
E%	100	100	92	42	10	2
Pd(II) ion						
pH	2.1	3.1	4.1	4.6	5.9	7.0
E%	98	100	98	52	12	10

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† Electronic supplementary information (ESI) available: 1. Extraction data; 2. Preparation and ^1H NMR spectrum of the Au(III)–**4** complex; 3. Spectroscopic data for the Pd(II)–**4** complex. See http://www.rsc.org/suppdata/cc/b2/b205303a/

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Table 2 The *E*% values of Au(III) and Pd(II) ions from sulfate or chloride media by thiacalix[4]aniline **4**[8]

Medium	SO_4^{2-}	SO_4^{2-}	Cl^-	Cl^-	Cl^-	Cl^-	Cl^-
pH	1.2	2.1	2.2	3.1	3.6	5.0	7.9
E%[a]	100	100	100	100	99	42	0

[a] *E*% < 0.4% is defined to be *E*% = 0.

that **4** has higher binding ability toward Au(III) than does chloride ion.

Although scrutiny of the detailed extraction mechanisms of the present systems is beyond the scope of this communication, the coordination of thiacalix[4]aniline **4** toward Au(III) and Pd(II) is deduced from some evidences other than the above-mentioned extraction behavior. First, ^{1}H NMR of the organic phase: Interestingly, upon extraction of Au(III) ion, the chloroform phase exhibited a deep-purple color, which coincides with that observed for Au-complexes of *o*-(methylthio)aniline (MA) and MA-dimer, each having aryl amine and aryl sulfide donor sets, obtained by reaction of $NaAuCl_4$ and the ligands in chloroform–methanol solution.[9] This led us to synthesize a complex of **4** in the same fashion as for the MA complexes.† Importantly, the ^{1}H NMR pattern of the resulting isolated complex was identical to that obtained by solvent extraction,[10] showing that the extracted species of Au(III) with **4** was the Au(III) complex. Since structurally analogous ligands **4** and MA form Au(III) complexes under the same conditions, it may be assumed that the coordination environment for Au(III) provided by thiacalix[4]aniline **4** is quite similar to that by MA. Second, X-ray analysis of a complex of Pd(II) with **4** clearly indicates the coordination of amide NH^- and bridging S (Fig. 2),[11] although the isolation of single crystals of the Au(III) complex is so far unsuccessful. In addition, the extraction *via* formation of ion-pairs between cationic **4**, such as $H^+\cdot$**4** and $(H^+)_2\cdot$**4**, and anionic chloro complexes, such as $AuCl_4^-$ and $PdCl_4^{2-}$, should be excluded: Although part of the amino groups in **4** may be protonated under such highly acidic pH conditions, the NMR pattern observed for the organic phase extracting Au(III) ion coincided with the Au(III) complex (*vide supra*), which was clearly different from those expected for $H^+\cdot$**4** and $(H^+)_2\cdot$**4**. From the above, it is concluded that Au(III) and Pd(II) were extracted by forming complexes with thiacalix[4]aniline **4**.

Finally, the highly specific extractability of **4** toward Au(III) and Pd(II) ions encouraged us to attempt competitive extraction of these ions from mixtures of soft metal ions Hg(II), Cd(II), Zn(II), Pb(II) and Cu(II) in highly acidic nitrate media (Table 3),[12] confirming again the specificity of **4** toward Au(III) and Pd(II) and suggesting the potential application to selective recovery of these precious metal ions from, for example, industrial waste and seawater.

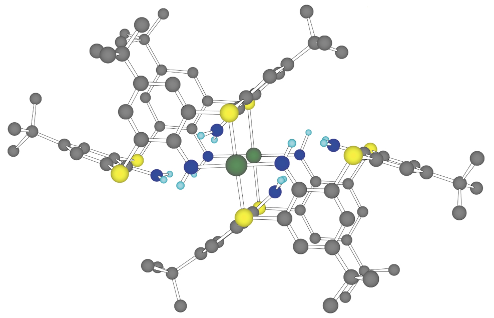

Fig. 2 X-Ray structure of the 2 : 2 (= **4**:Pd(II)) complex, in which two **4** in cone conformation was fused at the lower rim by binding to two Pd(II) ions with coordination of anilido NH^- and thioether S.

Table 3 Selective extraction of Au(III) and Pd(II) ions from aqueous solutions containing other soft ions by thiacalix[4]aniline **4**[12]

Au(III) system					
Metal	Au(III)	Hg(II)	Cd(II)	Zn(II)	Pb(II)	Cu(II)
E%[a]	100	2	0	0	0	0
Pd(II) system						
Metal	Pd(II)	Hg(II)	Cd(II)	Zn(II)	Pb(II)	Cu(II)
E%	100	12	2	2	2	11

[a] *E*% less than 0.4% is defined to be *E*% = 0.

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7 To a 30-cm^3 vial tube was pipetted a solution of thiacalix[4]aniline **4** (0.5 mM) in chloroform (10 cm^3) and an aqueous solution (10 cm^3) containing a metal ion ($[M]_{aq,init}$ = 0.1 mM) and pH buffer (50 mM). The mixture was shaken at 300 strokes/min for 24 h. The concentration of the metal ion remaining in the aqueous phase, $[M]_{aq}$, was determined by ICP-AES or flame AAS. The percent extraction, *E*%, was calculated by $E\% = ([M]_{aq,init} - [M]_{aq})/[M]_{aq,init} \times 100\%$.

8 In sulfate media, pH of the aqueous phase was adjusted to be 1.2 and 2.1 with 50 and 5 mM H_2SO_4, respectively, while in chloride media, pH was adjusted by a suitable buffer (50 mM) with HCl.

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10 To a 5-cm^3 vial tube was pipetted a solution of **4** (5 mM) in $CDCl_3$ (1 cm^3) and an aqueous solution (1 cm^3) containing Au(III) (5 mM). The mixture was shaken at 300 strokes min^{-1} for 24 h, and the $CDCl_3$ solution was separated with a pipette for the ^{1}H NMR measurement.

11 $Pd(OAc)_2$ (45 mg, 0.20 mmol) was added to a solution of **4** (0.12 g, 0.17 mmol) in $CHCl_3$ (15 cm^3) and then refluxed for 72 h. The dark-red reaction mixture was evaporated to dryness and washed with PhH (20 cm^3) to give a crude product. Recrystallization from $CHCl_3$–MeOH solution afforded dark-green needles (31.0 mg, 23%). *Crystal/refinement data*: $C_{80}H_{100}N_8S_8Pd_2\cdot3.5CHCl_3$, M_w = 2060.83, monoclinic, space group $P2_1/c$, a = 16.0963(4), b = 35.1851(4), c = 17.7567(9) Å, β = 104.0085(4)°, V = 9757.4(6) Å^3, Z = 4, D_c = 1.403 g cm^{-3}, μ(Mo-Kα) 8.72 cm^{-1}, $F(000)$ = 4236, T = 230 K. Data were collected on a Rigaku CCD diffractometer. A total of 64044 reflections collected, 17047 were independent (R_{int} = 0.030). The structure was solved by direct methods and refined using SHELXS-97 program. Final R_1 = 0.052 for 11045 data [$I > 2\sigma(I)$] and wR_2 = 0.150 for all data, and GOF = 0.984. CCDC reference number 188014. See http://www.rsc.org/suppdata/cc/b2/b205303a/ for crystallographic data in CIF or other electronic format.

12 Chloroform phase (10 cm^3): [**4**] = 50 mM, aqueous phase (10 cm^3): [Au(III) or Pd(II)] = [Hg(II)] = [Cd(II)] = [Zn(II)] = [Pb(II)] = [Cu(II)] = 0.1 mM, $[HNO_3]$ = 10 mM.