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Selective Ion Extraction by a Calix[6]arene Derivative Containing Azo Groups[1)]

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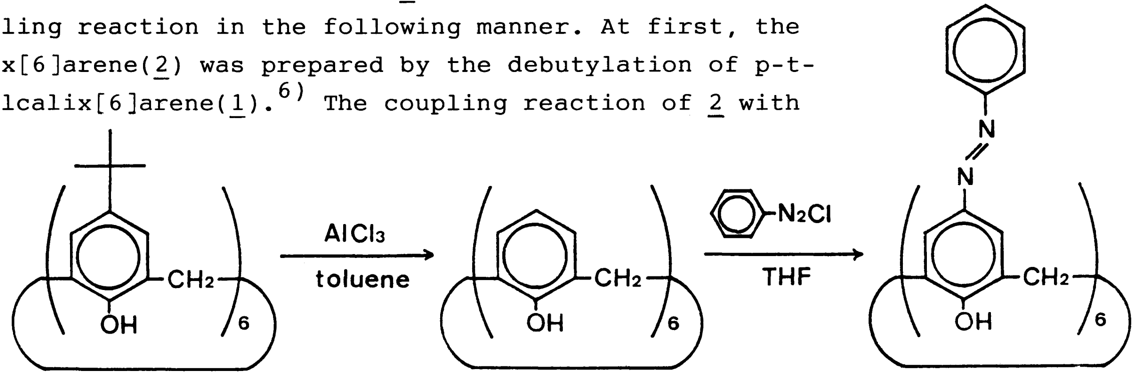
A calix[6]arene derivative containing azo groups was synthesized. The solvent extraction of metal picrates by this compound was selective for Ag^+,Hg^+, and Hg^{2+}.

Calixarenes have been paid much attention during the last decade because of their potential as a sort of host molecule.[2)] Calixarenes, which are appropriately designed, exhibit a large variety of functions; e.g., as inclusion compounds,[3)] selective complexing agents for metal ions,[4)] and catalysts.[5)]

We have been interested in azo groups contained in compounds because of their properties as binding sites for complexation or as chromophores of dyes. We report here the synthesis of 5,11,17,23,29,35-hexa-p-phenylazo-37,38,39,40,41,42-hexahydroxycalix[6]arene(p-phenylazocalix[6]arene)(3) and its binding properties for metal ions on solvent extraction comparing with the binding properties of p-t-butylcalix[6]arene(1) and 4-phenylazo-2,6-dimethylphenol(4).

p-Phenylazocalix[6]arene(3) was obtained by the diazo-coupling reaction in the following manner. At first, the calix[6]arene(2) was prepared by the debutylation of p-t-butylcalix[6]arene(1).[6)] The coupling reaction of 2 with benzenediazonium chloride in aqueous THF gave p-phenylazocalix[6]arene(3) in an 85% yield. It was recrystallized from DMSO and dried under reduced pressure at room temperature for 8 d to give an orange solid; Found: C, 62.32; H, 5.48; N, 9.40%. Calcd for $C_{78}H_{60}N_{12}O_6 \cdot 6C_2H_6OS$: C, 62.48; H, 5.59; N, 9.71%. The orange solid was dried under reduced pressure at 100 °C for 4 d to give a red one; mp>280 °C dec; IR(KBr) 3400(OH), 1600, 1525, 1475, 1123, 772, and 695 cm^{-1}. Found: C, 74.43; H, 4.77; N, 13.06%. Calcd for $C_{78}H_{60}N_{12}O_6$: C, 74.27; H, 4.79; N, 13,33%.



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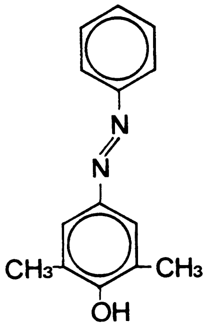

4

Table 1. Extraction of metal picrates with ligands[a)]

Ligand	Picrate salt extracted / %											
	Na^+	K^+	Cs^+	Ag^+	Hg^+	Hg^{2+}	Cr^{2+}	Cu^{2+}	Zn^{2+}	Pb^{2+}	Cd^{2+}	Al^{3+}
1	0	0	0	0	0	0	0	0	0	0	0	0
3	0	0	0	22	8	18	0	0	0	0	0	0
4	31	7	35	23	31	32	29	26	24	28	31	26

a) Aqueous phase, [metal nitrate] = $1X10^{-2}$ mol dm^{-3}, [picric acid] = $2X10^{-5}$ mol dm^{-3}; organic phase, chloroform, [ligand] = $1X10^{-3}$ mol dm^{-3} (1 or 3), $6X10^{-3}$ mol dm^{-3}(4); at 25 °C for 24 h.

The binding ability of 3 to metal ions was evaluated by the extraction of metal picrates from the aqueous phase into chloroform. The extraction was performed by shaking at 25 °C for 24 h. The another extraction by pure chloroform was carried out for comparison at the same time. The extractability was determined from the difference in the absorbance by a metal picrate between the two aqueous phases. The results summarized in Table 1 show that the calixarene 3 has the binding ability only to Ag^+, Hg^+, and Hg^{2+} among the metal ions tested, whereas 1 has no binding ability to any of the metal ions. It is clear that this extractability arises from phenylazo groups conjugated to calix[6]arene. In addition, 4, which is a monomer-type of 3, has the binding ability to all the metal ions tested; it possesses no selectivity. These results show that the selective extractability of 3 is concerned with its specific structure which is a cyclic oligomer.

Further, we examined the electronic spectrum of 3. The maximal absorption of 3 in THF was 347 nm. On addition of Ag^+, the absorption showed a remarkable decrease in absorbance with a slight red shift, and a shoulder appeared at ca. 450 nm. Based on the molar ratio method, it was suggested that 3 formed a 1:12 complex with Ag^+, on the other hand, 4 formed a 1:1 complex with Ag^+.

Another work is now in progress to examine the properties of 3 as a function dye which reveals piezochromism.

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