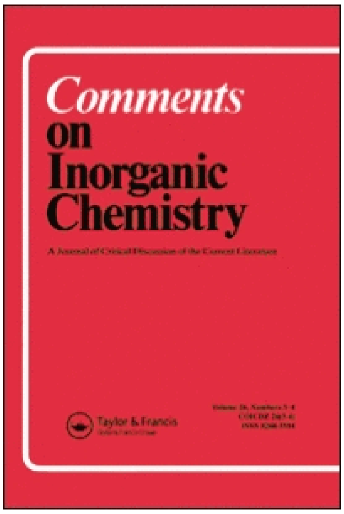

Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

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To cite this Article Yordanov, Alexander T. , Wolf, Nicholas J. , Georgiev, Emil M. , Koch, H. Fred , Falana, Olusegun M. and Roundhill, D. Max(1999) 'Derivatized Calix[4]arenes as Selective Phase Transfer Extractants for Heavy Metal and Oxyion Salts', Comments on Inorganic Chemistry, 20: 4, 163 — 175

To link to this Article: DOI: 10.1080/02603599908021442

URL: http://dx.doi.org/10.1080/02603599908021442

Derivatized Calix[4]arenes as Selective Phase Transfer Extractants for Heavy Metal and Oxyion Salts

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Calix[4]arenes with 2-methylthioethoxy, 2-thiophenecarboxyethoxy, 2-*N,N*-dimethyldithiocarbamoylethoxy and 2-mercaptoethoxy groups on the lower rim, and with methanethiomethyl and *N,N*-dimethyldithiocarbamoylmethyl groups on the upper rim, have been used for the transfer of Sn(II), Hg(II), Ag(I), Pd(II), Au(III), Ni(II), Pt(II), MeHg(II), Pb(II) and Cd(II) from aqueous solution into chloroform. These compounds generally extract Hg(II), Ag(I), Au(III) and Pd(II), but not Ni(II), Pt(II), Pb(II) and Cd(II). A series of calix[4]arenes with amide and amine functionalities bound to the lower rim have been used as extractants for the anions HPO_4^{2-} , SeO_4^{2-} , VO_3^- , ReO_4^-, CrO_4^{2-} , WO_4^{2-} , and MoO_4^{2-} . The extraction data into chloroform from solutions having a pH of 0.85 and 7.0 generally show that the amines are better extractants than the amides, and that the former are most effective from acidic solutions.

Keywords: *calixarenes, heavy metals, oxyions, extraction*

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Comments Inorg. Chem.
1999, Vol. 20, No 4-6, pp. 163-175
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Science Publishers imprint.
Printed in Malaysia

1. INTRODUCTION

The removal of heavy metals from polluted sites is particularly important for metals that are radioactive or chemically toxic. These sites can be soils, natural waters, or prepared storage facilities. Although the challenge of removing metals from these different sites have similarities, each presents unique problems. A particular problem with soils is that the metal is often positively charged and therefore strongly held by the negatively charged zeolite soil matrix. The removal is particularly challenging if the soil is at a site where it cannot be temporarily removed for cleansing. A problem with waters and prepared facilities is that they often contain mixed metals in acidic or basic salt solutions.

One removal technique involves direct extraction in the absence of added complexant. Such a method is frequently used to cleanse soils, and may involve solvent washing or *in situ* electrokinetic extraction under an applied voltage. Each method has been used in conjunction with a complexant specifically chosen for its selectivity toward a particular metal. A disadvantage of using a complexant is that unless it is non-toxic or safely biodegradable it must be subsequently removed. For metals in aqueous media, complexants are often used to transfer the metal between the aqueous and organic phase. Alternately the complexant can be bound to a solid support where it acts as a metal selective absorbant.

The chosen complexant offers combinations of donor atoms, charge, geometry and coordination number that match those preferred by the metal. Specific requirements may also be important. Thus, for electrokinetic extraction from soils, it is necessary that metal complexes be charged and of low molecular weight to give high mobility under the applied potential. In addition both complexant and metal complexes must be stable to acid and base because both H^+ and OH^- are formed in the concurrent electrolysis of water. A final consideration of metal removal is the need for the metal to be readily released for recovery of both metal and complexant.

From environmental and economic viewpoints there is a need for more selective and effective extractants for toxic heavy metals. The challenge is to find extractants that selectively extract and release metals from mixtures. Solid wastes from the mining and processing of mineral ores contain toxic metal residues.[1] Leakage from residues and waste piles pollute aquifers. In designing extractants, similarities and differences among heavy metals must be considered. Sn and Pb are present in both divalent and tetravalent states in solution. Both Sn(II) and Pb(II) form complexes with O and S donors, but whereas Sn(II) gives pyramidal adducts, SnX_2L (X = halide) Pb(II) is mostly octahedral. Zn(II) and Cd(II) complexes have 4, 5 and 6-coordination, but 2-coordination is favored for Hg(II), although 4 + 2-coordination occurs. Common oxidation states for Cu, Ag and Au are +1 (Cu, Ag, Au), +2 (Cu) and +3 (Au). Ag(I) favors linear 2-coordination, whereas for Cu(II) and Au(III) it is 4, with both favoring square planar geometry. Ni(II) exists as the hexaaqua complex, but Pd(II), Pt(II) and Pt(IV) are usually present as halo complexes with Pd(II) and Pt(II) being planar and Pt(IV) octahedral.

2. COMPLEXANT DESIGN

Our approach to complexant design is to use the calixarene platform as a unit upon which to attach heavy metal specific functionalities. Calixarenes are chosen because of both their preorganization and their availability of multiple sites for incorporating ligating functionalities.[2] The chosen derivatives have thiolate or *N,N*-dimethylcarbamoylmethyl functionalities appended to the lower rim. These are chosen because of their strong affinity for metals such as Hg(II), Pd(II), Au(III) and Ag(I). The strong complexant ability of the thiolate group is, however, accompanied by low selectivity. By contrast the *N,N*-dimethylcarbamoylmethyl functionality confers strong and rapid binding in addition to good selectivity. The selectivity at least partially results from this *N,N*-dimethylcarbamoylmethyl moiety being uncharged because anionic dithiocarbamates like thiolates show low selectivity for heavy metals.[3–6] Our extension to methanethiomethyl calix[4]arenes, despite their lower binding metal than thiolates, is based on the expectation that this uncharged ligating group can give higher heavy metal selectivity, especially since such calix[4]arenes are silver selective.[7]

For cations, the metal can be directly bound to a host ligating group, but for oxyanions and uncharged oxides there is often no direct interaction between metal center and host. Despite numerous examples of hosts and complexants for cations, there are fewer for anion hosts.[8–11] Recently a number of chemically modified calixarenes have been synthesized that are hosts for simple anions.[12] From an environmental viewpoint a series of anions for which selective hosts would be useful are oxyanions. One such anion is chromate, and a calix[4]arene with ammonium functionalities on its lower rim is an extractant for anionic Cr(VI).[13] Anionic Cr(VI) is important because of its high toxicity[14–19] and its presence in soils and waters.[20] Cr(VI) is a carcinogen and chromates are mutagenic and genotoxic. Cr(VI) requires intracellular reduction for activation, and this *in vivo* reduction can produce reactive intermediates such as Cr(V), Cr(IV), free radicals, and reactive oxygenated species that can target and damage DNA.[19] By contrast, water soluble Cr(III) is not carcinogenic, possibly because it does not cross plasma membranes.[21,22]

Several methods have been used for Cr(VI) removal. One is reduction in the presence of oxide surfaces. Reductants include α-hydroxy carboxylic acids such as mandelic acid,[23] oxalic acid or substituted phenols.[24] Another method couples microbial reduction of Cr(VI) with anaerobic degradation of benzoate.[25] Cr(VI) can also be extracted from soils with a mixture of Na_2CO_3 and NaOH at 90–95°C.[26]

Our approach to designing a Cr(VI) extractant is to seek a compound such as a polyamine that functions as an anion binder.[27, 28] Since both lower[29–34] and upper[35] rim modified calix[4]arenes are effective cation extractants we have synthesized calix[4]arenes with polyamine functionalities on their lower rim as extractants for anionic Cr(VI).[36, 37] In designing extractants for oxyion guests, structural features can be incorporated into the host that are important in achieving selective binding. For extractants to be effective their structural features must be compatible with the oxyanion. Such compatibilities include matching host and guest geometries and achieving selectivity by hydrogen bonding.

By studying calix[4]arene amides and amines we can deduce whether there is selectivity if the extractant is a diamine, and whether a more hydrophobic *N,N*-diethyl substituent gives higher extractabilities. Among the reasons for targeting amides are the availability of both ketonic oxygens and tertiary nitrogens for hydrogen bonding with oxyanions, the presence of tertiary nitrogens for reversible protonation, and a higher oxidative stability than amines.

Two other environmentally important pseudotetrahedral oxyanions are phosphate and selenate. Phosphates are a concern because if released uncontrolled into aquifers they cause excessive plant growth. Selenate is a problematic product of nuclear reactions because of its high toxicity. We need hosts for these anions that show selectivity due to differences in structure, hydrogen bonding and charge.

3. PHASE TRANSFER EXTRACTABILITIES

In addition to being a selective complexant, for a compound to be an extractant it must also be an effective phase transfer reagent. Literature precedent confirms that calixarenes with their hydrophobic upper rim and hydrophilic lower rim can function in both of these capacities.[38,39]

3.1 Heavy Metal Cations

Extraction with the sulfur derivatized calix[4]arenes **1–6** (Fig. 1) shows them to be selective for heavy metal cations into chloroform from water. The extraction data for Sn(II), Hg(II), Ag(I), Pd(II), Au(III), MeHg(II), Pb(II) and Cd(II) are collected in Table I. These calix[4]arenes do not extract the lighter metals Fe(II), Mn(II), Co(II), Ni(II), Zn(II) or Pt(II) and Pt(IV). Furthermore, whereas dithiocarbamoyl **1** and thiol **3** at low pH are effective for Hg(II) and MeHg(II), they are ineffective for Pb(II), Cd(II), and only slightly so for Sn(II). Both **1** and **3** are effective for Au(III) and Ag(I) and ineffective for Ni(II) and Pt(II), with **1** being effective and **3** being moderately so for Pd(II). These data do not correlate well with size effects when ionic radii for either 4- or 8-coordinate ions are used.[40] If Pt is excluded a case can be made for the precious metals that an ionic radius of 0.8 is favored for **1.** This exclusion is justifiable because the poor extraction of Pt results from its kinetic inertness.[41] Nevertheless, this premise fails for other metals because Hg(II) (with an ionic radius of 1.10 Å) is extracted by **1.** Similarly 8-coordinate Hg(II) and Cd(II) have similar ionic radii, yet they are on the opposite ends of the extractability scale. Apparently size, polarizability effects and kinetics all play a role in the selectivities. The non-*t*-butylated dithiocarbamoyl **2** shows a similar extractability pattern except that it extracts MeHg(II) only poorly. This selectivity pattern may result from conformational differences because whereas **1** has a symmetric cone, **2** has an elongated cone conformation.[42]

Thioethers **4** and **5** show a slightly different pattern where the extractability order for Hg(II) and Ag(I) is reversed and Pd(II) is only ~70% extracted. Thioethers are softer ligands than dithiocarbamates, and with alkyl groups attached directly to the donor atom, they are more space demanding. The former may explain the preferable extractability of Ag(I) over Hg(II). Compounds **1, 2, 4** and **5** extract Pd(II) and Au(III)

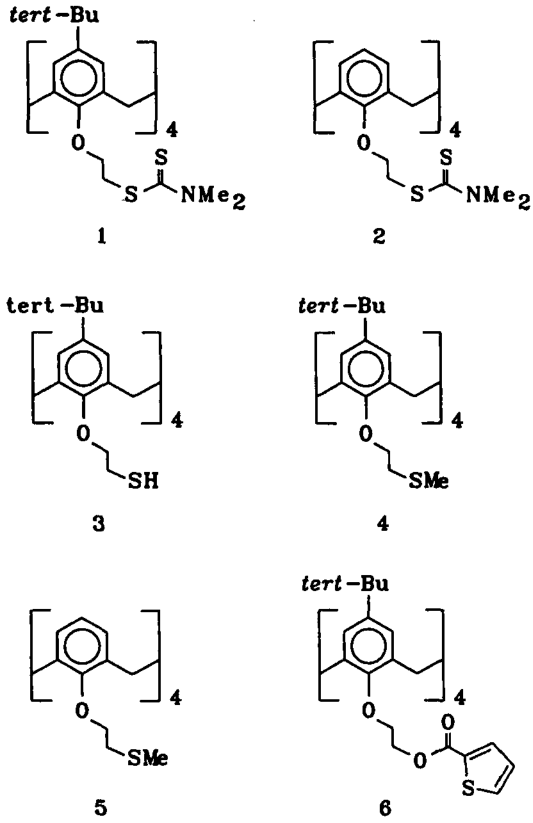


FIGURE 1 Structures of Calix[4]arenes **1–6**

completely, but **6** with a bound thiophene shows low extractability and selectivity. Free thiophene forms weak complexes because of the involvement of the unshared electron pairs on sulfur in the formation of a stable π electron sextet. Nevertheless **6** extracts Hg(II), Ag(I) and Pd(II) though the extractabilities are below 50%. Table II shows chosen selectivity ratios.

Upper rim *N*,*N*-dimethyldithiocarbamoylmethyl and methanethiomethyl substituted calix[4]arenes (Fig. 2) extract heavy metals with the highest values being observed for Pd(II) and Au(III) (Table III).[35]

TABLE I Extraction (%) of Heavy Metals by Calix[4]arenes **1–6**

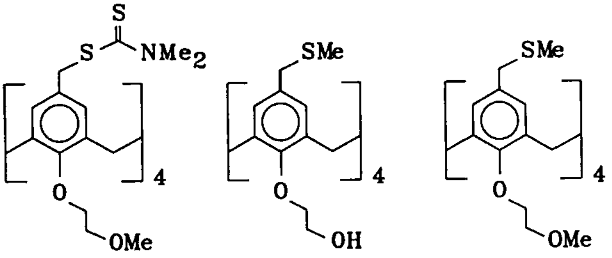
M (Å, CN)	*1*	*2*	*3*	*4*	*5*	*6*
Sn(II) 1.18, 3	10	-	17	<5	<7	<2
Hg(II) 1.02, 2	81	85	86	6	62	46
Ag(I) 1.15, 4	74	60	60	65	97	39
Pd(II) 0.86, 4	100	100	41	70	63	31
Au(III) 0.85, 4	100	97	64	100	99	8
MeHg(II) -, 4	38	2	81	-	-	-
Pb(II) 1.19, 6	<3	11	<6	-	-	-
Cd(II) 0.95, 4–6	<4	9	<3	-	-	-

TABLE II Selectivity Ratios for Calix[4]arenes **1–6**

	1	*2*	*3*	*4*	*5*	*6*
Au/Ag	1.4	1.6	1.1	1.5	1.0	0.2
Ag/Hg	0.9	0.7	0.7	10.8	1.6	0.9
Au/Pd	1.0	1.0	1.6	1.4	1.6	0.3
Hg/Au	0.8	0.9	1.3	0.06	0.6	5.8
Hg/Sn	8.1	-	5.1	>1.2	>8.8	>23
Hg/Cd	>20.3	9.4	>28.7	-	-	-

TABLE III Extraction (%) of Heavy Metals by Calix[4]arenes **7–9**

M	*7*	*8*	*9*
Ag(I)	14	14	<1
Hg(II)	73	<1	92
Pd(II)	100	63	100
Pt(II)	<1	3	<1
Au(III)	99	97	100



7 **8** **9**

FIGURE 2 Structures of Calix[4]arenes **7–9**

3.2 Oxyions

Data for amides **10–12** and amines **13–16** (Fig. 3) as phase transfer extractants for a series of oxyions from aqueous solution into chloroform are collected in Table IV.[43] Data in column A refer to an aqueous phase pH of 0.85 and initially equimolar concentrations of calix[4]arene and oxyion in each phase. By contrast data in column B refer to an aqueous phase pH of 7.0.

An important aspect of interpreting these data are the solution structures of the oxyions at pH 1 and 7. These structures are shown in Table V. Where species have different overall charges at pH 1 and 7, these structures offer an explanation of some of our data. Thus the failure to extract V(V) from acidic solution by either protonated amides or amines may be due to its being the cationic VO_2^+. Similarly P(V) may not extract from acidified solution because it is present as uncharged phosphoric acid. Nevertheless such generalizations have limitations because for W(VI) and Mo(VI) the uncharged trioxide is extracted from acidic solutions by amines, and it may be greater than from neutral solution. Apparently a combination of both charge compatibility and hydrogen bonding between oxyion and calix[4]arene are factors in determining extractability.

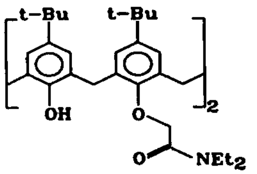
TABLE IV Extraction of Oxyions by Calix[4]arene Amides and Amines

C		HPO_4^{2-}		SeO_4^{2-}		VO_3^-		ReO_4^-		CrO_4^{2-}		WO_4^{2-}		MoO_4^{2-}	
		A	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*
10	D	-	0.04	0.31	0.03	-	-	-	-	0.01	0.01	0.02	-	0.10	-
	E(%)	-	4	23	3	-	-	-	-	1	1	1.5	-	9	-
11	D	-	0.03	0.16	0.06	-	0.03	0.01	-	-	0.06	-	0.01	-	0.03
	E(%)	-	3	14	6	-	3	1	-	-	6	-	1	-	3
12	D	-	-	0.39	0.07	0.05	0.02	0.41	0.64	0.01	0.05	0.07	0.05	-	0.04
	E(%)	-	-	28	6	5	2	29	39	1	5	6	4.5	-	3.5
13	D	-	-	0.15	0.03	-	0.08	0.10	-	0.12	0.10	12.0	0.11	0.14	0.05
	E(%)	-	-	13	3	-	7.5	9	-	11	9	92	10	12	4
14	D	-	1.93	0.22	6.81	-	1.87	0.11	0.57	0.2	7.33	17.6	17.5	0.46	2.77
	E(%)	-	66	18	87	-	65	10	36	16	88	95	95	32	73.5
15	D	-	0.03	0.27	0.02	-	0.01	0.37	0.55	-	-	0.07	0.05	-	0.02
	E(%)	-	2	22	2	-	1	27	36	-	-	6	4.5	-	2
16	D	-	-	0.23	-	0.1	-	-	-	-	-		-	0.02	-
	E(%)	-	-	19	-	9	-	-	-	-	-	-	-	2.0	-

1) For column A the **mole ratio** of amide or amine (C) to anion is 1.0 and the pH of the aqueous layer is 0.85.
2) For column B the **mole ratio** of amide or amine (C) to anion is 1.0 and the pH of the aqueous layer is 7.0.
3) The distribution coefficient D is given by [anion in $CHCl_3$]/[aqueous anion].
4) The % extraction E is given by [initial aqueous anion] – [final aqueous anion]/[initial aqueous anion] × 100.
5) The structures and stoichiometries of the anionic species in aqueous solution are dependent on the solution pH.

TABLE V Structures of P(V), Se(VI), V(V), Re(VII), Cr(VI), Mo(VI) and W(VI) Oxyanions at pH 1 and 7

pH 1	H_3PO_4	$HSeO_4^-$	VO_2^+	ReO_4^-	$Cr_2O_7^{2-}$	$WO_3{\cdot}2H_2O$	$MoO_3{\cdot}2H_2O$
pH 7	HPO_4^{2-}	SeO_4^{2-}	$V_{10}O_{28}^{6-}$	ReO_4^-	CrO_4^{2-}	WO_4^{2-}	MoO_4^{2-}



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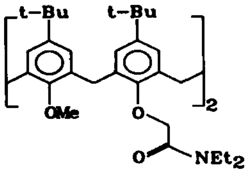

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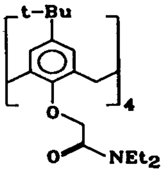

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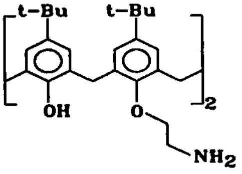

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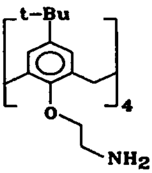

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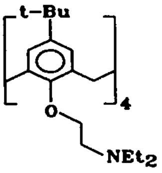

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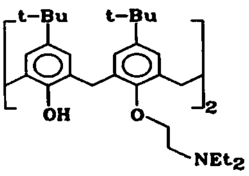

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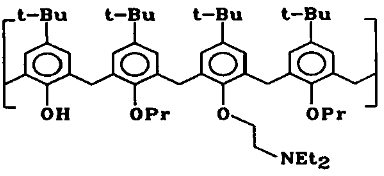

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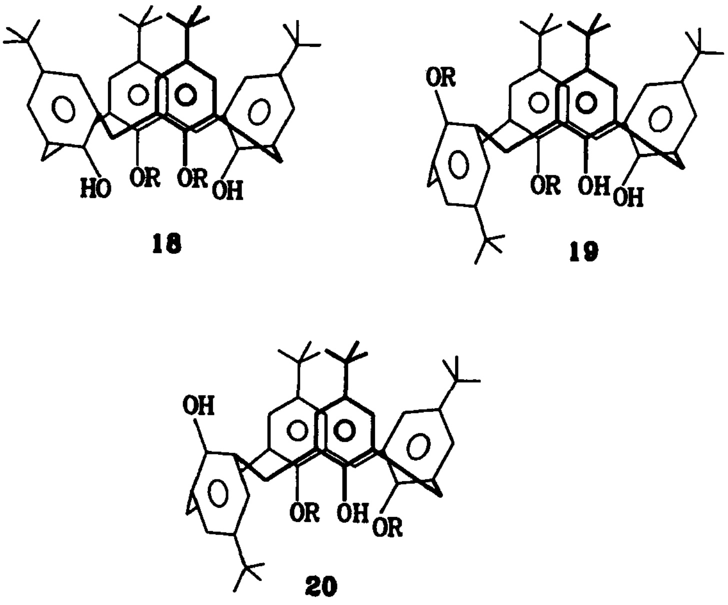
FIGURE 3 Structures of Calix[4]arenes **10–16**

3.3 Hydrophobic Extractants

Another approach to understanding transport across boundaries is to consider the lipophilicities of the extractants. The lipophilicities of **13**, **14** and **17** (Fig. 3) that have been estimated from their partition coefficients between 1-octanol and water are collected in Table VI. These high lipophilicities suggest that extractions of oxyions into more hydrophobic organic phases than chloroform should be achievable. The hydrophobic amide **18** and the isomeric amides **19** and **20** (Fig. 4) extract U(VI), Mo(VI), Cr(VI) and Se(VI) from aqueous solution at pH 0.85 into toluene or isooctane (Table VII).[44] Both UO_2^{2+} and MoO_3 have slight preferences for isooctane over toluene with the reverse being observed for the two oxyanions. The selectivity differences between **18**, **19** and **20** are less apparent, but it appears that **20** is the extractant of choice for isooctane. Interestingly this isomer has the amides in a potentially chelating geometry with a hydrophobic *tert*-butyl group projecting into the lower rim binding cavity.



18 **19** **20**

FIGURE 4 Structures of Calix[4]arenes **18–20** (R = $CH_2C(O)NBu^n_2$)

TABLE VI Partition Coefficients between 1-Octanol and Water

Compound	*pH 1–2*	*pH 6–7*	*pH 11–12*
13	33	11.5	6
14	8	9	17
17	11.5	12	8

TABLE VII Extraction (%) of Oxyions by 18–20

Compound	*Solvent*	UO_2^{2+}	$MoO_3.aq$	$Cr_2O_7^{2-}$	$HSeO_4^-$
18	Toluene	3	<1	20	1
	Isooctane	31	20	<1	<1
19	Toluene	13	7	20	11
	Isooctane	25	20	<1	<1
20	Toluene	14	<1	32	13
	Isooctane	39	40	<1	15

Acknowledgments

Our calixarene extraction research is supported by the U.S. Army Research Office, the U.S. Department of Energy through the Pacific Northwest Laboratory, and the North Atlantic Treaty Organization.

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