

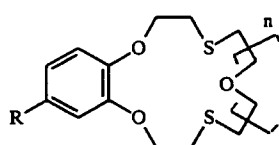
STUDY OF THE EXTRACTION OF STRONTIUM(II) AND LEAD(II) BY CROWN AND DITHIACROWN ETHERS

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A study was carried out on the extraction of strontium(II) and lead(II) picrates by chloroform solutions of crown and dithiacrown ethers. The benzene ring substituents in benzodithia-18-crown-6 only slightly affect the extraction of strontium and lead cations and their separation. The introduction of an adamantyl group onto the benzene ring markedly increases the extraction of lead and the separation selectivity of these cations. The use of dithia derivatives of benzo-18-crown-6 is less efficient for the extraction of both strontium and lead, though the selectivity of their separation is almost the same as in the extraction with benzo-18-crown-6.

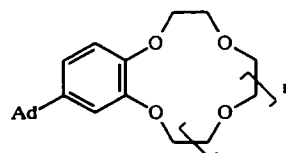
In a study of the extraction of strontium, lead, and other cations by chloroform solutions of 1,10-dithia-18-crown-6, Zolotov et al. [1] did not give partition coefficients or extraction constants, which are found in our previous work for strontium and lead picrates by some thiacycrown ethers [2]. The extraction of the same cations by different crown ethers has been studied rather thoroughly as, for example, in the work of Vogtle and Weber [3].

In the present work, we compared the extraction of strontium(II) and lead(II) picrates by chloroform solutions of benzo- and dibenzocrown ethers IV, V, VII, and VIII and benzodithiacrown ethers I-III and VI and elucidated the effect of various substituents in the benzene ring on the extraction of these cations into the organic phase.



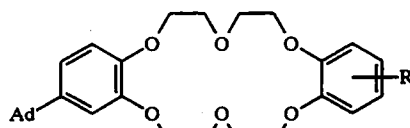
I-III, VI

I R = H, n = 2; II R = Br, n = 2;
III R = CHO, n = 2; VI R = NO₂, n = 1



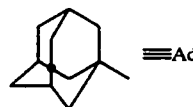
IV, V

IV n = 3; V n = 1



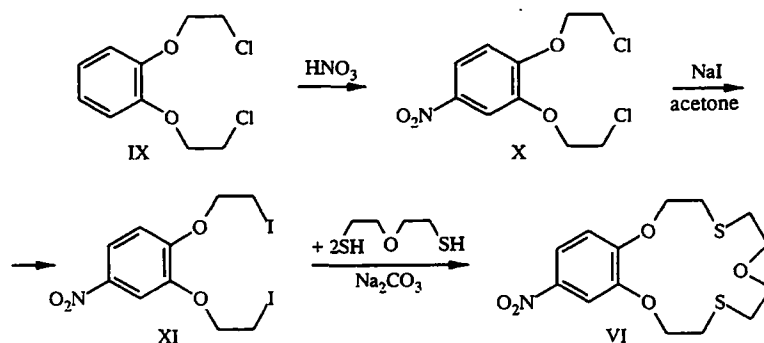
VII, VIII

VII R = H; VIII R = Ad



≡ Ad

Crown ether I was prepared according to Nazarenko [4], while bromo derivative II and formyl derivative III were prepared according to our previous report [5]. The syntheses of adamantyl derivatives IV, V, VII, and VIII were described in our previous work [6]. All the crown ethers were purified by chromatography on a Silpearl silica gel column. Nitro derivative VI was synthesized according to the general scheme:



Strontium(II) and lead(II) have somewhat different ionic radii r . In the case of strontium with coordination number 6, we find $r = 1.13 \text{ \AA}$ [3, 7] and 1.18 \AA [8]. In the case of lead, $r = 1.19 \text{ \AA}$ [3, 7, 8]. These cations may freely enter the cavity of 18-crown-6 and dithia-18-crown-6 and their benzo derivatives to give 1:1 complexes. On the other hand, 1:2 complexes are probably formed with adamantylbenzo-14-crown-4 since the cations cannot penetrate into the crown ether cavity [3]. With all other conditions equal, 1:1 complexes are more stable than 1:2 complexes [3].

The extraction of strontium(II) and lead(II) was carried out from aqueous solutions of lithium picrate. Due to its small radius ($r = 0.66 \text{ \AA}$ [3] and 0.59 \AA [8] for coordination number 4), lithium does not form sufficiently strong complexes with 15-crown-5 and 18-crown-6 and their dithia analogs, and is hardly extracted. However, lithium is extracted by 14-crown-4 rather well. Thus, in the extraction of strontium and lead from solutions of lithium picrate, we may disregard the binding of 15-crown-5 and 18-crown-6 and their thia analogs with lithium and the extraction of their complexes into the organic phase.

The molar partition coefficients D of strontium(II) and lead(II) were determined radiometrically using strontium-90 and lead-210. The method for measuring the radioactivity, determining the partition coefficients D , and calculating the extraction constants K_{ex} were described in our previous work [2].

The experimental and calculated data are given in Tables 1 and 2. The extraction constants K_{ex} were calculated for the extractants starting from the partition coefficients using the following equation:

$$K_{ex} = D/[L] \times [Pi]^2,$$

where L is the extractant and Pi is the picrate ion. In the case of extractants V and VI, the following equation was used:

$$K_{ex} = D/[L]^2 \times [Pi]^2.$$

The dithia analogs of benzo-18-crown-6 extract both strontium(II) and lead(II) much less readily (see Table 2). Substituents such as Br and COH on the benzene ring have only a slight effect on the extraction of these cations. However, some change in the partition coefficients and extraction constants of these metals was noted. For comparison, Table 3 gives the selectivities ($\log K_{ex} \text{ Pb} / \log K_{ex} \text{ Sr}$) of the extractants studied and the literature data [3, 7, 9, 11] for 18-crown-6 and their benzo derivatives. Table 3 shows that although the extraction constants of strontium(II) and lead(II) for the extractants studied are sometimes less than for 18-crown-6 and its benzo derivatives, the separation selectivity of these ions is virtually the same. We note that the replacement of hydrogen in the benzene ring of crown ether I by an adamantyl group enhances the extraction constant of lead (II). As a result, the selectivity for extraction using adamantyl crown ethers is much higher. The greatest selectivity was found for a 1:1 mixture of VII and VIII.

The extraction of strontium(II) by chloroform solutions of 1,2,9,11-dibenzotetracyclohexo-6,15-dithia-18-crown-6 [2] ($\log K_{ex} \text{ Sr} = 4.4$) was much less than for the dithiacrown ethers studied in this work. The extraction of lead(II) by 1,2,3,11-dibenzotetracyclohexohexathia-18-crown-6 ($\log K_{ex} \text{ Pb}^{+2} = 5.12$) was also lower [2]. The stability of the complexes of both strontium and lead is probably reduced due to steric hindrance, leading to their less efficient extraction.

TABLE 1. Extraction of Strontium-90 from 0.01 Mole/Liter Aqueous Lithium Picrate by 0.005 Mole/Liter Solutions of Extractants in Chloroform *

Extractant, L	Partition coefficient, D	Extraction constant, K_{ex}
I	0,030	$6,0 \times 10^4$
II	0,040	$8,0 \times 10^4$
III	0,040	$8,0 \times 10^4$
IV	0,030	$6,0 \times 10^4$
V	0,030	$1,2 \times 10^7$
VII	1,60	$3,2 \times 10^6$
VIII	0,40	$8,0 \times 10^5$
Mixture of VII and VIII	0,20	$4,0 \times 10^5$
VI	0,040	$1,6 \times 10^7$

* $C_{Sr}^{+2} = 10^{-2}$ mole/liter; $t_{ex} = 30$ min; $T = 20 \pm 5^\circ C$.

TABLE 2. Extraction of Lead-210 from Aqueous Lithium Picrate Solutions by 0.005 Mole/Liter Extractant Solutions in Chloroform *

Extractant, L	Lithium picrate concentration, mole/liter	Partition coefficient, D	Extraction constant, K_{ex}
I	0,01	1,30	$2,6 \times 10^6$
II	0,01	1,37	$2,74 \times 10^6$
III	0,01	1,28	$2,56 \times 10^6$
IV	0,01	1,79	$3,58 \times 10^6$
V	0,01	1,10	$4,40 \times 10^8$
VII	0,001	9,90	$1,98 \times 10^9$
Mixture of VII and VIII	0,001	3,80	$7,9 \times 10^8$

* $C_{Pb(II)} = 10^{-6} \dots 10^{-5}$ mole/liter; $t_{ex} = 30$ min; $T = 20 \pm 5^\circ C$.

TABLE 3. Selectivity in the Extraction of Strontium(II) and Lead(II) by Crown and Thiocrown Ethers

Extradant, L	$\lg K_{ex}$		Selectivity $\lg K_{ex} Pb / \lg K_{ex} Sr$
	Sr	Pb	
18-Crown 6 [7, 10]	9,70; 9,43	11,80; 11,70	1,21
Benzo-18-crown-6 [7]	6,62	9,18	1,39
Dibenzo-18-crown-6 [7, 10]	4,90	6,60	1,35
VII	6,50	9,29	1,43
1:1 Mixture of VII and VIII	5,60	8,89	1,59
IV	4,78	6,55	1,37
I	4,78	6,41	1,34
II	4,90	6,44	1,31
III	4,90	6,40	1,31
V	7,08	8,64	1,22

The rather good extraction by V and VI was rather surprising. These compounds probably form sandwich complexes with lead and strontium.

In the framework of the hard and soft acids and basis theory of Pearson [9, 11], "hard" strontium is extracted less well by "soft" dithiacrown ethers than an intermediate, more likely "soft" lead(II). The distortion of symmetry in the interaction of macrocyclic thiocrown ethers with cations reduces the strength of these complexes.

The introduction of an adamantyl moiety directly into the crown ethers and their thia-analogs as in adamantylbenzo-18-crown-6 and diadamantyl-dibenzo-18-crown-6 probably leads to the formation of very strong complexes with the

cations such that good extraction is possible (high K_{ex} values). These extractants probably extract strontium(II) and lead(II) better and may prove more efficient than an extractant such as dicyclohexoxohexano-18-crown-6.

EXPERIMENTAL

The ^1H NMR spectra were taken for CDCl_3 solutions on a Varian T-60 spectrometer with HDMS as the internal standard. The IR spectra were taken on a UR-20 spectrometer for Vaseline mulls.

1,2-Di(2-chloroethoxy)benzene (IX) was obtained from 1,2-di(2-hydroxyethoxy)benzene and SOCl_2 and corresponded in its melting point and PMR spectrum to an authentic sample [12].

3,4-Di(2-chloroethoxy)nitrobenzene (X). Product IX was nitrated as in the procedure proposed for monobenzocrown ethers [13] in 74% yield, mp 82-84°C. IR spectrum: 1550 (as), 1360 (s) (NO_2), 1660 cm^{-1} (arom.). PMR spectrum: 3.80 (4H, m, CH_2Cl), 4.30 (4H, m, CH_2OAr), 6.80 and 7.70 ppm (3H, m, Ar).

3,4-Di(2-iodoethoxy)nitrobenzene (XI) was obtained according to our previous procedure [5] in 91% yield, mp 47-50°C. The product was purified by preparative chromatography on an alumina column. PMR spectrum: 3.60 (4H, m, CH_2I), 4.30 (4H, m, CH_2OAr), 6.27 and 7.80 ppm (3H, 2m, Ar).

1,10-Dithia-4,7,13-trioxa-5,6-(4-nitrobenzo)-5-cyclopentadecene (VI) was obtained in 58% yield by a procedure proposed for the synthesis of the analogous bromocrown ether [5] by heating equal amounts of diiodide XI and 4-oxa-1,5-pentadithiol in 50% aq. ethanol in the presence of Na_2CO_3 for 36 h, mp 125-126°C (from ethanol). Found: C, 48.30; H, 5.38; N, 4.04%. Calculated for $\text{C}_{14}\text{H}_{19}\text{NO}_5\text{S}_2$: C, 48.69; H, 5.54; N, 4.05%. IR spectrum: 1590 (Ar ring), 1520 and 1330 cm^{-1} (NO_2). PMR spectrum: 2.87 (8H, m, CH_2S), 3.60 (4H, m, CH_2O), 4.30 (4H, m, CH_2OAr), 6.95 and 7.70 ppm (3H, 2m, Ar).

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