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EXTRACTION OF STRONTIUM(II), SILVER(I), AND LEAD(II) WITH SOME OXATHIA- AND THIACROWN COMPOUNDS*

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The extracting power of 12- and 18-membered oxathia- and thiacrowns in relation to strontium, silver, and lead ions from aqueous solutions in the presence of anions with various degrees of hardness was investigated with radiometric determination of the metal content. The best results for the extraction of lead were obtained with the 18-membered macrocycles.

Among the products from the operation of atomic power stations, special attention has been paid to the long-lived radioisotopes and primarily to ^{90}Sr, the isolation of which from the waste products of nuclear processes is essential for the protection of the environment. Until now the problem of extracting this radioactive isotope from aqueous solutions has remained practically unresolved [1, 2]. Of the radioactive isotopes of heavy metals that accumulate in the environment, one of the most hazardous is the isotope ^{210}Pb. The most promising direction in the search for selective and effective extractants for the cations of metals with various degrees of "hardness" involves the use of crown ethers and their heteroatomic analogs and particularly oxathia- and thiacrown ethers. By varying the size of the macrocycle and the number and type of heteroatoms, it is possible to create extractants having high extracting power and selectivity for the cations of metals at various positions in the periodic system.

In the present work we studied the extracting power of 12- and 18-membered macrocyclic compounds (I-V, VIII, IX), containing various numbers of sulfur and oxygen atoms in the ring, and also the two podands (VI, VII) with respect to the ions of strontium(II), silver(I), and lead(II). During the investigation, the liquid extraction process for the "hard" cation strontium(II), the "soft" cation silver(I), and "intermediate" cation lead(II) by "soft" ligands, which were the synthesized oxathiacrowns, was compared with the action of the "hard" extractant dibenzo-18-crown-6, which among the heteroatoms only contains oxygen atoms in the macrocycle. The "soft" picrate anion and "hard" nitrate anion in various salts were used as counterions. Such division of cations, anions, and ligands (extractants) into "soft" and "hard" [3] is widely used in extraction chemistry [4].

The oxathiacrown compounds (I-V) are 12-membered heterocyclic compounds having various numbers of sulfur and oxygen atoms in the macrocycle, while the total number of heteroatoms is four. Compounds (VI) and (VII) are podands with various numbers of sulfur atoms in their molecules, while compounds (VIII) and (IX) are 18-membered macrocycles also with various numbers of sulfur atoms in their molecules and must have cavities which all the cations that we investigated can enter. The oxathiacrowns (I-V), which contain four heteroatoms with variable numbers of sulfur and oxygen atoms in the macrocycle, probably have such a small aperture that even the strontium(II) cation having the smallest radius is unable to enter it. It can therefore be supposed that the formation of sandwich structures will be observed for the thiacrown compounds having four heteroatoms in the macrocycle; the podands (VI) and (VII) can also form 1:2 compounds with all the investigated cations. We observed the formation of such a 1:2 complex during investigation of the reaction of the thiacrown (V) with the silver(I) cation by means of the shift of the equilibrium.

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*Dedicated to Prof. É. Ya. Lukevits on his sixtieth birthday.

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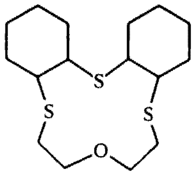

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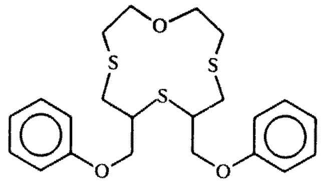

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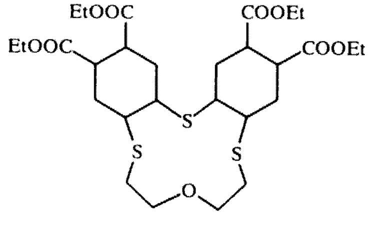

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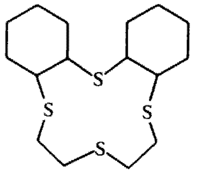

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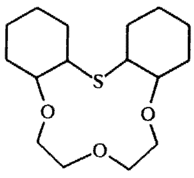

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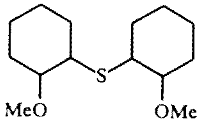

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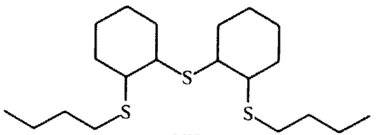

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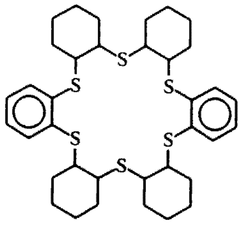

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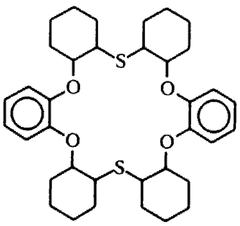

IX

The fact that the podands (VI) and (VII) exhibit lower extracting power than the oxathiacrown compounds (I-V) (Tables 1 and 2) toward strontium(II) and lead(II) is somewhat unusual. The "hard" strontium(II) is extracted worse by the oxathiacrowns (V-I) than by dibenzo-18-crown-6. In contrast, the "soft" silver(I) is extracted much better by the "soft" oxathiacrowns (I-V) both with the "soft" picrate anion and with the "hard" nitrate anion (Tables 1-3). The difference in the distribution coefficients is due to competition by the hydrogen, lithium, and sodium ions for bonding with the ligand.

The "hard" strontium(II) is extracted into the organic phase with the "hard" nitrate ion better than with the "soft" picrate ion. Lead(II), which is intermediate in hardness, behaves in a contradictory manner; with the "soft" picrate anion it is extracted by the "hard" dibenzo-18-crown-6 worse than by the "soft" oxathiacrowns (I-V).

The distribution coefficients for lead(II) during extraction with the oxathiacrowns (I-V) are larger than for strontium(II) but less than for silver(I). The results on the extraction of lead(II) (Table 2) make it possible to trace the effect of substituents at the periphery of the macrocycle and the replacement of sulfur by oxygen on this process. With gradual replacement of the sulfur atoms by oxygen in the 12-membered macrocycle of the oxathiacrowns [from (IV) through (I) and (II) to (V)], the distribution of lead(II) at first increases slightly and then decreases. The appearance of substituents in the cyclohexane fragments of the oxathiacrowns (I) and (III) has little effect on the extractability of strontium(II) and lead(II). The best results on the extraction of lead (II) were obtained with the 18-membered macrocycles (VIII) and (IX). This is due to the large size of the cavity, which is suitable for all the investigated cations and best of all for the "soft" lead(II).

On the basis of the obtained distribution coefficients for the extraction of strontium, silver, and lead by dibenzo-18-crown-6 from a solution of lithium picrate we calculated the logarithms of the concentration constants for the extraction of the compounds $SrLiPi_2$, AgLiPi, and $PbLiPi_2$ (5.20, 3.30, and 6.60 respectively), which differed little from the published data [5].

In conclusion it can be noted that some of the data on the extraction of the cations of metals with various degrees of hardness by oxathiacrowns obtained in the present work provide grounds for asserting that Pearson's concept of soft and hard cations, anions, and neutral ligands makes it possible at a qualitative level to predict the extraction of metals by macrocyclic compounds.

TABLE 1. Distribution Coefficients of Strontium(II) ($C_{Sr(II)} = 10^{-5}$ M)

Compound	Extractant *S* in chloroform	Composition of aqueous phase		
		0,01 M LiPi	3 M HNO_3	5 M $LiNO_3$
I	$[S] - 2{,}2\cdot10^{-3}$ M	0,050	0,015	0,02
II	$[S] - 2{,}2\cdot10^{-3}$ M	0,015	—	—
III	$[S] - 2{,}2\cdot10^{-3}$ M	0,020	—	—
IV	$[S] - 2{,}2\cdot10^{-3}$ M	0,005	0,004	—
V	$[S] - 2{,}2\cdot10^{-3}$ M	0,002	0,0015	0,050
VI	$[S] - 2{,}2\cdot10^{-3}$ M	0,040	—	—
VII	$[S] - 2{,}2\cdot10^{-3}$ M	0,020	0,015	—
VIII	$[S] - 6{,}0\cdot10^{-3}$ M	—	0,015	0,035
IX	$[S] - 1{,}6\cdot10^{-2}$ M	0,040	0,052	0,026
	DB-18-crown-6 $[S] - 2{,}0\cdot10^{-2}$ M	0,600	—	—
	DB-18-crown-6 $[S] - 0{,}10$ M	2,1	—	—

TABLE 2. Distribution Coefficients of Lead(II) ($C_{Pb(II)} = 10^{-6}$ to 10^{-5} M)

Compound	Extractant *S* in chloroform	Composition of aqueous phase		
		0,01 M LiPi	3 M HNO_3	5 M $LiNO_3$
I	$[S] - 2{,}2\cdot10^{-3}$ M	5,73	0,26	0,10
II	$[S] - 2{,}2\cdot10^{-3}$ M	4,50	0,24	0,26
III	$[S] - 2{,}2\cdot10^{-3}$ M	6,17	0,40	0,10
IV	$[S] - 2{,}2\cdot10^{-3}$ M	3,23	0,10	0,18
V	$[S] - 2{,}2\cdot10^{-3}$ M	1,80	0,10	0,14
VI	$[S] - 2{,}2\cdot10^{-3}$ M	3,7	0,11	0,29
VII	$[S] - 2{,}2\cdot10^{-3}$ M	2.92	0,24	0,20
VIII	$[S] - 6{,}0\cdot10^{-3}$ M	0,080	0,75	0,65
IX	$[S] - 1{,}6\cdot10^{-2}$ M	(0,001 M LiP i)	0,80	0,90
	DB-18-crown-6 $[S] - 2{,}0\cdot10^{-2}$ M	—	0,072	0,18
	DB-18-crown-6 $[S] - 0{,}10$ M	0,410	—	—

TABLE 3. Distribution Coefficients of Silver(I) ($C_{Ag(I)} = 10^{-5}$ M)

Compound	Extractant *S* in chloroform	Composition of aqueous phase			
		0,01 M LiPi	3 M HNO_3	5 M $LiNO_3$	5 M $NaNO_3$
V	$[S] - 1{,}0\cdot10^{-2}$ M	140	10	74	38
VI	$[S] - 6{,}0\cdot10^{-3}$ M	—	67	31	—
IX	$[S] - 3{,}6\cdot10^{-3}$ M	—	27	46	23,5
	DB-18-crown-6 $[S] - 5{,}0\cdot10^{-3}$ M	0,11	0,034	0,18	0,028

EXPERIMENTAL

Oxathiacrowns (I, III-V, VIII, IX) and Podands (VI, VII). These compounds were obtained by the reaction of di(2-chlorocyclohexyl) sulfides with the respective thiols, glycols, and alcohols. The oxathiacrown (II) was obtained by the reaction of 1,5-diphenoxy-2,4-dichloromethyl-3-thiapentane with di(β-mercaptoethyl) ether [6]. The obtained macrocyclic compounds were used in the form of chloroform solutions. The distribution coefficients were determined by means of the radionuclides strontium-90 in equilibrium with yttrium-90, silver-110m, and lead-210.

Extraction of Sr(II), Ag(I), and Pb(II) Cations. Extraction was carried out at 20±5°C in extraction tubes for 30 min with vigorous agitation. On the attainment of equilibrium equal volumes of the solutions were taken from the aqueous and organic phases, and the content of the cation was determined radiometrically. The distribution coefficients D of the metals were calculated by dividing the molar concentration of the metal cation in the organic phase by the concentration in the aqueous phase.

Radioactivity of Strontium-90. The radioactivity in Cerenkov radiation of the daughter yttrium-90 was measured on a Mark III liquid-scintillation counter (Tracor Europa, the Netherlands). The measurements were made with standard strontium-90 in equilibrium with yttrium-90 to the attainment of radioactive equilibrium.

Radioactivity of Lead-210. The radioactivity was measured on the same apparatus by means of Brey's solution with Amersham tritium standard; the maximum energies and the form of the β-particle spectrum of lead-210 and tritium are extremely similar. The radioactivity of the daughter bismuth-210 and the grandchild polonium-210 was recorded in a different energy channel. In order to obtain reliable results, repeated measurements were made for lead-210 after five and ten days, and these measurements showed a negligibly small contribution from the activity of the daughter isotopes to the determined radioactivity of lead-210 in the tritium channel.

Radioactivity of Silver-110m (the sixth γ-radiation). This radioactivity was measured on a standard Russian γ-scintillation counter, in which the radiation detector was a large crystal of sodium iodide activated with thallium with a well for the samples. As determined by special tests, the efficiency with which the γ-radiation of silver-110m was recorded did not depend on the composition of the aqueous and organic phases.

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