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Extractability of Copper(II) and Zinc(II) with Crown Ethers as Picrates

Yuko Hasegawa,* Hiroaki Tanabe, and Satoshi Yoshida
Department of Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162

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Synopsis. The extraction of copper(II) and zinc(II) with picrate ion and 12-crown-4(1,4,7,10-tetraoxacyclododecane) or 15-crown-5(1,4,7,10,13-pentaoxacyclopentadecane) into benzene or chloroform has been measured. The extraction of copper(II) is better than that of zinc(II), in spite of the similar ionic size, although the difference is much smaller than that in the extraction of these metal ions with β-diketones.

The study of extractions of metal ions with crown ethers has been developed in relation to the agreement between the size of the metal ion and the cavity size of the crown ether.

Since both copper and zinc ions are stable in the divalent state and have about equal size, and their size is also close to the cavity size of 12-crown-4(12C4) or 15-crown-5(15C5), a similar extraction may be expected.

On the other hand, it has been reported that the extraction of copper(II) with a given β-diketone is much better than that of zinc(II).[1]

In the present paper, the extraction of copper and zinc ions with 12C4 and 15C5 from lithium picrate solution into benzene or chloroform has been measured, in order to compare the extractability of these metal ions as ion pairs to the extractability as the chelates.

Experimental

All the procedures were performed at 25±0.5 °C. The crown ethers were obtained from the Aldrich Chemical Co., USA and Merck Inc., West Germany. The lithium picrate solution was prepared by neutralizing picric acid solution with lithium hydroxide. All other reagents were employed without purification.

An aqueous solution containing metal(II) nitrate (2.5×10^{-2} M, 1 M=1 mol dm^{-3}) and lithium picrate and the same volume of benzene or chloroform containing a certain amount of 12C4 or 15C5 were placed in a stoppered glass tube and agitated mechanically for an hour. The two phases were then centrifuged and the metal(II) in the organic phase was back extracted with 0.1 M perchloric acid. The amount of the metal(II) was measured by an atomic absorption method. The metal(II) concentration in the aqueous phase was regarded as the total concentration added initially. The distribution ratio was defined by the following equation.

$$D = [M(II)]_{o,total}/[M(II)]_{a,total}$$

The distribution constants of 12C4 and 15C5 were determined as follows: the crown ethers were distributed between water and benzene or chloroform. The concentration of each crown ether distributed between both phases was measured spectrometrically using sodium chloride and lithium dipicrylamide. The detailed procedure was reported elsewhere.[2]

Results and Discussion

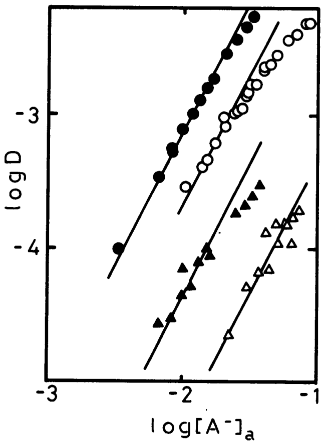

Fig. 1. Extraction of copper(II) (circles) and zinc(II) (triangles) into benzene (open symbols) or chloroform (closed symbols) containing 15C5 as a function of picrate ion concentration.

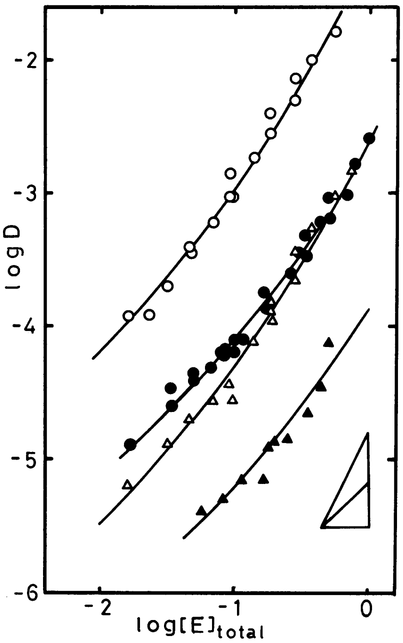

Fig. 2. Distribution ratio of copper(II) (circles) and zinc(II) (triangles) with 12C4 (closed symbols) or 15C5 (open symbols) at 2.5×10^{-2} M picrate concentration as a function of crown ether concentration in benzene.

Figure 1 shows the dependence of the picrate ion concentration on the extraction of copper and zinc ion with 15C5 into benzene or chloroform. The slopes of the curves are +2, except in the higher picrate concentration region. When 12C4 was used, the distribution ratio also increased in proportion to the second order of the picrate ion concentration. Since the extraction was not good, a higher concentration of

TABLE 1. SUMMARY OF CONSTANTS

Org. solvent	Ether[b]	log K_D	Cu(II)[a]		Zn(II)[a]	
			log Kex_1	log Kex_2	log Kex_1	log Kex_2
C_6H_6	12C4	−0.82	0.0_9	0.5_0	-1.0_5	-0.7_2
	15C5	−0.84	1.0_4	2.0_2	-0.2_6	0.6_4
$CHCl_3$	12C4	0.90	0.6_4	3.0_7	-0.1_5	1.8_0
	15C5[4]	0.88	2.0_9	4.4_4	1.0_1	3.2_8

a) Diameter (nm)[3]: 0.15 for 4 coordination, 0.18 for 6 coordination. b) cavity size (nm)[2]: 0.1—0.13 *(12C4), 0.17—0.22 (15C5).*

the metal ions should be employed for an accurate determination of the distribution ratio. Consequently, the nitrate concentration was as high as 0.05 M. However, the species extracted does not seem to include nitrate ions, because the value of the slope of +2 indicates that two picrate ions were present and there was no room for additional anions.

Figure 2 shows the dependence of the crown ether concentration on the extraction of these metal ions into benzene at a constant picrate concentration. The slope of the extraction curves seems to change from one to two. It suggests that the species extracted would have a 2:1 as well as a 1:1 stoichiometry of the crown ether to the metal ion.

From these results, the distribution ratio, D, can be represented as,

$$\begin{aligned} D &= \frac{[MEA_2]_o + [ME_2A_2]_o}{[M^{2+}]_a} \\ &= Kex_1[A^-]_a^2[E]_a + Kex_2[A^-]_a^2[E]_a^2 \qquad (1) \end{aligned}$$

here, the subscripts "o" and "a" denote the organic and the aqueous phases, respectively, $Kex_n=[ME_nA_2]_o/[M^{2+}]_a[A^-]_a^2[E]_a^n$, and $[E]_a=[E]_{total}/(1+K_D)$ and $K_D(=[E]_o/[E]_a)$ is the distribution constant of the crown ethers. The extraction data were analyzed by a successive approximation method. The extraction constants obtained are listed in Table 1 together with the distribution constants of these crown ethers.

As seen in Table 1, the frame size of the crown ether does not seem to change the general features of the extraction of the crown ether itself. The increase of hydrocarbon segments in the frame may be more favorable to the extraction, because the segments give more hydrophobic character to the crown ether. At the same time, the increase in the hydrophobic tendency should be cancelled out by the increase in the hydrophilic tendency of the molecule, because in a series of the crown ethers such as 12C4, 15C5, and 18C6, an increase of one hydrocarbon segment, $-CH_2-CH_2-$ in the frame always causes an increase of one oxygen atom, and the oxygen atom should give hydrophilic tendency to the molecule through hydration.

On the other hand, the extraction of the metal ions with 15C5 is always better than that with 12C4 by a factor of about one order of magnitude as seen in Fig. 2. That is, the frame size seems to change the extraction of metal ions definitely. Although the reason is not clear, it may reflect that on the complexation of the metal ion with the crown ether, the oxygen atoms in the crown ether interact with metal ions, and hence the balance between the hydrophilic and hydrophobic tendency would be broken, or the stability of the complex with 12C4 would be different from that with 15C5.

The difference of organic solvents influences the extraction of the crown ethers themselves more remarkably than that of the ion pairs of the metal(II), as is seen in Table 1. This fact may also reflect that the oxygen atoms in the frame of the crown ethers may solvate more easily with chloroform, probably through a hydrogen bond, than with benzene.

Table 1 also shows that the extraction of copper ion with either 12C4 or 15C5 is better by a factor of one order than that of zinc ion, when the metal ions are extracted with the same crown ether into the same organic solvent. The extraction constant of bis(acetylacetonato) copper(II) (log $Kex=-3.47$) is larger than that of zinc chelate (log $Kex=-10.69$). The difference has been explained in terms of the different electronic structure, that is, since zinc ion forms stable octahedral chelates with the coordination number of six, the central zinc ion in the chelate may interact more with water molecules than the central copper(II) ion in the chelate.[1] On the other hand, it has been reported[4] that zinc(II) takes four coordination when the metal ion is extracted as ion pairs with trioctylphosphine oxide and perchlorate or halide ions. If the zinc ion also takes on a tetrahedral structure instead of an octahedral one on extraction with the crown ethers and picrate ions, the zinc ion in the ion pairs should not hydrate more than the ion in the chelates. Accordingly, the difference of the extraction of these metal ions would be smaller than that with *β*-diketones.

Without information on the thermodynamic properties such as the changes in the free energy, the enthalpy, and the entropy on the complexation or the extraction, it is impossible to discuss the extractability of these ion pairs in more detail.

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