Inorganica Chimica Acta, 162 (1989) 105–111

Solubilization of Potassium Ethylenediaminetetraacetatocobaltate(III) in Organic Solvents by Using Macrocyclic Polyethers

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(Received November, 5, 1988; revised February 28, 1989)

Abstract

Solubilities of potassium ethylenediaminetetraacetatocobaltate(III) dihydrate, $K[Co(edta)]\cdot 2H_2O$, were determined at 25 °C by spectrophotometry in organic solvents (methanol, ethanol, acetonitrile, chloroform, acetone, tetrahydrofuran, etc.) containing a macrocyclic polyether: cryptand 222, 18-crown-6, 15-crown-5, 12-crown-4, dicyclohexyl 18-crown-6, dicyclohexyl 24-crown-8, dibenzo 18-crown-6 and dibenzo 24-crown-8 ethers. It was found that (i) the solubility in some organic solvents is markedly enhanced by the addition of these macrocyclic polyethers though the complex is sparingly soluble in pure solvents, and (ii) the magnitude of this solubility enhancement of the cobalt(III) complex increases as the stability constant of these macrocycles with the potassium ion, K^+, increases. Eventually, it was concluded that cryptand 222 that has the greatest stability constant is the best one of these reagents for solubilizing this cobalt(III) complex of a potassium salt. Furthermore, the examination of solvent dependence of the solubility suggests that the solubility enhancement of this complex depends not only on the dielectric constant but also on the electrophilic ability of the solvent; the latter is represented by the acceptor number (*AN*) that is proposed as a parameter of measuring the electrophilic ability of the solvent. This corresponds to the result that cryptand 222 solubilizes the complex in chloroform which has a small dielectric constant (ϵ) 4.8 (*AN* value = 23.1) but could not solubilize it in tetrahydrofuran (THF) that has a larger dielectric constant but a smaller *AN* value ($\epsilon = 7.4$ and $AN = 8.0$).

Introduction

Various inorganic salts have been found to be solubilized by macrocyclic polyether, so-called crown ether, in organic solvents since Pedersen reported that, for example, $KMnO_4$ is solubilized by dicyclohexyl 18-crown-6 in benzene [1]. These findings led to the development of new organic syntheses [2, 3]. On the other hand, the chemistry of anionic cobalt(III) complexes in organic solvents is still being developed. This may be due to the solubility problem of these complex salts. In general, the alkali salts of anionic cobalt(III) complexes are not soluble in a variety of organic solvents if they are not composed of some aromatic ligands such as phenanthroline, bipyridine, acetylacetone and so on. However, the spectroscopic properties [4] or reaction mechanisms [5] of anionic cobalt(III) complexes are quite interesting in organic solvents because the anion interacts more specifically with the solvent molecules as indicated in the literature [6]; the anion is strongly solvated by the protic solvent but exists as a naked anion in aprotic solvents.

The author thought that anionic cobalt(III) complexes could be solubilized by using macrocyclic polyethers like crown ethers. It is, however, somewhat surprising to note that macrocyclic polyethers had not been used for solubilizing the anionic cobalt(III) complexes until the author investigated them [7, 8] and only a few systematic studies even on simple inorganic salts have been reported on the solubilizing ability of macrocyclic polyethers in organic solvents. Therefore, as a first stage of the study on the anionic cobalt(III) complex in organic solvents how the salts of these complexes are solubilized by crown ethers and a cryptand [9] in organic solvents, was investigated, that is, what is the correlation between the solubilizing ability of macrocyclic polyethers and the properties of the polyethers and the organic solvents, and which polyether is the best solubilizing reagent for $K[Co(edta)]$. The macrocyclic polyethers used in this work are as follows: cryptand 222, 18-crown-6, 15-crown-5, 12-crown-4, dicyclohexyl 18-crown-6, dicyclohexyl 24-crown-8, dibenzo 18-crown-6 and dibenzo 24-crown-8 ethers, which are abbreviated as C222, 18C6, 15C5, 12C4, DC18C6, DC24C8, DB18C6 and DB24C8, respectively and are illustrated in Scheme 1.

This investigation was carried out by measuring the solubilities of $K[Co(edta)]\cdot 2H_2O$, which is one of the most familiar cobalt(III) complex salts, in a variety of organic solvents in the presence of some

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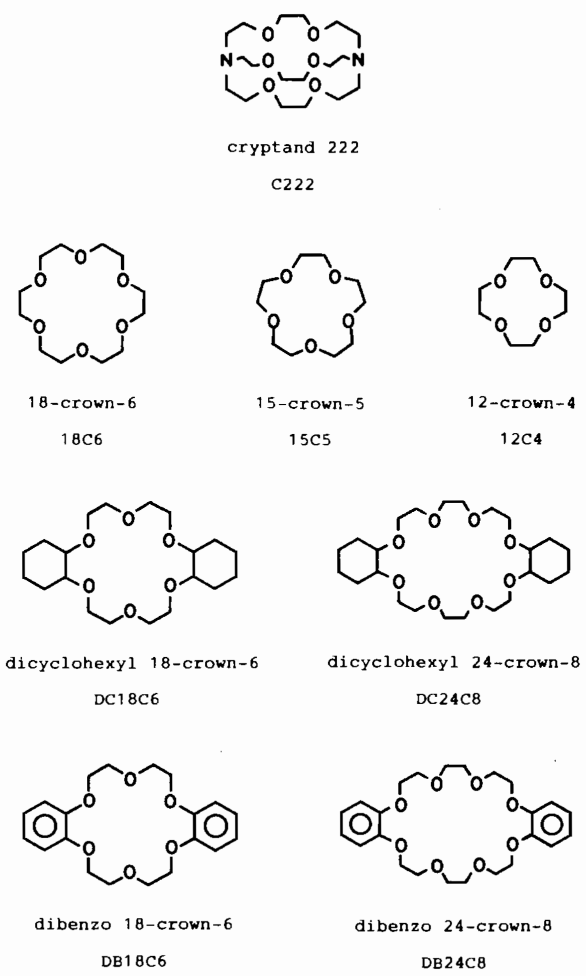

Scheme 1.

crown ethers and cryptand 222. The complex is quite stable in a variety of solvents and has an intense d–d absorption band (the extinction coefficient is 324 at 536 nm in water) in the visible region. The solubility is thus readily determined by the spectrophotometric method.

Experimental

Materials

K[Co(edta)]$\cdot$2H_2O was prepared by the usual method [10]. NH_4[Co(edta)]$\cdot$2H_2O was prepared by using ammonium acetate in place of potassium acetate in the above method. The purity of these complexes was checked by the spectroscopic method. The crown ether 18-crown-6 was a reagent of Tokyo Kasei Kogyo Co., Japan and 15-crown-5 and 12-crown-4 ethers were from Borregaard A.S., Norway (via Wako Pure Chemical Industries, Japan). Dicyclohexyl and dibenzo 18-crown-6 ethers were from Aldrich Chemical Co., U.S.A. and dicyclohexyl and dibenzo 24-crown-8 ethers were from Nisso Co., Japan. Cryptand 222 was purchased from Merck (Kryptofix 222). The other materials, KF, K_2SO_4 and $K_2Cr_2O_7$, were of reagent grade. The organic solvents were of purest grade commercially available and were used without further purification: methanol, ethanol, acetonitrile, chloroform, acetone, dioxane, benzene, carbon tetrachloride, tetrahydrofuran and hexane.

Measurements

Solubilities of K[Co(edta)]$\cdot$2H_2O

Solubilities were determined by measuring the absorption at 536 nm. The procedure of solubility measurements is as follows. Solution equilibration was attained in a glass vessel kept at 25.0 ± 0.1 °C with a Neslab circulator, Model RTE-9. The solid cobalt(III) complex was added to the organic solvent containing a macrocyclic polyether ranging in concentration from 0.01 to 0.05 M. This mixture was stirred magnetically for 1 to 2 days. (The complex is quite stable though C222 is slightly basic.) An aliquot of the solution was pipetted out through a glass filter and completely dried at 40 °C with an evaporator. This was diluted appropriately in a volumetric flask with water for measuring the absorption. The absorption was measured by a spectrophotometer, Shimadzu UV-240, at ambient temperature.

Solubilities of $K_2Cr_2O_7$

The solubilities of this salt were measured by the same procedure as that for K[Co(edta)]$\cdot$2H_2O but the solution pipetted out through a glass filter was diluted appropriately with the solvent acetonitrile*.

Solubilities of KF and K_2SO_4

The solutions for the determination of solubilities were obtained by the same procedure as that for the cobalt(III) complex salt, but solubilities were determined by measuring the concentration of potassium cation using emission spectrometry: Shimadzu AA-630-12 Atomic Absorption/Flame Emission Spectrophotometer at 766.5 nm with 1.9 Å of band width. This is because these salts are colorless and the absorption in the visible region cannot be measured. The measurement in the UV region has some problems: for example, the intense absorption of solvents themselves in this region.

Results and Discussion

Potassium ethylenediaminetetraacetatocobaltate(III), K[Co(edta)]$\cdot$2H_2O, easily dissolves in water

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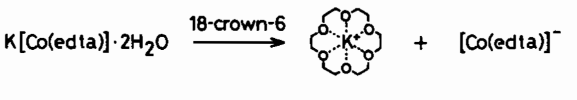
*$K_2Cr_2O_7$ is decomposed in acetonitrile solution and a dark green precipitate appears in several hours. The measurement is completed within 3 h and the absorption is measured in acetonitrile solution and not in aqueous solution.

because of the stabilization of K^+ and $[Co(edta)]^-$ by the solvation of water molecules as well as the large dielectric constant of water ($\epsilon = 78.5$). By contrast, this salt is sparingly soluble in organic solvents except for a solvent like $(CH_3)_2SO$ that has a large dielectric constant. This is because the ions generated from this salt are not fairly stabilized by the solvation.

$$K[Co(edta)]_{solid} \rightleftarrows K[Co(edta)]_{solution} \rightleftarrows K^+ + [Co(edta)]^- \rightleftarrows K^+\cdot solvent + [Co(edta)]^-\cdot solvent \quad (1)$$

In contrast to this, it was reported in the previous paper [7] that this salt is solubilized in acetonitrile by the addition of 18-crown-6 ether or other crown ethers. In this solution, K^+ is strongly complexed with the polyethers in place of the solvent molecules in eqn. (1) and is highly stabilized even in organic solvents that solvate this cation to a slight extent. This is the reason why the potassium salt is solubilized in organic solvents by the macrocyclic polyethers. The situation is schematically presented for 18-crown-6 ether as follows.



In organic (aprotic) solvents, the $[Co(edta)]^-$ anion that is not so markedly solvated dissolves in solvents compulsorily. Therefore, this anion is quite reactive and should exhibit the inherent properties without the solvent influence in the spectroscopies.

In the following sections, we will try to estimate the solubilizing ability of a macrocyclic polyether and elucidate the origin of this ability in several organic solvents. The discussion will mainly be done on the basis of the data in Tables 1 and 2. These data are visualized in some of the Figures.

Solubilities in Methanol

Figure 1 and Table 1 show the solubilities of $K[Co(edta)]\cdot 2H_2O$ in methanol (CH_3OH) solutions containing a crown ether: 18C6, 15C5, 12C4 and a cryptand C222. This complex is sparingly soluble in pure methanol ($S = 0.0010$ M), but is strikingly solubilized by these macrocycles, especially by 18C6 and C222, where the solubilization is stoichiometric (one molecule of macrocycle solubilizes an ion of K^+

TABLE 1. Solubilities (M) of $K[Co(edta)]\cdot 2H_2O$ in organic solvents containing a macrocyclic polyether at 25 °C

Solvent	Macrocycle (M)	Solubility (M)[a]							
		C222	18C6	15C5	12C4	DC18C6	DC24C8	DB18C6	DB24C8
CH_3OH	0	0.00101							
	0.01	0.0102	0.0099	0.0041	0.0012	0.0082	0.0062		
	0.02	0.0202	0.0190	0.0084	0.0015	0.0158	0.0109		
	0.03	0.0283	0.0293	0.0108	0.0017	0.0235	0.0159		
	0.04	0.0400	0.0383	0.0138	0.0022	0.0307	0.0202		
	0.05	0.0486	0.0468	0.0174	0.0024	0.0387	0.0257		
C_2H_5OH	0		0.00011						
	0.01		0.0091	0.0018					
	0.02		0.0174	0.0031					
	0.03		0.0269	0.0067					
	0.04		0.0351	0.0072					
	0.05		0.0440	0.0098					
CH_3CN	0	0.00020							
	0.01	0.0101	0.0079	0.0027	0.00043	0.0087	0.0053	0.0041	0.0016
	0.02	0.0202	0.0139	0.0049	0.00067	0.0148	0.0087	0.0064	0.0014
	0.03	0.0287	0.0193	0.0070	0.00080	0.0185	0.0105	0.0083	0.0016
	0.04	0.0391	0.0234	0.0092	0.00109	0.0221	0.0132		0.0016
	0.05	0.0496	0.0256	0.0094	0.00104	0.0254	0.0153		0.0019
$CHCl_3$	0	0[b]							
	0.01	0.0109	0.00026						
	0.02	0.0205	0.00028						
	0.03	0.0314	0.00078						
	0.04	0.0407	0.00061						
	0.05	0.0495	0.00046						

[a] These values are the averages of solubilities determined for the solutions, which were pipetted out more than 3 times in each 2 h after 1–2 days. [b] The solubility is too small to measure by this method.

TABLE 2. Solubilities (M) of $NH_4[Co(edta)]\cdot 2H_2O$ in methanol solutions containing a macrocyclic polyether at 25 ℃

Concentration (M) of macrocycles	Solubility (M)^a	
	18C6	15C5
0	0.0032	
0.01	0.0106	0.0042
0.02	0.0192	0.0054
0.03	0.0291	0.0065
0.04	0.0362	0.0080
0.05	0.0446	0.0090

^{a}These values are the averages of the solubilities determined for the solutions, which were pipetted out more than 3 times in each 2 h after 1–2 days.

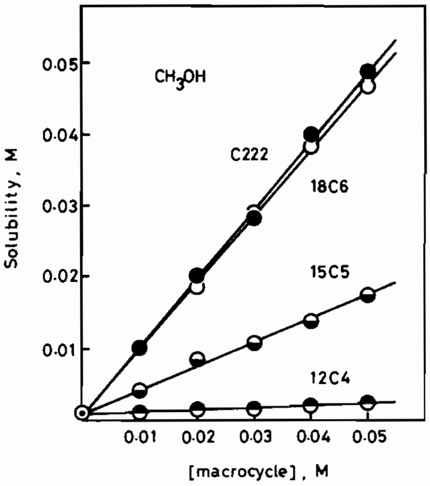


Fig. 1. Solubilities of $K[Co(edta)]\cdot 2H_2O$ in methanol (◉) and in methanol solutions of a macrocycle: cryptand 222 (●), 18-crown-6 (○), 15-crown-5 (◒) and 12-crown-4 (◓).

and $[Co(edta)]^-$). The solubility is enhanced by a factor of about 50 upon addition of 0.05 M 18C6 and C222. For the crown ethers the order of increasing solubility ($S_{18C6} > S_{15C5} > S_{12C4}$) seems to be closely correlated to that of increasing stability constant between a crown ether and a potassium ion. Reported values of stability constants in methanol are as follows [11]: $\log K_{18C6} = 6.08$, $\log K_{15C5} = 3.43$ and $\log K_{12C4} = 1.74$. Namely, $K_{18C6} > K_{15C5} > K_{12C4}$. As for C222, the stability constant ($\log K_{C222} = 10.6$) [12] of this ether with K^+ is much greater than that of 18C6. However, only a 1:1 complex of C222 with K^+ was formed in this concentration, this suggests a limit to the solubility enhancement. Therefore, the solubilizing ability of C222 is apparently similar to that of 18C6.

In this context, DC18C6 should be an excellent solubilizing reagent since this crown has a large stability constant ($\log K = 6.01$ or 5.38 in methanol [13]), which is similar to that of 18C6. In fact, the

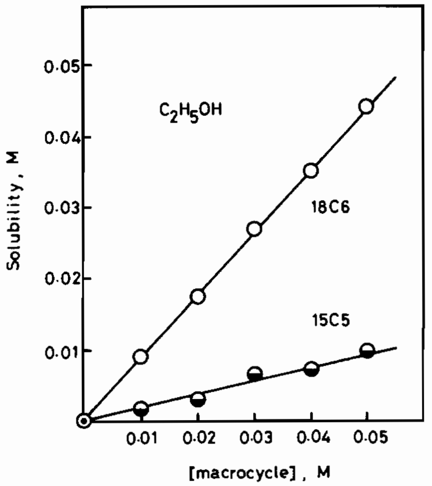


Fig. 2. Solubilities of $K[Co(edta)]\cdot 2H_2O$ in ethanol (◉) and in ethanol solutions of a macrocycle: 18-crown-6 (○) and 15-crown-5 (◒).

data in Table 1 indicate that DC18C6 enhances the solubility of the complex to the same magnitude as 18C6. This means that the solubilizing abilities of these crown ethers are primarily dependent on the magnitude of complex formation with the potassium ion. In Table 1, DC24C8 enhances the solubility to a less extent than DC18C6. The stability constant for DC24C8 is not known but it was reported that 24-crown-8 ether (24C8), which has the same hole size* as DC24C8, has a stability constant of $\log K = 3.50$ [11]. Therefore, the lower solubility enhancement by DC24C8 is due to the stability constant of DC24C6 being less than that of DC18C6. For the solubility enhancement, the influence of a 2:1 complex formation of K^+ with DC24C8 of a large hole size indicated in the literature [3] does not seem to appear in this case.

Furthermore, in methanol the solubilities of $NH_4[Co(edta)]\cdot 2H_2O$, where the size of NH_4^+ is similar to that of K^+, were also measured in the presence of 18C6 and 15C5 (Table 2). The enhancement of the solubility is quite similar to that for a potassium salt. The stability constant ($\log K_{18C6} = 4.21$) of NH_4^+ with a crown ether is less than that of K^+ [11]. Therefore, the magnitude of the solubility enhancement is slightly less than that for a potassium salt.

Solubilities in Ethanol

The dielectric constant of ethanol (C_2H_5OH) is 24.3, and is less than that of methanol ($\epsilon = 32.6$). However, a similar result was obtained as shown in Fig. 2 and Table 1. 18C6 increases the solubility of

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*The correlation between the stability constant of a crown ether with K^+ and the hole size of the ether is widely studied. It is known that the crown ether, whose hole size is fitted with the ion size of K^+, has a great stability constant with K^+.

K[Co(edta)]·$2H_2O$ to a stoichiometric extent (1:1 solubilization). The order of increasing solubility is as follows: $S_{18C6} > S_{15C5}$. 15C5 enhances the solubility to a slightly less extent than that in methanol. This could be due to the small dielectric constant of ethanol. Preliminarily, the solubility upon addition of C222 was measured, though the data are not listed in Table 1. C222 also solubilizes this complex to a stoichiometric extent.

Solubilities in Acetonitrile

In contrast to methanol and ethanol, the enhancement of the solubility in acetonitrile (CH_3CN) is not large and is not stoichiometric for 18C6, though the dielectric constant ($\epsilon = 36.0$) of acetonitrile is greater than those of methanol and ethanol (Fig. 3 and Table 1). Therefore, this less solubility enhancement should be due to a factor other than the dielectric constants of the solvents. According to the literature [14], the solubility of the salts increases as the donor and acceptor numbers of the solvents increase, where the numbers were proposed by Gutmann as measures of estimating the donor and acceptor properties of solvents, respectively. This is because the solvent molecules that have large values of these two parameters stabilize the cation and anion generated from the salt by the strong solvation. In this context, acetonitrile ($AN = 18.9$) that is an aprotic solvent and has a smaller AN value should stabilize $[Co(edta)]^-$ less than methanol ($AN = 41.3$) and ethanol ($AN = 37.1$) do, while the potassium ion is already stabilized by the complex formation with a crown ether and so the donor number of the solvent does not influence the solubility to a great extent. This could be the reason why K[Co(edta)]·$2H_2O$ is less solubilized in acetonitrile than in methanol and ethanol of smaller dielectric constants. In contrast to crown ethers, C222, that has the greatest stability constant ($\log K = 11.0$) in acetonitrile, solubilizes this complex to a stoichiometric extent.

This situation is the same in the case of DC18C6 and DC24C8. The solubilities of K[Co(edta)]·$2H_2O$ in the presence of these crown ethers are listed in Table 1. DC18C6 solubilizing the complex to the same magnitude as 18C6 solubilizes it to a less extent than in methanol. DC24C8 also solubilizes it less in acetonitrile. By contrast, the case of DB18C6 that was investigated only in acetonitrile, is different from 18C6 and DC18C6. The stability constant of DB18C6 with a potassium ion ($\log K = 4.83$ in acetonitrile) is less than that of DC18C6 [15]. So, the solubility enhancement is less than those for 18C6 and DC18C6. DC24C8 and DB24C8 enhance the solubility to a less extent than DC18C6 and DB18C6. These ethers have a large hole size in comparison with K^+, and so have a lower stability constant than those of the corresponding 18C6 ethers, as was described before.

Solubilities in Chloroform

In chloroform that is a low polar solvent of dielectric constant 4.8, 18C6 enhances the solubility of K[Co(edta)]·$2H_2O$ only slightly but C222 solubilizes this complex to a stoichiometric extent against the electrostatic interaction between K^+ and $[Co(edta)]^-$ (Fig. 4 and Table 1). Chloroform has a small dielectric constant (4.8) but has a rather large AN value (23.1). Therefore, in this solvent C222 that forms a complex with K^+ ion to a great extent solubilizes the potassium salt of the cobalt(III) complex against the low polarity of the environment. (C222 solubilizes this complex in a concentration of more than 0.5 M in chloroform.)

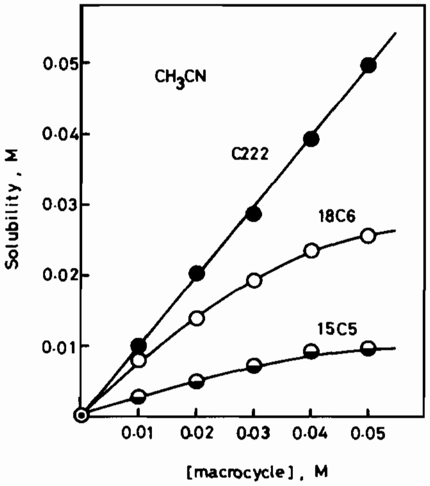

Fig. 3. Solubilities of K[Co(edta)]·$2H_2O$ in acetonitrile (◉) and in acetonitrile solutions of a macrocycle: cryptand 222 (●), 18-crown-6 (○) and 15-crown-5 (◒).

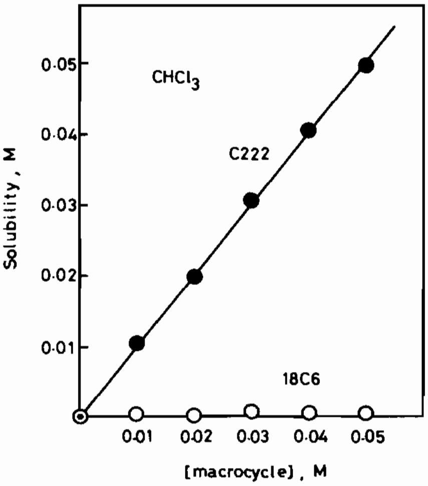

Fig. 4. Solubilities of K[Co(edta)]·$2H_2O$ in chloroform (◉) and in chloroform solutions of a macrocycle: cryptand 222 (●) and 18-crown-6 (○).

Solubilities in Other Solvents of Low Polarities

An attempt was made to solubilize the complex in other organic solvents of low polarities: acetone, dioxane, benzene, carbon tetrachloride, tetrahydrofuran and hexane. In acetone, 18C6 enhances the solubility of K[Co(edta)]$\cdot$2H_2O slightly but C222 solubilizes this complex to a stoichiometric extent, which is like chloroform, though the data are not shown in Table 1. This is due to the moderate dielectric constant and *AN* value of acetone ($\epsilon = 20.7$ and $AN = 12.5$). The solubilization is not successful for other solvents. Tetrahydrofuran has a greater dielectric constant but has a smaller *AN* value than chloroform (Table 3). The small *AN* value seems to be the reason why the complex is not solubilized in tetrahydrofuran. The other solvents have small dielectric constants and small *AN* values, leading to the small (unmeasurable) solubility enhancement even in the presence of C222 which has the greatest stability constant.

Comparison with Solubilities of KF, K_2SO_4 and $K_2Cr_2O_7$

The solubilities of KF and K_2SO_4 in acetonitrile are presented in Table 4. KF is sparingly soluble in pure acetonitrile but is solubilized to some extent by 18C6. KF in acetonitrile is used as a facile and efficient reagent for obtaining organic fluorine compounds in high yield [16] but the limit of the solubility when 18C6 is used, is about 0.0036 M. In contrast to this ether, a higher concentration of KF is obtained by using cryptand 222 which is the best of the solubilizing reagents investigated in this work. Therefore, if C222 is used, it becomes more facile to utilize KF for the reaction in organic solvents. The potassium salt of a singly charged anion including KF and K[Co(edta)] is solubilized by C222 to a stoichiometric extent in acetonitrile.

TABLE 3. Dielectric constants (ϵ) and acceptor numbers (*AN*) of solvents

Solvent	ϵ	*AN*
CH_3OH	32.6	41.3
C_2H_5OH	24.3	37.1
CH_3CN	36.0	18.9
$CHCl_3$	4.8	23.1
Acetone	20.7	12.5
Dioxane	2.2	10.8
Benzene	2.3	8.2
Carbon tetrachloride	2.2	8.6
Tetrahydrofuran	7.4	8.0
Hexane	1.9	0.0

TABLE 4. Solubilities of KF and K_2SO_4 in acetonitrile solutions of 0.05 M 18-crown-6 and cryptand 222 at 25 °C

	0	18C6	C222
KF	0.00014 M	0.0036 M	0.049 M
K_2SO_4	0.00010 M	0.00019 M	0.0065 M

As for K_2SO_4, even if cryptand 222 is used, the solubility in acetonitrile is quite small (0.0065 M for the addition of 0.05 M C222). This seems to be due to the doubly charged and small anion of SO_4^{2-}.

The solubilization of $K_2Cr_2O_7$ in acetonitrile is similar to that for K[Co(edta)]$\cdot$2H_2O. Table 5 shows that 18C6 and DC18C6 solubilize this salt in acetonitrile to the greatest extent and stoichiometrically, and the solubility increases in the same order (DC18C6 $\approx$ 18C6 $>$ 15C5 $>$ 12C4) as that for K[Co(edta)]$\cdot$2H_2O. This large solubility enhancement may be due to the large anion of $Cr_2O_7^{2-}$. Preliminary measurements of solubilities indicate that K_2[Co(ox)$_2$gly] and K_3[Co(ox)$_3$] are solubilized easily by 18C6 and C222 in acetonitrile, where ox = oxalate and gly = glycine. This is probably because the [Co(ox)$_2$gly]$^{2-}$ and [Co(ox)$_3$]$^{3-}$ are doubly and triply charged but are large anions.

Conclusions

The complex, K[Co(edta)]$\cdot$2H_2O, could be solubilized in several organic solvents by use of some macrocyclic polyethers though it is sparingly soluble in pure solvents, where C222 is the best reagent for the solubilization of this complex salt. The solubility enhancement is correlated to the magnitude of the complex formation of the macrocycles with K^+, the dielectric constants and the electrophilic abilities of the solvents. In this work the author succeeded in solubilizing one of the anionic cobalt(III) complexes, K[Co(edta)]$\cdot$2H_2O, in chloroform of a low polarity ($\epsilon = 4.8$) by using a macrobicyclic polyether, C222, which forms a complex with K^+ to a great extent ($\log K = 10.6$) [12].

TABLE 5. Solubilities of $K_2Cr_2O_7$ in acetonitrile solutions of 0.05 M crown ethers: 12-crown-4, 15-crown-5, 18-crown-6, dicyclohexyl 18-crown-6, and of 0.03 M[a] dibenzo 18-crown-6 at 25 °C

Crown ether	0	12C4	15C5	18C6	DC18C6	DB18C6
Solubility	0.005 M	0.009 M	0.017 M	0.025 M	0.026 M	0.016 M

[a] DB18C6 can be dissolved in acetonitrile in concentration up to 0.03 M.

This means that this kind of cobalt(III) complex could be solubilized by C222 in a solvent of a large *AN* value even if the polarity of the solvent is quite low.

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