



Conductance Study of 1 : 1 19-Crown-6 Complexes with Various Mono- and Bivalent Metal Ions in Water

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Abstract. Formation constants (K_{ML}) of 1 : 1 19-crown-6 (19C6) complexes with mono- (M^+) and bivalent metal ions (M^{2+}) were determined in water at 25 °C by conductometry. The K_{ML} value of 19C6 for M^+ and M^{2+} decreases in the order $Rb^+ \geq K^+ > Tl^+ > Na^+ = Ag^+ > Li^+ \approx Cs^+$ and $Pb^{2+} > Ba^{2+} > Sr^{2+} > Cd^{2+} > Ca^{2+}$, respectively. The selectivity for the neighboring alkali metal ions in the periodic table is lower for 19C6 than for 18-crown-6 (18C6) except for the case of Rb^+ and Cs^+ . The same is true for the alkaline earth metal ions. Generally, the K_{ML} values of 19C6 with M^{2+} are greater than those with M^+ . For Na^+ and the ions which are smaller in size than Na^+ (Li^+ , Ca^{2+} , Cd^{2+}), the K_{ML} value is larger for 19C6 than for 18C6, but the contrary holds for all the other ions of larger sizes than Na^+ . The limiting ionic molar conductivity (λ°) of the 19C6- K^+ complex in water at 25 °C was determined to be 43. Although 19C6 is larger than 18C6, the 19C6- K^+ complex is much more mobile in water than the 18C6- K^+ complex.

Key words: stability constant, limiting ionic molar conductivity, asymmetry, 19-crown-6, mono- and bivalent metal ions, complexes, water, conductometry

1. Introduction

19-Crown-6 (19C6) is larger in size than 18-crown-6 (18C6) by one methylene group. The structure of 19C6 is less symmetric, whereas that of 18C6 is symmetric. But 19C6 and 18C6 have the same number of donor ether oxygen atoms. Examinations of CPK molecular models show that the less symmetric arrangement of donor oxygen atoms causes an unfavorable conformation for complexation with size-fitting and size-misfitting larger metal ions compared with the symmetric 18C6. Extraction selectivity orders of 19C6 for alkali and alkaline earth metal ions are

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identical with those of 18C6, i.e., $K^+ > Rb^+ > Cs^+ > Na^+$ and $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$; 19C6 shows lower extractabilities for all the cations compared with 18C6 [1, 2]. In order to clarify the effect of the extra methylene group on extraction-selectivity and -efficiency of 19C6 for metal ions from the standpoint of equilibrium, it is necessary to analyze the overall extraction equilibrium by fundamental equilibria. The formation constant in water of a crown ether – metal ion complex is one of the fundamental equilibrium constants which constitute the overall extraction equilibrium constant of the crown ether – metal salt complex. Formation constants of crown ether – metal ion complexes in various solvents provide us with important information of solvent effects on stabilities of the crown ether complexes and the interaction between crown ethers and metal ions.

In this study, complex-formation constants in water of 19C6 with mono- and bivalent metal ions were determined at 25 °C by conductometry, and were compared with those of 18C6.

2. Experimental

2.1. MATERIALS

The preparation of 19C6 was as described in the previous paper [1]. 18-Crown-6 (Nisso Co., Ltd.) was recrystallized from acetonitrile and, prior to use, dried at 80 °C in a vacuum. Analytical-grade $LiCl \cdot H_2O$, $LiClO_4 \cdot 3H_2O$, $LiNO_3 \cdot 3H_2O$, NaCl, KCl, RbCl, CsCl, $Ca(NO_3)_2 \cdot 4H_2O$, $Sr(NO_3)_2$, $Ba(NO_3)_2$, AgNO₃, TlNO₃, and HClO₄ were purchased from Merck Japan Ltd.; analytical-grade $Cd(NO_3)_2 \cdot 4H_2O$ and $Pb(NO_3)_2$ from Wako Pure Chemicals Ltd. They were used without further purification. The conductivity of water was $< 7 \times 10^{-7} \text{ S cm}^{-1}$.

2.2. APPARATUS AND PROCEDURE

The conductivity measurements were made on a Fuso conductivity apparatus, Model 362B, at 25 ± 0.02 °C. Cells with cell constants of 0.1885 and 0.08624 cm^{-1} were used.

The experimental procedure to obtain formation constants of crown ether complexes with cations in water was almost the same as that described in the previous paper [3]. For Ag, Cd, and Pb, the conductivity measurements were performed at pH 2.8–5.2 to prevent the hydrolysis of these metal ions. The concentration ranges of the metal salts and perchloric acid were $(1.3\text{--}4.9) \times 10^{-3} \text{ M}$ (1 M = 1 mol dm^{-3}).

The limiting molar conductivity (Λ°) of the 19C6–KCl 1 : 1 : 1 complex in water was determined at 25 ± 0.01 °C in the same way as previously described [3]. For each conductivity measurement, total concentrations of KCl and 19C6 were kept below 9×10^{-3} and $9 \times 10^{-2} \text{ M}$, respectively.

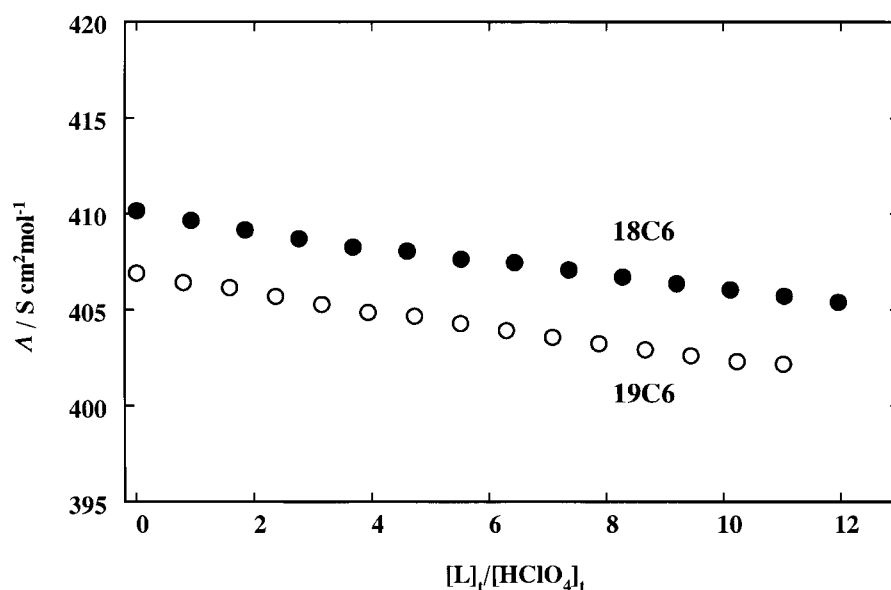


Figure 1. Λ vs. $[L]_t/[HClO_4]_t$ curves for 19C6 and 18C6 in water. $[HClO_4]_t = 3.52 \times 10^{-3}$ mol dm $^{-3}$ (19C6), 3.02×10^{-3} mol dm $^{-3}$ (18C6).

Table I. $\log K_{ML}$ and Λ_{MLA} values of 19C6 with LiCl, LiNO $_3$, and LiClO $_4$ in H $_2$ O at 25 °C^a

Salt	$\log K_{ML}$	$\Lambda_{MLA}/S\text{ cm}^2\text{ mol}^{-1}$	$[M]_t \times 10^3/\text{mol dm}^{-3}$
LiCl	0.79 ± 0.07	100.4	3.9876
LiNO $_3$	0.72 ± 0.18	93.74	3.4821
LiClO $_4$	0.77 ± 0.08	93.56	3.3405

^a Each $\log K_{ML}$ value is the average of 5-7 measurements. The uncertainties are the standard deviations. These Λ_{MLA} values are the Λ values of the MLA complexes at $[MLA] = [M]_t$.

3. Results and Discussion

The procedure for determining formation constants (K_{ML}) and limiting ionic molar conductivities (λ°) of crown ether – metal ion 1 : 1 complexes was described elsewhere [3], where $K_{ML} = [ML^{m+}]/[M^{m+}][L]$; M^{m+} and L refer to a metal ion and a crown ether, respectively. It is assumed that the association between a cation and an anion is negligible in water. Corrections for viscosity changes due to solute were neglected. The λ° value of the 19C6–KCl 1:1:1 complex in water was determined to be 119.5 ± 1.6 at 25 °C.

The molar conductivity (Λ) vs. $[L]_t/[HClO_4]_t$ plots are given in Figure 1, $[L]_t$ and $[HClO_4]_t$ denoting total concentrations of crown ether and perchloric acid, respectively. Scarcely any change in Λ despite an increase in the crown ether

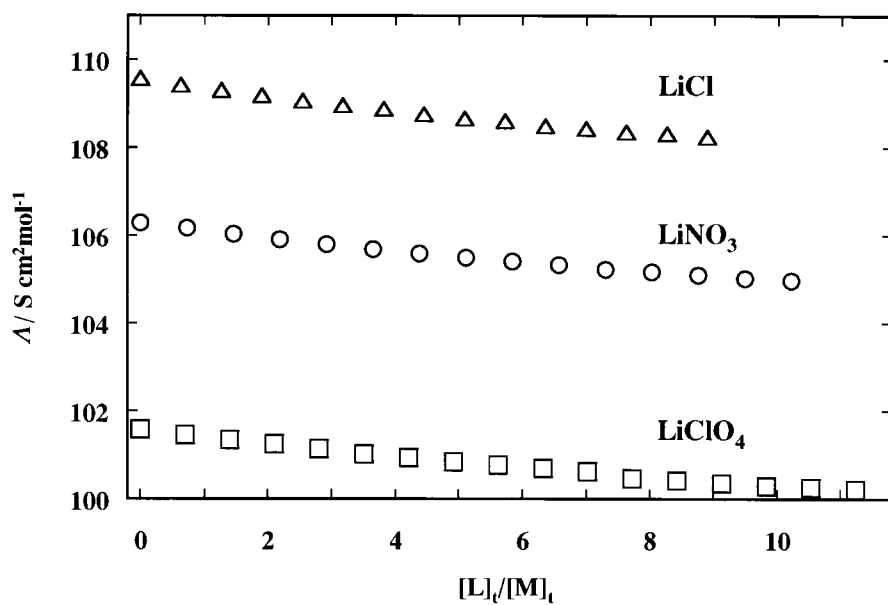


Figure 2. Δ vs. $[L]_t/[M]_t$ curves for 19C6 – lithium salt systems in water.

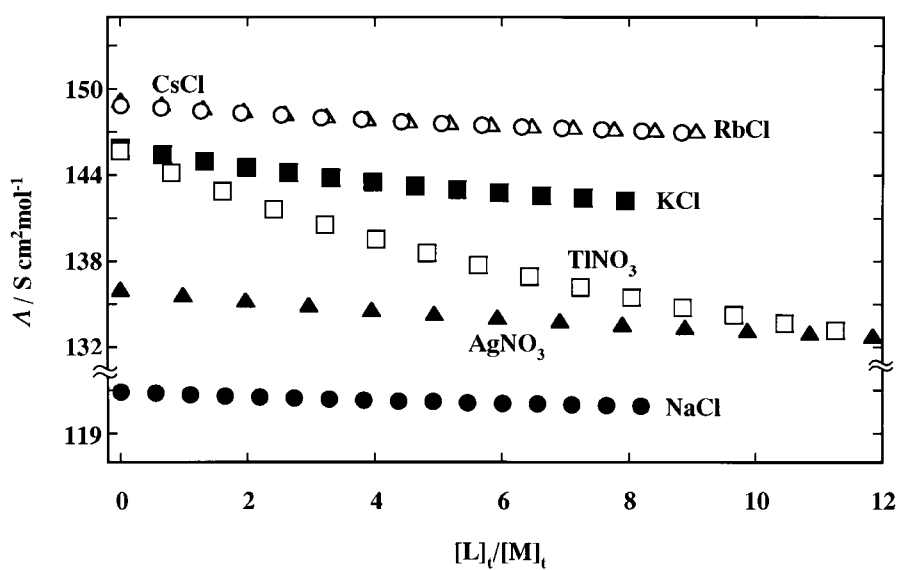


Figure 3. Δ vs. $[L]_t/[M]_t$ curves for 19C6 – monovalent metal salt systems in water.

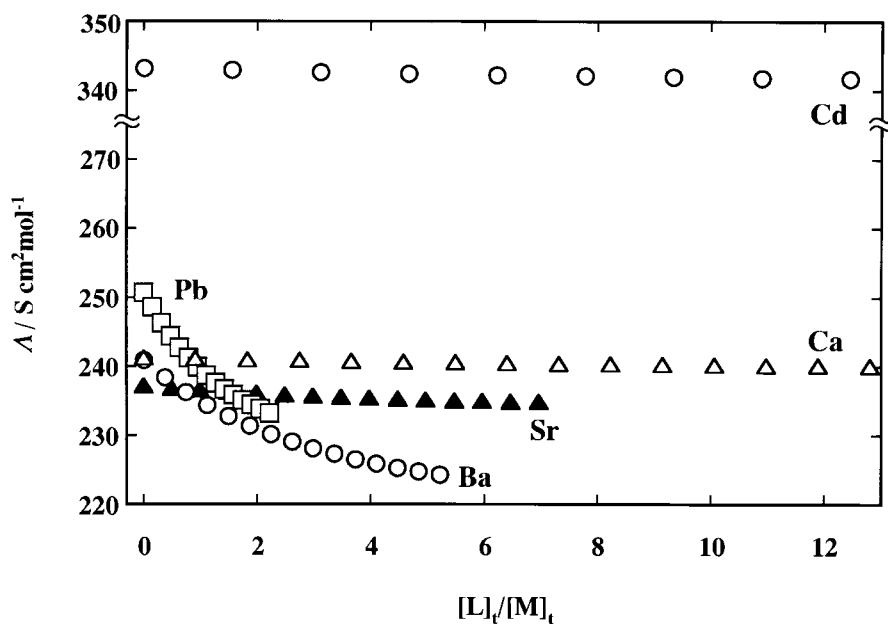


Figure 4. Λ vs. $[L]_t/[M]_t$ curves for 19C6 – bivalent metal nitrate systems in water.

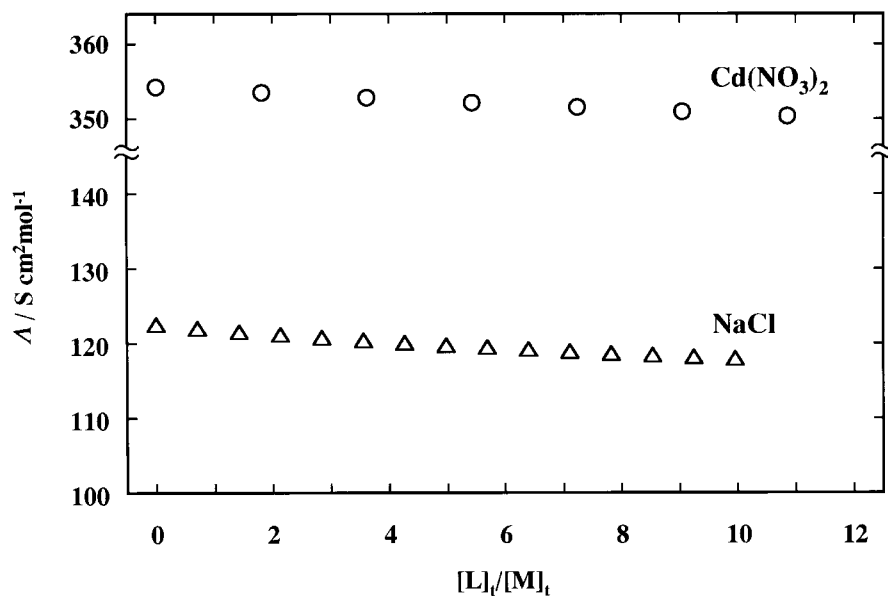


Figure 5. Λ vs. $[L]_t/[M]_t$ curves for 18C6 – metal salt systems in water.

Table II. $\log K_{ML}$ values of 19C6 and 18C6 with metal ions in H₂O at 25 °C^a

Metal ion	Ionic radius (Å) ^b	19C6	18C6
Li ⁺	0.74	0.76 ± 0.11	0.0 ^c
Na ⁺	1.02	0.93 ± 0.07	0.73 ± 0.01 0.8 ^d
K ⁺	1.38	1.27 ± 0.02	2.03 ^{d,e}
Rb ⁺	1.49	1.33 ± 0.07	1.56 ^d
Cs ⁺	1.70	0.71 ± 0.06	0.99 ^d
Ag ⁺	1.15	0.93 ± 0.06	1.50 ^d
Tl ⁺	1.50	1.08 ± 0.03	2.27 ^d
Ca ²⁺	1.00	1.26 ± 0.09	0.48 ^f
Sr ²⁺	1.16	1.83 ± 0.11	2.72 ^d
Ba ²⁺	1.36	1.95 ± 0.03	3.87 ^d
Cd ²⁺	0.95	1.54 ± 0.04	-0.053 ± 0.035
Pb ²⁺	1.19	2.38 ± 0.05	4.27 ^d

^a Each value determined in this study is the average of 5–8 measurements. The uncertainties are the standard deviations.

^b R.D. Shannon and C.T. Prewitt: *Acta Crystallogr.* **B25**, 925 (1969).

^c Y. Kudo, Y. Takeda and H. Matsuda: *J. Electroanal. Chem.* **396**, 333 (1995).

^d R.M. Izatt, R.E. Terry, B.L. Haymore, L.D. Hansen, N.K. Dalley, A.G. Avondet and J.J. Christensen: *J. Am. Chem. Soc.* **98**, 7620 (1976).

^e Y. Takeda and O. Arima: *Bull. Chem. Soc. Jpn.* **58**, 3403 (1985).

^f H. Høiland, J.A. Ringseth and T.S. Brun: *J. Solution Chem.* **8**, 779 (1979).

concentration is observed for both 19C6 and 18C6. A constant Λ is caused by low stability of a crown ether – cation complex and/or nearly equal mobilities of the complex and the cation. Because proton mobility is extremely high in water (proton-jump mechanism), it can be concluded that 19C6 and 18C6 scarcely form any complexes with protons in water. Thus, it was possible to determine the K_{ML} value in water of 18C6 with Cd²⁺ and those of 19C6 with Ag⁺, Cd²⁺, and Pb²⁺ under acidic conditions.

The Λ vs. $[L]_t/[M]_t$ plots are given in Figures 2–5, $[M]_t$ designating the total concentration of a metal salt. The $\log K_{ML}$ values of the 19C6–Li⁺ complex in water were measured at 25 °C for LiCl, LiNO₃, and LiClO₄. They are listed in Table I. Table I shows that anion effect on the $\log K_{ML}$ values is negligible. The $\log K_{ML}$ value of the 19C6–Li⁺ complex in Table II is the average of the $\log K_{ML}$ values in Table I.

The K_{ML} value of 19C6 for mono- and bivalent metal ions decreases in the order Rb⁺ ≥ K⁺ > Tl⁺ > Na⁺ = Ag⁺ > Li⁺ ≈ Cs⁺ and Pb²⁺ > Ba²⁺ > Sr²⁺ > Cd²⁺ > Ca²⁺, respectively (Table II). The selectivity orders of 19C6 and 18C6 for

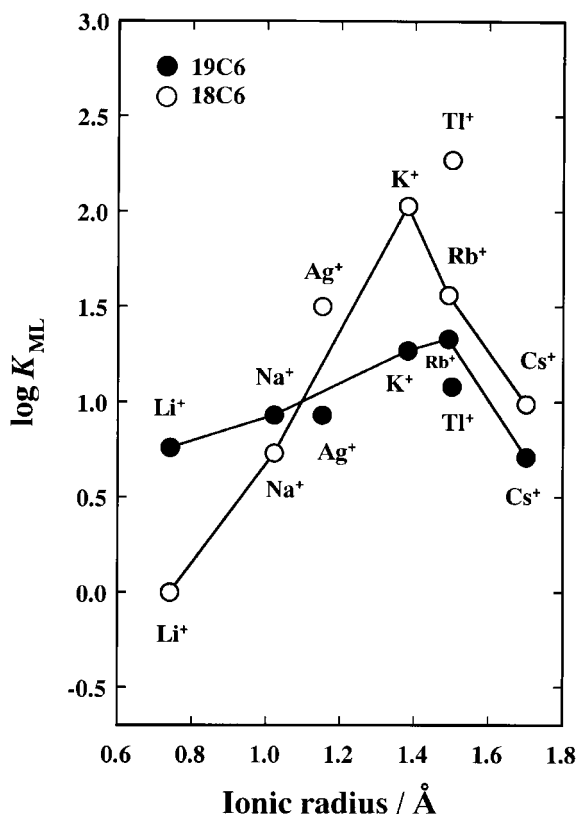


Figure 6. $\log K_{ML}$ vs. ionic radius plots for monovalent metal ions.

monovalent metal ions are different from each other, but those for bivalent metal ions are the same except for Cd^{2+} . The highest selectivity of 19C6 is found for Rb^{+} among the monovalent metal ions (Figure 6). For alkali metal ions, the differences between the largest and the smallest $\log K_{ML}$ values are 0.62 for 19C6 and 2.03 for 18C6; for alkaline earth metal ions, these are 0.69 for 19C6 and 3.39 for 18C6. The selectivity for the neighboring alkali metal ions in the periodic table is lower for 19C6 than for 18C6 except for the case of Rb^{+} and Cs^{+} (Figure 6). The same is true for the alkaline earth metal ions (Figure 7). The increased flexibility of 19C6 over 18C6 lowers the selectivity for *s*-block metal ions.

The sizes of Rb^{+} and Tl^{+} are almost the same. The K_{ML} value of 19C6 is greater for Rb^{+} than for Tl^{+} , but the reverse is true for 18C6 (Figure 6). 18-Crown-6 forms a more stable complex with Ag^{+} than with Na^{+} , but the K_{ML} values of Ag^{+} and Na^{+} with 19C6 are equal (Table II and Figure 6). The ionic sizes of Ca^{2+} and Cd^{2+} are almost the same. The Gibbs energy of hydration (ΔG_h° [4]) is smaller for Cd^{2+} ($-1801 \text{ kJ mol}^{-1}$) than for Ca^{2+} ($-1593 \text{ kJ mol}^{-1}$). 18-Crown-6 forms a more stable complex with Ca^{2+} in water than with Cd^{2+} as is to be expected. But the contrary holds for 19C6. Sr^{2+} and Pb^{2+} are nearly equal in size. ΔG_h° [4]

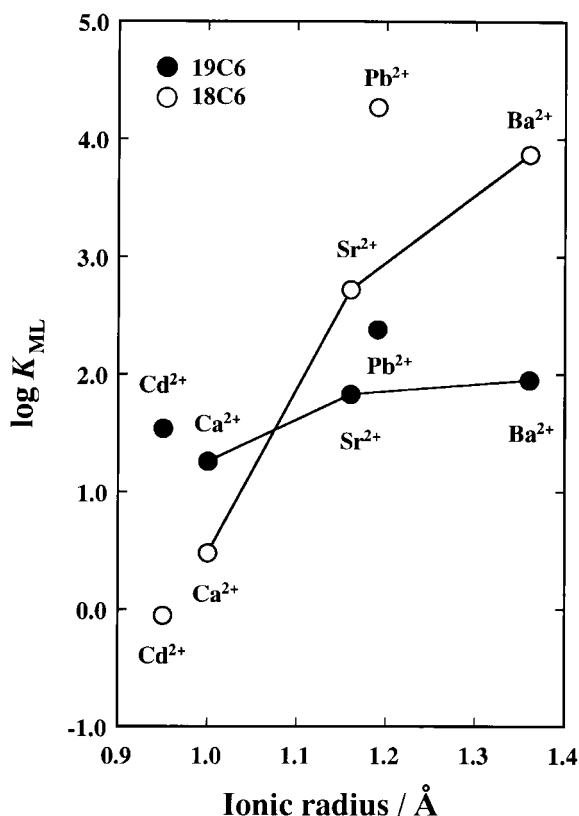


Figure 7. $\log K_{ML}$ vs. ionic radius plots for bivalent metal ions.

of Sr^{2+} ($-1447 \text{ kJ mol}^{-1}$) and Pb^{2+} ($-1497 \text{ kJ mol}^{-1}$) are much the same. But the 19C6 complex with Pb^{2+} is more stable in water than that with Sr^{2+} . Although the bivalent metal ions undergo much stronger hydration than the monovalent metal ions [4], the K_{ML} values of 19C6 with M^{2+} are greater than or nearly equal to those with M^{+} . This is due to the stronger intrinsic interaction of 19C6 with M^{2+} and the stronger hydration of the 19C6- M^{2+} complex compared with M^{+} . The K_{ML} value of 18C6 with Cd^{2+} is the smallest of all the bivalent metal ions, and is lower than or nearly equal to those with M^{+} . This is attributed to the smallest crystal ionic radius, next to Li^{+} , and the greatest $-\Delta G_h^\circ$ value of the size-misfitted Cd^{2+} . For Na^{+} and the ions which are smaller in size than Na^{+} (Li^{+} , Ca^{2+} , Cd^{2+}), the K_{ML} value is greater for 19C6 than for 18C6, but the reverse is true for all the other ions of larger sizes than Na^{+} . It follows from this that, for Li^{+} , Na^{+} , Ca^{2+} , and Cd^{2+} , the donor oxygen atoms of 19C6 are more favorably oriented to the small ion than those of 18C6 because 19C6 is larger than 18C6, resulting in the stronger interaction of the donor oxygen atoms of 19C6 with the small ion compared with 18C6; for the other metal ions of larger sizes than Na^{+} , the donor oxygen atoms of 19C6 are less favorably oriented to the ion than those of 18C6 owing to the

Table III. Λ_{MLA} values of 19C6 and 18C6 with alkali metal chlorides in H_2O at 25 °C

Salt	19C6		18C6	
	$\Lambda_{\text{MLA}}^{\text{a}}$ $\text{S cm}^2 \text{ mol}^{-1}$	$[\text{M}]_{\text{t}} \times 10^3$ mol dm^{-3}	$\Lambda_{\text{MLA}}^{\text{a}}$ $\text{S cm}^2 \text{ mol}^{-1}$	$[\text{M}]_{\text{t}} \times 10^3$ mol dm^{-3}
NaCl	115.5	3.7413	85.07	3.6740
	115.5	3.8605	87.84	3.7558
	116.8	3.9839	83.88	3.7949
KCl	133.4	3.1273	92.59	3.2385
	134.2	3.2499	94.07	3.7555
	132.6	3.4079		
	133.4	3.7580		
RbCl	141.8	3.7925		
CsCl	136.7	3.7823		

^a The Λ_{MLA} values are the Λ values of the MLA complexes at $[\text{MLA}] = [\text{M}]_{\text{t}}$.

unsymmetrical structure of 19C6. To the best of our knowledge, the 19C6 complex with Li^+ is much the most stable in water among all the crown ether complexes with Li^+ ; the same is true for the 19C6 complex with Ca^{2+} . The effect of the extra methylene group on the stability of the crown ether complex from 18C6 to 19C6 is small for Na^+ , Rb^+ , and Cs^+ , whereas that is large for the other metal ions (Figures 6 and 7).

Tables I and III show that the mobility of the 19C6–alkali metal ion complex in water decreases in the order $\text{Rb} > \text{Cs} \geq \text{K} > \text{Na} > \text{Li}$. Generally, the smaller the alkali metal ion, the larger is the moving entity in water of the 19C6–alkali metal ion complex (stronger hydration of the 19C6 complex ion). Great decreases in the mobility of the 19C6 – alkali metal ion complex are found from heavy alkali metal ions (K^+ , Rb^+ , Cs^+) to light ones (Li^+ , Na^+). Although 19C6 is larger than 18C6, the 19C6 complexes with K^+ and Na^+ are much more mobile in water than the 18C6 complexes with K^+ and Na^+ , respectively (Table III). It thus appears that the interaction between the crown ether complex ion and water is weakened by the extra methylene group. The limiting ionic molar conductivity of the 19C6– K^+ complex in water at 25 °C is calculated to be 43 from the λ° value of Cl^- (76.39[5]) and from the Λ° value of the 19C6–KCl complex determined in this study. The λ° value of the 19C6– K^+ complex is much higher than that of the 18C6– K^+ complex (25.3 [6]), and is comparable to that of $(\text{CH}_3)_4\text{N}^+$ in water at 25 °C (44.42 [5]).

Appendix

Table IV. Apparent molar conductivities ($\Lambda/S \text{ cm}^2 \text{ mol}^{-1}$) of aqueous solutions containing crown ethers and metal salts for K_{ML} -determination at 25 °C

	Salt	$[L]_t \times 10^3 / \text{mol dm}^{-3}$	$[L]_t / [M]_t$	Λ
L = 19C6				
	LiCl	0.0000	0.0000	109.6
		2.4737	0.6358	109.4
		4.8295	1.2717	109.3
		7.0758	1.9075	109.2
		9.2200	2.5434	109.1
		11.268	3.1792	109.0
		13.228	3.8151	108.9
		15.105	4.4509	108.8
		16.903	5.0868	108.7
		18.628	5.7226	108.6
		20.284	6.3585	108.5
		21.874	6.9943	108.4
		23.404	7.6302	108.4
		24.876	8.2660	108.3
	26.294	8.9018	108.2	
	LiNO ₃	0.0000	0.0000	106.3
		2.4793	0.7298	106.2
		4.8405	1.4596	106.0
		7.0919	2.1894	105.9
		9.2409	2.9192	105.8
		11.294	3.6490	105.7
		13.258	4.3788	105.6
		15.139	5.1086	105.5
		16.941	5.8384	105.4
		18.670	6.5682	105.3
		20.330	7.2980	105.2
		21.924	8.0278	105.2
		23.457	8.7576	105.1
		24.933	9.4875	105.0
	26.353	10.217	105.0	
	LiClO ₄	0.0000	0.0000	101.6
		2.2895	0.7025	101.5
		4.4700	1.4050	101.3
		6.5490	2.1075	101.2
		8.5335	2.8100	101.1
		10.429	3.5125	101.0
		12.243	4.2150	100.9
		13.980	4.9175	100.8
		15.644	5.6201	100.8
		17.241	6.3226	100.7
	18.773	7.0251	100.6	

Table IV. Continued.

Salt	$[L]_t \times 10^3 / \text{mol dm}^{-3}$	$[L]_t / [M]_t$	Λ
L = 19C6			
LiClO ₄ (contd)	20.246	7.7276	100.5
	21.662	8.4301	100.4
	23.024	9.1326	100.4
	24.336	9.8351	100.3
	25.600	10.537	100.3
	26.819	11.240	100.2
NaCl	0.0000	0.0000	121.9
	1.9924	0.5459	121.8
	3.8899	1.0917	121.7
	5.6992	1.6376	121.6
	7.4262	2.1834	121.6
	9.0764	2.7293	121.5
	10.655	3.2751	121.4
	12.166	3.8210	121.3
	13.614	4.3668	121.3
	15.003	4.9127	121.2
	16.337	5.4585	121.1
	17.619	6.0044	121.1
	18.851	6.5502	121.1
	20.036	7.0961	121.0
21.178	7.6419	121.0	
22.278	8.1878	120.9	
KCl	0.0000	0.0000	145.9
	2.2028	0.6625	145.4
	4.3008	1.3251	144.9
	6.3011	1.9876	144.5
	8.2105	2.6502	144.2
	10.035	3.3127	143.8
	11.780	3.9753	143.5
	13.451	4.6378	143.2
	15.052	5.3004	143.0
	16.588	5.9629	142.8
	18.063	6.6255	142.6
	19.479	7.2880	142.4
20.842	7.9506	142.2	
RbCl	0.0000	0.0000	149.2
	2.2711	0.6475	148.9
	4.4340	1.2949	148.7
	6.4963	1.9424	148.5
	8.4649	2.5898	148.3
	10.346	3.2373	148.1
	12.145	3.8847	147.9
	13.868	4.5322	147.8
15.519	5.1796	147.7	

Table IV. Continued.

Salt	$[L]_t \times 10^3 / \text{mol dm}^{-3}$	$[L]_t / [M]_t$	Δ
L = 19C6			
RbCl	17.102	5.8271	147.5
(contd)	18.622	6.4745	147.4
	20.083	7.1220	147.4
	21.487	7.7694	147.2
	22.839	8.4169	147.2
	24.140	9.0643	147.1
CsCl	0.0000	0.0000	148.8
	2.5163	0.6310	148.7
	4.9129	1.2620	148.5
	7.1979	1.8930	148.3
	9.3791	2.5240	148.2
	11.463	3.1550	148.0
	13.457	3.7861	147.9
	15.365	4.4171	147.7
	17.195	5.0481	147.6
	18.949	5.6791	147.5
	20.634	6.3101	147.4
	22.252	6.9411	147.3
	23.808	7.5721	147.2
	25.305	8.2031	147.1
	26.747	8.8341	147.0
AgNO ₃	0.0000	0.0000	136.1
	2.5011	0.9878	135.7
	4.8832	1.9756	135.3
	7.1544	2.9635	134.9
	9.3224	3.9513	134.6
	11.394	4.9391	134.3
	13.375	5.9269	134.1
	15.272	6.9148	133.9
	17.091	7.9026	133.6
	18.835	8.8904	133.4
	20.509	9.8782	133.2
	22.117	10.866	133.0
	23.664	11.853	132.8
	25.152	12.841	132.6
	26.586	13.829	132.5
TiNO ₃	0.0000	0.0000	145.7
	2.3908	0.8048	144.2
	4.6678	1.6096	142.9
	6.8388	2.4143	141.6
	8.9112	3.2191	140.5
	10.891	4.0239	139.5
	12.785	4.8287	138.6
	14.599	5.6335	137.7

Table IV. Continued.

Salt	$[L]_t \times 10^3 / \text{mol dm}^{-3}$	$[L]_t / [M]_t$	Λ
L = 19C6			
TlNO ₃ (contd)	16.337	6.4382	136.9
	18.004	7.2430	136.2
	19.604	8.0478	135.5
	21.142	8.8526	134.8
	22.620	9.6574	134.2
	24.043	10.462	133.7
	25.413	11.266	133.2
Ca(NO ₃) ₂	0.0000	0.0000	241.3
	2.6310	0.9145	241.2
	5.1367	1.8289	241.0
	7.5258	2.7434	240.9
	9.8064	3.6579	240.8
	11.985	4.5723	240.7
	14.070	5.4868	240.6
	16.065	6.4012	240.5
	17.978	7.3157	240.4
	19.812	8.2302	240.3
	21.574	9.1446	240.3
	23.266	10.059	240.3
	24.893	10.973	240.2
	26.458	11.888	240.2
27.966	12.802	240.1	
Sr(NO ₃) ₂	0.0000	0.0000	237.2
	1.3912	0.4970	236.8
	2.7161	0.9940	236.5
	3.9795	1.4910	236.3
	5.1854	1.9880	236.1
	6.3377	2.4850	235.9
	7.4399	2.9820	235.7
	8.4952	3.4790	235.6
	9.5065	3.9760	235.4
	10.476	4.4729	235.3
	11.407	4.9699	235.1
	12.302	5.4669	235.0
	13.162	5.9639	235.0
	13.990	6.4609	234.9
14.787	6.9579	234.9	
Ba(NO ₃) ₂	0.0000	0.0000	240.9
	1.1731	0.3722	238.4
	2.2903	0.7444	236.2
	3.3555	1.1166	234.4
	4.3724	1.4889	232.8
	5.3440	1.8611	231.4
	6.2734	2.2333	230.1

Table IV. Continued.

Salt	$[L]_t \times 10^3 / \text{mol dm}^{-3}$	$[L]_t / [M]_t$	Λ	
L = 19C6				
Ba(NO ₃) ₂ (contd)	7.1632	2.6055	229.1	
	8.0160	2.9777	228.1	
	8.8340	3.3499	227.3	
	9.6192	3.7221	226.5	
	10.373	4.0944	225.9	
	11.099	4.4666	225.3	
	11.797	4.8388	224.8	
	12.469	5.2110	224.3	
	Cd(NO ₃) ₂	0.0000	0.0000	343.2
		2.2215	1.5547	342.9
		4.3372	3.1095	342.7
		6.3545	4.6642	342.5
		8.2801	6.2190	342.3
		10.120	7.7737	342.2
11.880		9.3285	342.0	
13.565		10.883	341.8	
15.180		12.438	341.7	
16.729		13.992	341.6	
18.216		15.547	341.5	
19.644		17.102	341.5	
21.018		18.656	341.4	
22.340		20.211	341.3	
23.613	21.766	341.2		
Pb(NO ₃) ₂	0.0000	0.0000	250.7	
	0.5176	0.1581	248.6	
	1.0105	0.3162	246.3	
	1.4805	0.4744	244.4	
	1.9291	0.6325	242.7	
	2.3578	0.7906	241.2	
	2.7678	0.9487	239.9	
	3.1604	1.1068	238.7	
	3.5367	1.2649	237.6	
	3.8976	1.4231	236.7	
	4.2440	1.5812	235.9	
	4.5769	1.7393	235.1	
	4.8969	1.8974	234.4	
	5.2049	2.0555	233.8	
5.5015	2.2136	233.2		
L = 18C6				
NaCl	0.0000	0.0000	122.5	
	2.6049	0.7109	122.0	
	5.0857	1.4218	121.5	
	7.4512	2.1327	121.2	
	9.7091	2.8436	120.8	

Table IV. Continued.

Salt	$[L]_t \times 10^3 / \text{mol dm}^{-3}$	$[L]_t / [M]_t$	Λ	
L = 18C6				
NaCl (contd)	11.866	3.5545	120.4	
	13.930	4.2654	120.1	
	15.906	4.9763	119.8	
	17.800	5.6872	119.5	
	19.616	6.3981	119.2	
	21.360	7.1090	118.9	
	23.035	7.8199	118.6	
	24.646	8.5308	118.4	
	26.196	9.2417	118.2	
	27.688	9.9526	117.9	
	Cd(NO ₃) ₂	0.0000	0.0000	354.3
		4.8541	1.8086	353.6
		9.4771	3.6172	352.9
		13.885	5.4258	352.2
18.092		7.2343	351.6	
22.113		9.0429	351.0	
25.959		10.851	350.4	
29.641		12.660	349.8	
33.170		14.468	349.3	
36.554		16.277	348.8	
39.804		18.085	348.4	
42.925		19.894	347.9	
45.927		21.703	347.5	
48.816		23.511	347.1	
51.597	25.320	346.7		

References

1. M. Ouchi, Y. Inoue, T. Kanzaki and T. Hakushi: *J. Org. Chem.* **49**, 1408 (1984).
2. Y. Inoue, M. Ouchi and T. Hakushi: *Bull. Chem. Soc. Jpn.* **58**, 525 (1985).
3. Y. Takeda, H. Yano, M. Ishibashi and H. Isozumi: *Bull. Chem. Soc. Jpn.* **53**, 72 (1980).
4. H. L. Friedman and C. V. Krishnan: in F. Franks (ed.), *Water*, Vol. 3, p. 55, Plenum Press, New York (1973).
5. R. L. Kay and D. F. Evans: *J. Phys. Chem.* **70**, 2325 (1966).
6. Y. Takeda: *Bull. Chem. Soc. Jpn.* **56**, 866 (1983).

