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Investigation of the Cation Complexation by Macrocyclic Ethers using ^{13}C NMR Spin–Lattice Dipolar Relaxation Time Measurements

Çakıl ERK[1,*], Matthias HEYDENREICH[2], and Erich KLEINPETER[2,†]
[1] *İstanbul Technical University, Chemistry Department, Sciences Faculty, Maslak, 34469, İstanbul, TURKEY*
[2] *Universität Potsdam, Chemisches Institut, Postfach 60 15 53, D-14415 Potsdam, GERMANY*
e-mail: kp@chem.uni-potsdam.de

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The binding constants (K_a) of [18]crown-6 ether with Na^+, K^+, and Ba^{2+} thiocyanates were determined by $^{13}C\{^1H\}$ NMR spin–lattice dipolar relaxation time measurements. The observed relaxation times (T_{obs}) for ^{13}C nuclei are dependent upon the relaxation times of the complexed (T_{1a}) and free crown ether (T_{1f}), and were measured in [D4]methanol using inversion–recovery measurements in the extreme narrowing limit (75 MHz). The observed ^{13}C relaxation times of the metal complexes were found to be smaller than those of the cation-free macrocyclic ether due to reduced internal flexibility of the macrocycles in the complexes. The relationship $1/T_{obs} = P_a/T_{1a} + P_f/T_{1f}$ was used to estimate K_a for the n:m stoichiometry of the cation complexes in [D4]methanol and were found to run in the order $Ba^{2+} > K^+ > Na^+$. The T_1 measurements within the temperature range of 280–301 K yielded energy barriers for the internal interconversion of the –O–CH_2–CH_2–O– structural fragments in free and complexed [18]crown-6 ether. The results indicated that the energy barriers of complexed crown ether are lower than those of the cation-free molecule, indicating the stabilization of preferred conformations in the cation-complexed crown ethers.

Introduction

A large number of macrocyclic ether (crown ether) applications of metal binding have been reported[1,2] and include such applications as cation extraction, membrane transport, ion-selective electrodes, calorimetric measurements, and, quite recently, functionality of molecular structure using NMR spectroscopy[2–12]. The interaction mechanism of cations with the donor oxygen atoms of the macrocycle was examined herein by studying the influence of the cationic interactions on the internal molecular mobility of the crown ether ligand. This was based on the premise that the formation of rather rigid complexes should notably alter

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†Corresponding author

the flexibility of the macrocyclic backbone[9−11]. In order to quantitatively determine the binding effect of diamagnetic cations using NMR methods, we recently reported the Na^+−benzocrown ether association in acetonitrile, using ^{13}C dipolar relaxation time measurements[9]. The main contribution to spin–lattice relaxation arises from dipole–dipole interactions, with directly bound protons having the largest effect on the T_1 value of the corresponding ^{13}C nuclei[13]. Thus, measurements of the ^{13}C relaxation rates were performed in order to ascertain the effect of the preferential cation binding, which, at the same time, leads to detailed information about the macrocyclic backbone flexibility involving the carbon atoms[14].

The cation association process of n:m stoichiometry can be formulated[9−14] in the following manner (where A^+ and L indicate the cation and macrocyclic ether, respectively):

$$nA^+ + mL \rightleftharpoons A_n^+L_m \tag{1}$$

From the solution concentrations, $[A_0^+] = n[A_n^+L_m] + [A^+]$ and $[L_0] = m[A_n^+L_m] + [L]$, for the cation and the macrocycle, respectively, the binding constant of the complex formation expressed in Eq. (1) can be derived if complexation is 1:1 (i.e. m = n = 1); then the mole fraction of the cation–crown ether complex ($P_a = [A^+L]/[L_0]$) can be introduced into Eq. (1), yielding $K_a = P_a/\{(1 - P_a[A_0^+])(1 - P_a[L_0])\}$. For this reason, the experimental solution concentrations of the analytes were used in identical measures (i.e. $[A_0^+] = [L_0]$), which leads to Eq. (2). P_a and P_f are thus obtainable from Eqs. (2) and (3) by calculating T_{1a} from T_{obs} for the 1:1 stoichiometric complex[6,7].

$$K_a = P_a/\{[L_0](1 - P_a)^2\} \tag{2}$$

$$1/T_{obs} = P_a/T_{1a} + P_f/T_{1f} \tag{3}$$

In the present study, ^{13}C NMR relaxation time measurements of free and Na^+, K^+, and Ba^{2+} thiocyanate complexes of [18]crown-6 ether were measured at different temperatures in order to determine the 1:1 binding constants (K_a), the relaxation times (T_{1a}) of the 1:1 complexes, and the energy barriers to segmental motion in the free and the cation-complexed crown ether in [D4]methanol. The cation–crown ether interaction influences the molecular motion of the macrocyclic ring via the C−O dipoles; therefore, preferential binding of the cations can be studied via the segmental mobility of the macrocyclic ring system. The correlation time (τ_{CH}) of this dynamic process is given by Eq. (4); in the extreme narrowing limit, τ_{CH} is much smaller than the reciprocal of the ^{13}C resonance frequency, $1/\omega_{CH}$, as it is required to be[15].

$$1/T_1 = (\mu_0/4\pi)^2 h\gamma_C^2\gamma_H^2 r_{CH}^{-6}\tau_{CH} \tag{4}$$

The experimentally observed relaxation rate of the ^{13}C nuclei (T_{obs}) is a confluence of both the free (T_{1f}) and the 1:1 complex (T_{1a}) of the crown ether, as the 2 species are in fast exchange[11,12]. The reorientation process of the macrocyclic ring system in solution strongly determines the correlation times (τ_{CH}) of the C–H bonds; these τ_{CH} values can be readily obtained from ^{13}C NMR T_1 data and were shown to be markedly dependent on cation binding (see Table 3)[9,13,14]. The experimental correlation times, τ_{CH}, thus obtained, are based on the fastest dynamic process of lowest energy, i.e. on the internal skeletal interconversion process. Considering Eq. (4), the corresponding energy barrier ($\Delta E = \Delta H - T\Delta S$) of the correlation time, τ_{CH}, can be derived from Eq. (5) (cf. Figures 1 and 2):

$$\tau_{CH} = \tau_{0CH} * e^{-\Delta E/RT} \tag{5}$$

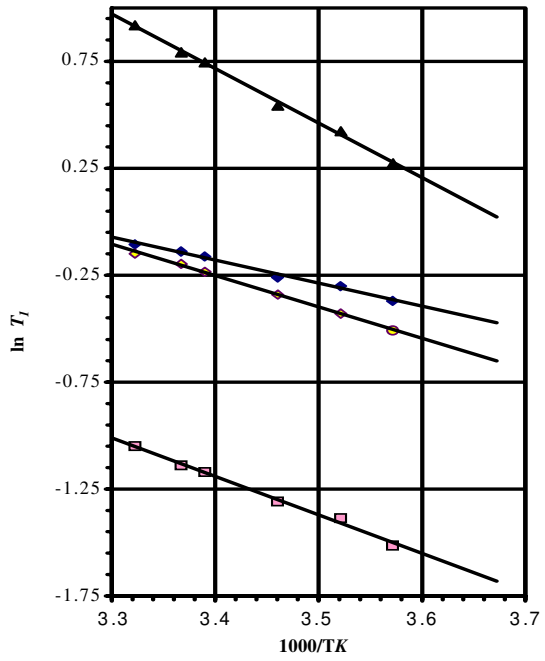

Figure 1. Relaxation times of free (▲) [18]crown-6 ether ([0.26] M) and its 1:1 complexes with Na^+ (♦), K^+ (○), and Ba^{2+} (□) ions at various temperatures in [D4]methanol.

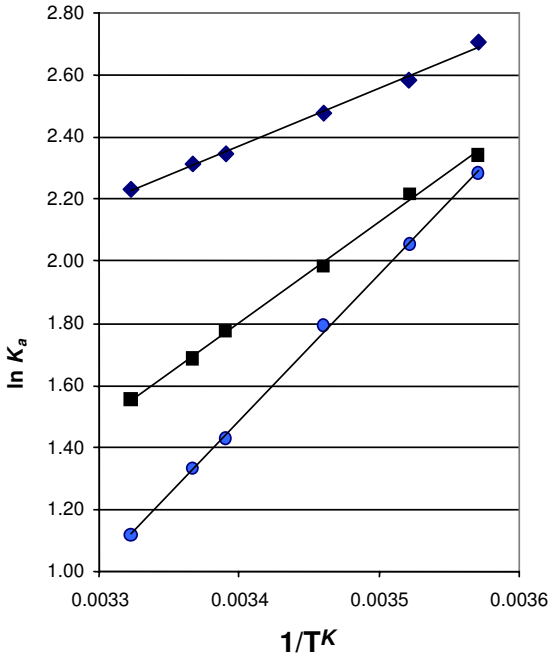

Figure 2. Association constants, K_a, of 1:1 complexes of Na^+ (♦), K^+ (■), and Ba^{2+} (●) with [18]crown-6 ether at various temperatures in [D4]methanol.

Results and Discussion

Cation binding of macrocyclic crown ethers originates from interactions of the backbone oxygen atoms with the strongly electropositive cations. In solution, the cation is involved in a dynamic binding process, which is mainly determined by the thermodynamic stability of the complex. Different experimental methods have been applied to determine the binding constant quantitatively, and the cation binding selectivity of such macrocyclic ligands for diamagnetic cations (in particular, alkali and alkaline earth cations) has been the subject of numerous studies[10−17]. For analytical methods, both electrochemical and calorimetric procedures, in addition to NMR spectroscopy of the complexing nuclei, have been employed to investigate the complex formation quantitatively. With regard to the optimum choice of method, however, IR, optical spectroscopy, and dynamic NMR appear to be best at representing these complex systems because the response to complexation comes directly from the molecules detected experimentally.

The results of the present study, shown in Table 1, can be readily employed to assess the cation binding activities of [18]crown-6 ether. Of the ions examined, Na^+ proved to have optimal binding; due to this effect, the internal skeletal interconversion enthalpy was the lowest obtained ($\Delta H = 8.69$ kJ/mol), since the cation resides completely within the cavity of the 6 oxygen atoms of the crown ether. The binding of K^+, too large to fit completely into the crown cavity, was of intermediate internal skeletal interconversion enthalpy (13.65 kJ/mol), while for the alkaline earth cation Ba^{2+} (not much different in size compared to K^+, but of a higher charge) the highest internal skeletal interconversion enthalpy was obtained (17.36 kJ/mol). In the complexes studied, the lone pair electrons of the macrocyclic ring systems must be delocalized over the complexing cation, determining both the binding strength and the distance from the cation to the average center of the macrocyclic ring system. However, the free crown ether has no cation effect to diminish electron density from the donor oxygen atoms; thus, the highest internal skeletal interconversion enthalpy (21.73 kJ/mol) was obtained. Although T_{1f} varied by almost 50% within the temperature range examined, there is nothing present to hinder the internal skeletal interconversion. This is significant because complexation is not a simple, singular process, but instead involves a number of different steps[16,17], that is to say, complex formation of macrocyclic ethers with cations is a sequence of several steps involving such things as molecular conformational changes, the relevant ones of which are determined by the cavity size preferences of the crown ether under study. Experimentally, only the first and last steps of the equilibrium given in Eq. (6) are observed; whereby T_{1f} reflects the skeletal interconversion of the free crown ether depending on its rotational diffusion, and both T_{obs} and T_{1a} reflect the corresponding dynamic process in the complex, $[A^+_{n-1}\ L_{m-1}]$, in the solution equilibrium.

$$mL + nA^+ \rightleftharpoons (conform.changes)mL + nA^+ \rightleftharpoons A^+_n L_m \rightleftharpoons A^+_{n-1}L_{m-1} + A^+ + L \qquad (6)$$

The results obtained by T_1 measurements are sufficiently reliable to assess cation binding as well as the molecular dynamics of [18]crown-6 ether and of its complexes, as the skeletal interconversion barriers due to cation binding of [18]crown-6 ether determined here are in excellent agreement with earlier reports $Ba^{2+} < K^+ < Na^{+}$[1,4,13−16]. In consideration of the stoichiometry and statistics of the electrostatic interactions of the species, the T_1 NMR experiments imply that the last step in Eq. (6) can be quantitatively studied using the methodology provided by the application of Eqs. (1)–(3). However, when treating the problem from the point of stoichiometry, it must be considered that the macrocyclic ether–cation–anion system is a rather complicated multi-stoichiometric system. Furthermore, it is not known how much of mL is ready

to react with nA^+ in the second step of Eq. (6), and the exact structure of $[A^+_{n-1}\ L_{m-1}]$ is unknown. In fact, it is not easy to determine the free energy of the complex formation within such a complex equilibrium as presented in Eq. (6). Much of the data on macrocyclic complex formation have been reported using a single analytical method[3−6,8,11]. However, a single method is insufficient to satisfactorily represent the cation binding and binding selectivity, and accordingly more extensive work has to be conducted under ideal conditions. Therefore, the present T_{obs} and T_{1f} measurements at 75 MHz of these well-known macrocyclic ether structures, which are primarily present, do correctly represent the binding and cation selectivity of [18]crown-6 ether.

Table 1. Barrier to interconversion relaxation times T_1 of free (T_{1f}) and 1:1 Na^+, K^+, and Ba^{2+} complexes of [18]crown-6 ether (T_{1a}) at various temperatures.

Temp. (K)	Na^+/T_{1a} (s)	K^+/T_{1a} (s)	Ba^{2+}/T_{1a} (s)	Free/T_{1f} (s)
332	0.91	0.86	0.35	2.50
337	0.87	0.82	0.32	2.20
339	0.87	0.79	0.31	2.10
344	0.82	0.71	0.27	1.72
352	0.77	0.65	0.25	1.50
357	0.74	0.60	0.22	1.30
ΔH (kJ/mol)	8.69	13.65	17.36	21.73
ΔS (kJ/mol)	28.06	44.23	38.97	79.74

Table 2. Binding constants (ln K_a) of 1:1 complexes of Na^+, K^+, and Ba^{2+} with [18]crown-6 ether at various temperatures and the corresponding binding energies.

Temp. (K)	$Na^+/\ln K_a$	$K^+/\ln K_a$	$Ba^{2+}/\ln K_a$
332	1.12	1.55	2.23
337	1.33	1.68	2.31
339	1.43	1.76	2.35
346	1.80	1.98	2.49
352	2.05	2.22	2.58
357	2.28	2.34	2.71
ΔG_{298} (kJ/mol)	−3.15	−4.10	−5.65
ΔH (kJ/mol)	−38.95	−26.92	−15.57
ΔS (J/mol)	120.11	76.59	33.29

The binding constants K_a of 1:1 complexes of [18]crown-6 ether run in the order $Ba^{2+} > K^+ > Na^+$ in [D4]methanol (see Table 2). The corresponding energies are somewhat lower compared with data obtained by other analytical methods[15−17], although conductivity measurements[18,19] of ion pair interactions of crown ethers were very close to those values determined here. Thus, the results here can be satisfactorily explained employing the ion pairs theory[20], whereby increasing temperatures decrease T_{1a} as well as T_{1f} values due to endothermic internal motions that lower the association constants (cf. Table 2, and Figures 1 and 2). According to the theory, by reducing the temperature, the association constants, K_a, are increased due to increasing distances between the cations and counter ions; therefore, the encapsulation of the cation by the macrocyclic ether is enhanced (cf. Tables 2 and 3). For the same reason, the formation of the crown complexed (crown-separated) ion pairs is actually an exothermic association, even in polar solvents such as methanol, and may be similar to the equilibrium of free ions[20]. Therefore, it is clear that this method is

well suited to determining the thermodynamic parameters of the strong complexation of [18]crown-6 ether in methanol. Furthermore, it should be noted that methanol solvates the cations better when compared with polar solvents that do not bear hydroxyl groups. For this reason, the binding constants in methanol are smaller than those observed in acetonitrile[9,13,14].

Table 3. Observed relaxation data, T_{obs}, T_{1f}, and T_{1a}, and calculated binding constants (K_a) of the 1:1 complex of Na^+-[18]crown-6 ether at various temperatures (cf. Figure 3).

[Lo]	**1/[Lo]**	$\boldsymbol{T_{1f}}$	$\boldsymbol{1/T_{1f}}$	$\boldsymbol{T_{obs}}$	$\boldsymbol{1/T_{obs}}$	$\boldsymbol{P_1}$	$\boldsymbol{(1-P_1)^2/P_1}$
0.40	2.50	2.390	0.418	1.420	0.704	0.420	0.801
0.28	3.57	2.400	0.417	1.510	0.662	0.360	1.138
0.25	4.00	2.500	0.400	1.570	0.637	0.339	1.289
0.22	4.55	2.550	0.392	1.620	0.617	0.319	1.458
$\boldsymbol{T_{1a}}$	$\boldsymbol{1/T_{1a}}$	**Correl**	$\boldsymbol{K_{ass}}$	**ln** $\boldsymbol{K_{ass}}$	$\boldsymbol{-\Delta G}$ **(kJ)**	$\boldsymbol{T}$ **(K)**	**Intcpt.**
0.91	1.10	0.9998	3.101	1.13	2.763	307.00	0.030
[Lo]	**1/[Lo]**	$\boldsymbol{T_{1f}}$	$\boldsymbol{1/T_{1f}}$	$\boldsymbol{T_{obs}}$	$\boldsymbol{1/T_{obs}}$	$\boldsymbol{P_1}$	$\boldsymbol{(1-P_1)^2/P_1}$
0.40	2.50	2.150	0.465	1.300	0.769	0.444	0.695
0.28	3.57	2.200	0.455	1.390	0.719	0.381	1.005
0.25	4.00	2.212	0.452	1.415	0.707	0.365	1.104
0.22	4.55	2.282	0.438	1.460	0.685	0.347	1.230
$\boldsymbol{T_{1a}}$	$\boldsymbol{1/T_{1a}}$	**Correl**	$\boldsymbol{K_{ass}}$	**ln** $\boldsymbol{K_{ass}}$	$\boldsymbol{-\Delta G}$ **(kJ)**	$\boldsymbol{T}$ **(K)**	**Intcpt.**
0.87	1.155	0.9980	3.786	1.33	3.251	297.00	−0.163
[Lo]	**1/[Lo]**	$\boldsymbol{T_{1f}}$	$\boldsymbol{1/T_{1f}}$	$\boldsymbol{T_{obs}}$	$\boldsymbol{1/T_{obs}}$	$\boldsymbol{P_1}$	$\boldsymbol{(1-P_1)^2/P_1}$
0.40	2.50	2.080	0.481	1.260	0.794	0.459	0.639
0.28	3.57	2.120	0.472	1.340	0.746	0.397	0.914
0.25	4.00	2.150	0.465	1.370	0.730	0.380	1.014
0.22	4.55	2.170	0.461	1.400	0.714	0.361	1.131
$\boldsymbol{T_{1a}}$	$\boldsymbol{1/T_{1a}}$	**Correl**	$\boldsymbol{K_{ass}}$	**ln** $\boldsymbol{K_{ass}}$	$\boldsymbol{-\Delta G}$ **(kJ)**	$\boldsymbol{T}$ **(K)**	**Intcpt.**
0.86	1.16	0.9990	4.121	1.42	3.457	295.00	−0.155
[Lo]	**1/[Lo]**	$\boldsymbol{T_{1f}}$	$\boldsymbol{1/T_{1f}}$	$\boldsymbol{T_{obs}}$	$\boldsymbol{1/T_{obs}}$	$\boldsymbol{P_1}$	$\boldsymbol{(1-P_1)^2/P_1}$
0.40	2.50	1.520	0.658	1.000	1.000	0.534	0.407
0.28	3.57	1.600	0.625	1.060	0.943	0.473	0.589
0.25	4.00	1.665	0.601	1.090	0.917	0.454	0.657
0.22	455	1.676	0.597	1.110	0.901	0.433	0.741
$\boldsymbol{T_{1a}}$	$\boldsymbol{1/T_1}$	**Correl**	$\boldsymbol{K_{ass}}$	**ln** $\boldsymbol{K_{ass}}$	$\boldsymbol{-\Delta G}$ **(kJ)**	$\boldsymbol{T}$ **(K)**	**Intcpt.**
0.77	1.30	0.9997	6.101	1.81	4.415	290.00	0.003
[Lo]	**1/[Lo]**	$\boldsymbol{T_{1f}}$	$\boldsymbol{1/T_{1f}}$	$\boldsymbol{T_{obs}}$	$\boldsymbol{1/T_{obs}}$	$\boldsymbol{P_1}$	$\boldsymbol{(1-P_1)^2/P_1}$
0.40	2.50	1.500	0.67	0.950	1.053	0.564	0.338
0.28	3.57	1.518	0.66	0.990	1.010	0.507	0.479
0.25	4.00	1.520	0.66	1.000	1.000	0.493	0.520
0.22	4.55	1.560	0.64	1.030	0.971	0.464	0.618
$\boldsymbol{T_{1a}}$	$\boldsymbol{1/T_1}$	**Correl**	$\boldsymbol{K_{ass}}$	**ln** $\boldsymbol{K_{ass}}$	$\boldsymbol{-\Delta G}$ **(kJ)**	$\boldsymbol{T}$ **(K)**	**Intcpt.**
0.74	1.35	0.9960	7.420	2.00	4.893	284.00	−0.232
[Lo]	**1/[Lo]**	$\boldsymbol{T_{1f}}$	$\boldsymbol{1/T_{1f}}$	$\boldsymbol{T_{obs}}$	$\boldsymbol{1/T_{obs}}$	$\boldsymbol{P_1}$	$\boldsymbol{(1-P_1)^2/P_1}$
0.40	2.50	1.280	0.78	0.840	1.190	0.613	0.245
0.28	3.57	1.310	0.76	0.875	1.143	0.553	0.361
0.25	4.00	1.340	0.75	0.890	1.124	0.537	0.400
0.22	4.55	1.380	0.72	0.910	1.099	0.516	0.453
$\boldsymbol{T_{1a}}$	$\boldsymbol{1/T_1}$	**Correl**	$\boldsymbol{K_{ass}}$	**ln** $\boldsymbol{K_{ass}}$	$\boldsymbol{-\Delta G}$ **(kJ)**	$\boldsymbol{T}$ **(K)**	**Intcpt.**
0.69	1.45	0.9993	9.823	2.28	5.578	280.00	0.073

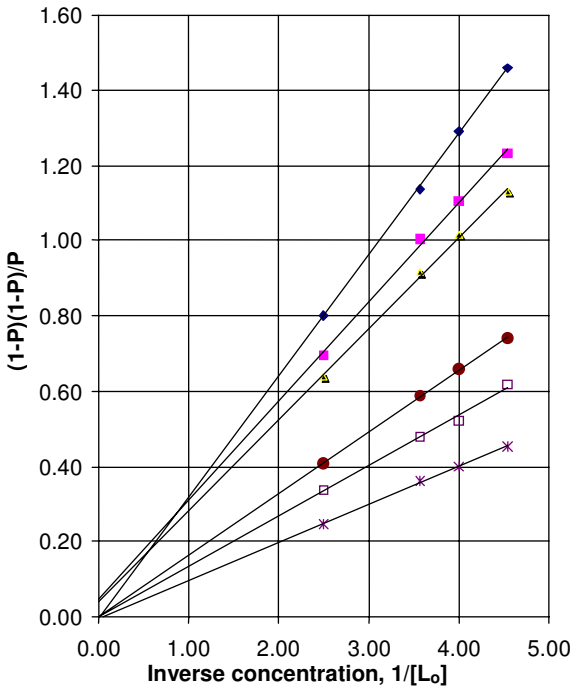

Figure 3. Estimation of the 1:1 association constants of Na^+−[18]crown-6 ether complex at various temperatures from the plots of $(1 - P_1)^2/P_1$ versus inverse initial concentration, $1/[L_0]$, (see Eq. (3) and Table 3). Temperatures: 307 (♦), 297 (■), 295 (▲), 290 (●), 284 (□), and 280 (×) K.

Experimental

[18]Crown-6 ether and thiocyanate salts were purchased from Fluka and used without further purification. Solutions of free and $Na^+/K^+/Ba^{2+}$-complexed [18]crown-6 ether (wherein identical molar amounts of salt and crown ether were employed) for T_1 measurements were prepared in 5 mm NMR tubes using dry [D4]methanol, and the resulting solutions were degassed by several freeze-pump-thaw cycles at low pressure before being finally sealed. The ^{13}C NMR relaxation times were measured at 75 MHz with a Bruker Avance 300 NMR spectrometer using the standard software of the inversion–recovery experiment (pulse sequence 180°–t–90°–acq), with 10 different values of t. Acquisition was performed using 32 K data points. All measurements were conducted at 6 different NMR temperatures (probe temperature calibration was performed using a methanol NMR thermometer with a precision of ±1.0 K). Table 1 presents the T_{1a} and T_{1f} values of [18]crown-6 ether and its Na^+, K^+, and Ba^{2+} complexes in [D4]methanol (maximum error limit of less then ±0.1%). In a number of cases, NOE measurements were also conducted in order to ascertain if the interactions studied were purely dipolar, wherein experimental values were obtained for η_{CH} that were very close to 1.98. Binding constants (K_a) were calculated for the 1:1 complexes using Eqs. (1)–(3)[9,13], and corresponding thermochemical data were obtained using Eq. (5). Results are presented in Tables 1–3.

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