Optical Determination of Thallium(I) and Cesium(I) with a Fluorogenic Calix[4]arenebis(crown-6 ether) Containing One Pendent Dansyl Group

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A fluorogenic derivative of *1,3-alternate* calix[4]arenebis-(crown-6) (1) containing a dansyl group in the proton-ionizable side arm has been employed in selective sensing of Tl⁺ and Cs⁺ at low concentration levels in MeCN−H₂O (1:1) mixed solvent. Optical recognition of these two metal cations by 1 occurs in contrasting modes. On the basis of the results of fluorescence, matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MAL-DI-TOF MS), and ¹H NMR studies, Tl⁺ and Cs⁺ react with 1 via formation of 1:1 complexes that differ in coordination arrangement around the metal ion.

New methods and reagents for selective recognition of hazardous ionic species contaminating the environment as a result of human activities continue to be important scientific objectives. During the past decade, encouraging results on optical sensing of heavy metal ions were obtained by employment of calixarene and calixcrown macrocyclic receptors incorporating fluorescent probes.[1] In particular, a number of *1,3-alternate* calix[4]arene-crown-6 and -bis(crown-6) derivatives containing coumarin, anthracene, and some other types of fluorophores were utilized in determination of Cs⁺.[2] We suggested that a similar calixcrown scaffold would be a good fit for Tl⁺ as well, and we recently reported the synthesis and preliminary complexation studies of a new fluorogenic *1,3-alternate* calix[4]arenebis(crown-6 ether) with one pendent dansyl group (**1**) as the first calixarene-based optical chemosensor for selective recognition of thallium(I).[3] In the design of **1**, nonfluorogenic mono-proton-ionizable calixbiscrown *N*-(X-sulfonyl)carboxamides **2** known for efficient separation of cesium[4] served as the structural prototypes. Hence it was no surprise that, concurrently with Tl⁺, **1** was found capable of selective sensing of Cs⁺ in a mixture with other alkali metal cations. Coordination of Tl⁺ and Cs⁺ generated contrasting spectral responses of the fluorogenic calixbiscrown. This observation indicated that **1** has a potential for serving as a multipurpose fluorescent probe for determination of both of these hazardous metal ions, which very rarely are present in waste solutions simultaneously. From continued development of this work, herein we present a detailed study of metal ion recognition by **1** using optical fluorescence spectroscopy and investigation of the corresponding complexes by matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry and ¹H NMR spectroscopy.
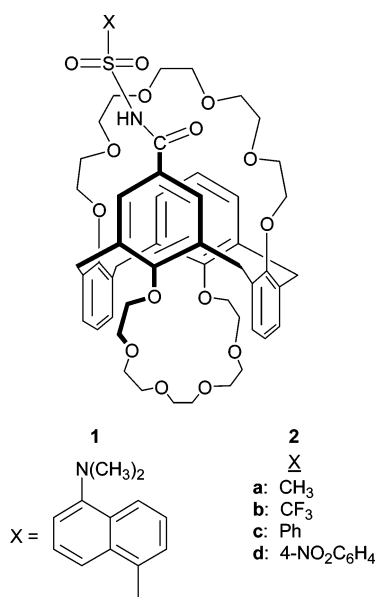
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EXPERIMENTAL SECTION

Materials. Fluorogenic calixbiscrown **1** was synthesized by a recently published procedure.[3] Nonfluorogenic proton-ionizable calixbiscrown **2a** was prepared as described earlier.[4] Thallium(I) nitrate, thallium(I) carbonate, cesium nitrate, cesium carbonate, and rubidium carbonate from Aldrich and Strem, all of the highest quality available, and HPLC-grade MeCN from Fisher were used as received; ACS-grade chloroform from Fisher was washed with deionized water and dried over Na_2CO_3. **CAUTION!** Compounds of thallium(I) are poisonous and may cause severe health effects if ingested, inhaled, or adsorbed through skin.

Methods and Instrumentation. The corrected fluorescence spectra were obtained with a Shimadzu RF-5301PC spectrofluorometer. ^{1}H NMR spectra were recorded with Bruker Avance 400.13 and 600.13 MHz spectrometers. MALDI-TOF mass spectra of the metal complexes were measured by use of a methyl ester of α-cyano-4-hydroxycinnamic acid[5] matrix on a Perkin-Elmer Biosystems Voyager-DE STR Workstation equipped with a two-stage acceleration ion source.

Preparation of Thallium and Alkali Metal Salts of 1 and 2a for ^{1}H NMR Studies. To ensure that only 1:1 complexes were obtained, for which an excess of Cs^+, Tl^+, or Rb^+ as well as the presence of any inorganic anions in solution should be avoided, **1** was reacted with the appropriate metal carbonates in $CHCl_3$, similarly to the earlier reported procedure.[4] The mixture was filtered. After evaporation of the solvent, the residue was dried in vacuo. The solid was dissolved in $CDCl_3$ and the ^{1}H NMR spectrum was measured. Unfortunately, employment in this study of CD_3CN alone or in a mixture with D_2O was unfeasible because of inappropriate quality of the spectra obtained in these solvents, that is, significant broadening of peaks due to exchange processes.

RESULTS AND DISCUSSION

In our earlier work,[3] the pH profile of fluorescence for the proton-ionizable calixbiscrown **1** was studied in a mixed solvent of MeCN–H$_2$O (1:1 v/v). In the absence of any coordinating metal ions in acidic solutions (pH ≤ 3.5), it was found that this ligand exists predominantly in its neutral form and produces fluorescence emission at 541 nm upon excitation at 330 nm. The dansyl group NH-proton dissociation of **1** resulted in a gradual increase of the fluorescence intensity, I, along with a hypsochromic shift of the emission band up to 495 nm (λ_{em} for **1**$^-$; observed at pH > 5.0). These observations were accounted for in the further metal recognition studies of **1**.

As a proton-ionizable ligand, neutral **1** reacts with a unicharged metal ion, M^+, via replacement of the acidic dansyl group NH-proton in accordance with

$$M^+ + \mathbf{1} \rightleftharpoons [M^+\mathbf{1}^-] + H^+ \tag{1a}$$
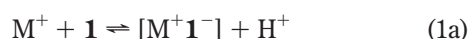
Under the conditions when the anion **1**$^-$ dominates in solution, complex formation takes place as ion pairing:

$$M^+ + \mathbf{1}^- \rightleftharpoons [M^+\mathbf{1}^-] \tag{1b}$$
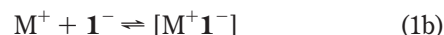
As shown earlier for the nonfluorogenic analogues **2**,[4] the metal ion in the complex $[M^+(\mathbf{2})^-]$ is encapsulated in the ligand cavity and resides in close proximity to the proton-ionizable side arm. Obviously, both Coulombic interactions and donor−acceptor bonding, which includes coordination of M^+ with crown ether oxygens and any cation−π interactions involving the calixarene aromatic framework,[6] contribute to the thermodynamic stability of the complex.

Due to the presence of two crown ether loops in **1**, the probability of incorporation of a second metal ion into the complex exists. Formation of cesium complexes with metal-to-ligand stoichiometry of 2:1 was reported earlier for *1,3-alternate* calix-[4]arenebis(crown-6)[6] (named CBC6, vide infra) as well as several fluorogenic derivatives.[2b,f,g] With only one proton-ionizable group available in **1**, the second metal-coordination step must proceed through formation of a complex ion pair involving the metal salt anion, X$^-$:

$$[M^+\mathbf{1}^-] + M^+ + X- \rightleftharpoons [(M^+)_2\mathbf{1}^-]X^- \tag{2}$$
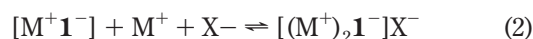
Driven by the donor−acceptor interactions only, with conflicting electrostatic repulsion between the two cations inside of the ligand cavity, reaction 2 must have a dramatically smaller equilibrium constant than reactions 1a,b.

Optical Sensing of Tl$^+$ by 1: *Recognition of Tl$^+$ by Neutral* **1**. Initial testing of Tl$^+$ complexation with **1** was carried out in MeCN−H$_2$O (1:1 v/v) at pH 3.5 (HNO$_3$).[3] Such a choice of the medium acidity was determined by the goal to investigate reaction of the metal ion with the non-ionized ligand (eq 1a). It was found that addition of Tl$^+$ produces gradual quenching of the ligand fluorescence, rationalized in terms of photoinduced electron transfer (PET) within the formed complex. As demonstrated in Figure 1a, the general decrease in the emission intensity was accompanied by a hypsochromic shift of the emission maximum from its original value of 541 nm (λ_{ex} = 330 nm), consistent with ligand ionization due to the NH-proton replacement by the metal ion. Indeed, formation of the anion **1**$^-$ caused enhancement of the fluorescence intensity at 495 nm (I_{495}), which took place simultaneously with an intensity decrease at the wavelength corresponding to the emission of the neutral ligand, I_{541}. These contrasting fluorescence changes, ΔI_{495} and ΔI_{541}, as a function of the analytical concentration of thallium (C_{Tl}) are shown in Figure 1b.

Thus, as a summary effect from the two conflicting trends (fluorescence quenching via PET and emission increase due to the dansyl NH-group deprotonation), a modest overall fluorescence quenching was observed upon Tl$^+$ coordination with nonionized **1** (see Figure 1a). It was envisioned that employment in Tl$^+$ recognition of anionic species **1**$^-$ instead of neutral **1** would eliminate the above contradiction. Accordingly, a working pH of

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(6) For solid-state and solution structures of Cs$^+$ complexes with 1,3-alternate calix[4]arene-bis(crown-6), see Asfari, Z.; Naumann, C.; Vicens, J.; Nierlich, M.; Thuery, P.; Bressot, C.; Lamare, V.; Dozol, J.-F. *New J. Chem.* **1996**, *20*, 1183−1194.
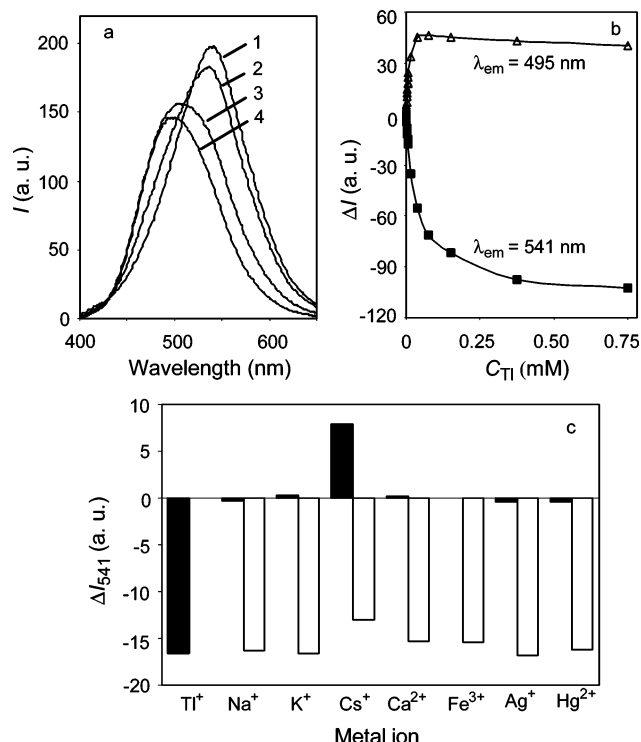
Figure 1. Tl^+ recognition by neutral **1** in $MeCN-H_2O$ (1:1 v/v) at pH 3.5 (HNO_3), $C_1 = 7.5 \times 10^{-6}$ M. (a) Corrected fluorescence emission spectra of **1** (1) and its mixtures with $TlNO_3$ with $C_{Tl}/C_1 = $ 1.00 (2), 10.0 (3), and 100 (4) at $\lambda_{ex} = 330$ nm. (b) Plot of ΔI as a function of C_{Tl} for the emission wavelengths of 495 ($\triangle$) and 541 ($\blacksquare$) nm. (c) Variation in the emission intensity of **1** (black bars) and its 1:1 mixture with $TlNO_3$ (white bars) upon addition of equimolar amounts of different competing metal ions.

5.5 was chosen for the further study of $\mathbf{1}-Tl^+$ complexation in $MeCN-H_2O$ (1:1 v/v). As judged from the pH profile of the emission band shift for **1**,[3] under such conditions of pH and solvent, the ligand is predominantly ionized.

The selectivity of neutral **1** for Tl^+ over other hard and soft metal cations, M^{n+}, was probed in single-species and competitive experiments. The change in the free ligand fluorescence, ΔI_{541}, observed for the solution containing **1** and Tl^+ in the ratio of analytical concentrations $C_{Tl}/C_1 = 1$ was compared with those observed for the equimolar binary solutions of **1** and M^{n+}, as well as tricomponent mixtures $\mathbf{1}/Tl^+/M^{n+}$. As shown in Figure 1c, addition of the competing metal ions produced no significant deviation in the fluorescence of free **1** and its Tl^+ complex. The only notable exception was Cs^+, which caused appreciable restoration of the ligand emission intensity quenched due to Tl^+ coordination. (Cs^+ sensing by **1** will be described below).

Practical Determination of Tl^+ with the Anionic Form of the Ligand, $\mathbf{1}^-$. Fluorescence of $\mathbf{1}^-$ was studied as a function of analytical concentration of Tl^+ in $MeCN-H_2O$ (1:1 v/v) at pH 5.5. It should be taken into account that maintaining such a pH requires employment of a buffer that brings into the system a relatively high concentration of potentially interfering metal cations (most often Na^+). To probe for an effect of the buffer cation, Tl^+ recognition by $\mathbf{1}^-$ was tested in the presence of two 0.10 M acetate buffers with pH 5.5, prepared with NaOH and LiOH. (For **1**, Li^+
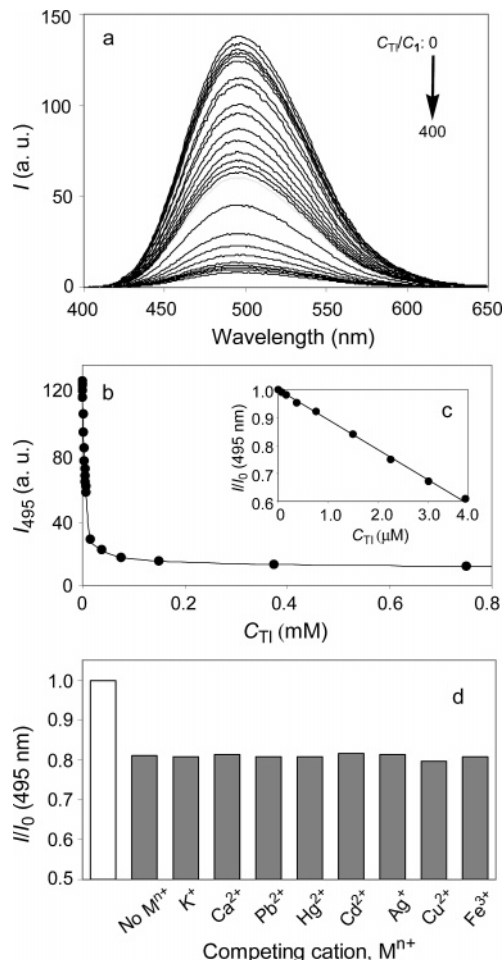

Figure 2. Tl^+ recognition by the anion $\mathbf{1}^-$ in $MeCN-H_2O$ (1:1 v/v) at pH 5.5 (0.10 M sodium acetate buffer), $C_1 = 3.8 \times 10^{-6}$ M. (a) Evolution of the fluorescence emission spectrum of $\mathbf{1}^-$ with increasing concentration of $TlNO_3$ at $\lambda_{ex} = 330$ nm. (b) Changes in the fluorescence intensity I_{495} with varied C_{Tl}. (c) Calibration plot of I/I_0 vs C_{Tl}. (d) Changes in the fluorescence intensity of the buffered equimolar mixture of $\mathbf{1}^-$ with $TlNO_3$ in the presence of 100-fold excess of different competing metal nitrates (gray bars), with that for free $\mathbf{1}^-$ shown as a white bar.

is believed to be a noncoordinating ion due to its known negligibly weak complexation with analogues **2**).[4] Since no significant deviation was observed in the results of these two experiments, Na^+ was concluded not to interfere with determination of Tl^+ under the given experimental conditions. Hence, the following study of Tl^+ sensing by $\mathbf{1}^-$ was carried out with Na^+-containing 0.10 M acetate buffer.

At pH 5.5, $\mathbf{1}^-$ showed strong fluorescence emission at 495 nm ($\lambda_{ex} = 330$ nm). In the presence of increasing concentrations of Tl^+, gradual quenching of the ligand fluorescence at unchanged wavelength was observed (Figure 2a). Such a mode of I_{495} variation as a function of C_{Tl} for $\mathbf{1}^-$ (Figure 2b) diverges from the tendency for moderate fluorescence increase at the same wavelength due to ionization of **1** observed in the studies conducted at pH 3.5 (Figure 1b). As a result, the magnitude of the overall Tl-induced fluorescence quenching for $\mathbf{1}^-$ was appreciably larger than that found for **1** under otherwise identical conditions.

ΔI_{495} and I/I_0 (where I is the current emission intensity and I_0 is the emission intensity of $\mathbf{1}^-$ in the absence of Tl^+ at $\lambda_{em} = 495$
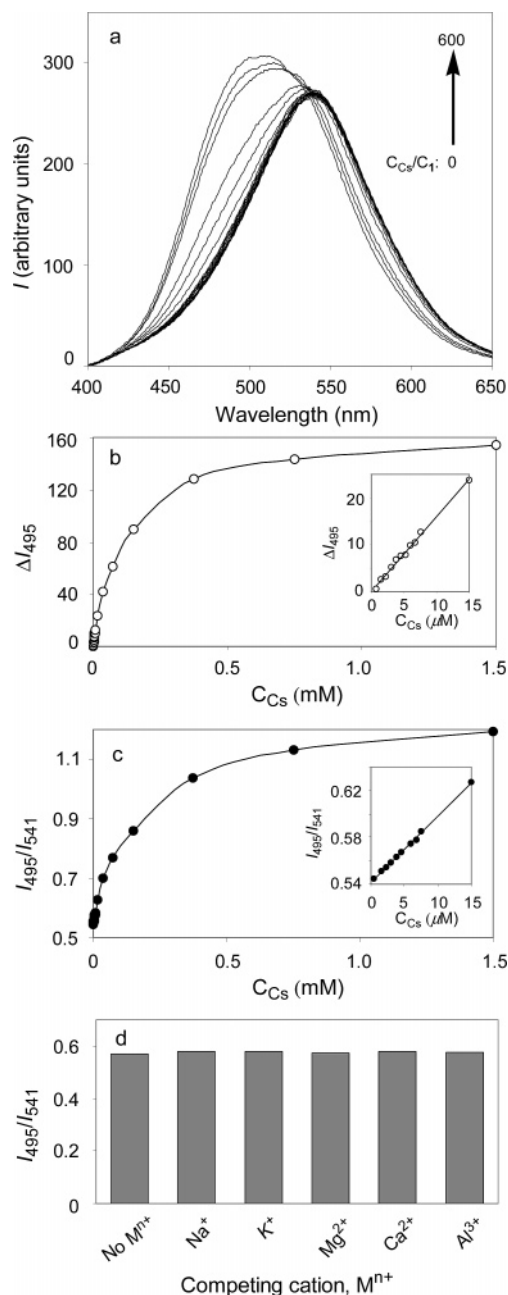
Figure 3. Cs^+ recognition by **1** in MeCN–H_2O (1:1 v/v) at pH 3.5 (HNO₃), $C_1 = 7.5 \times 10^{-6}$ M. (a) Evolution of the fluorescence emission spectrum of **1** with increasing concentration of $CsNO_3$ at $\lambda_{ex} = 330$ nm. (b) Single-wavelength characterization: plot of ΔI_{495} as a function of C_{Cs}. (c) Dual-wavelength characterization: plot of I_{495}/I_{541} as a function of C_{Cs}. (d) Changes in I_{495}/I_{541} of an equimolar mixture of **1** and $CsNO_3$ in the presence of 100-fold excess of different competing metal ions.

nm) were plotted against C_{Tl}. With $C_{Tl}/C_1 \leq 1$, both of these dependences are linear (as shown in Figure 2c for I/I_0 vs C_{Tl}) and may be used as calibration plots for determination of microconcentrations of Tl^+. With $C_1 = 3.8 \times 10^{-6}$ M under the indicated conditions of solvent and pH, the detection limit for Tl^+, defined as 3 times the signal-to-noise ratio, was 5×10^{-8} M or 10 μg/L.

The above study of Tl^+ complexation by **1**$^-$ in 0.10 M sodium acetate buffer demonstrated high selectivity of the ligand for Tl^+ over Na^+. To probe for interference from other metal ions (M^{n+}),
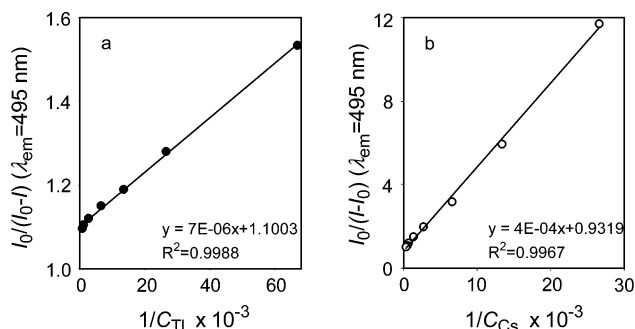
Figure 4. Determination of the complex stoichiometry and K_f^{app} for (a) [Tl^+**1**$^-$] (pH 5.5, 0.10 M sodium acetate buffer; $C_1 = 3.8 \times 10^{-6}$ M) and (b) [Cs^+**1**$^-$] (pH 3.5, HNO₃; $C_1 = 7.5 \times 10^{-6}$ M) in MeCN–H_2O (1:1 v/v), with $\lambda_{ex} = 330$ nm.

a series of tricationic (Tl^+/Na^+/M^{n+}) solutions was prepared by adding a 100-fold excess of K^+, Ca^{2+}, Pb^{2+}, Cu^{2+}, Fe^{3+}, Ag^+, Cd^{2+}, or Hg^{2+} to the buffered equimolar mixture of Tl^+ and **1** ($C_{Tl} = C_1 = 3.8 \times 10^{-6}$ M). As is evident from Figure 2d, the magnitude of I/I_0 for the Tl^+–**1** complex under the given experimental conditions is essentially unaffected by the excess M^{n+}, which indicates no significant interference of those metal ions with determination of Tl^+ by use of **1**$^-$.

Optical Sensing of Cs^+ by 1. Complexation of Cs^+ by **1** was studied in MeCN–H_2O (1:1 v/v) at pH 3.5 (HNO₃). The results are presented in Figure 3. As mentioned above, under these conditions, the ligand exists predominantly in the neutral form and emits fluorescence at 541 nm upon excitation at 330 nm. Addition of increasing amounts of Cs^+ (C_{Cs}/C_1 from 0 to 600 with $C_1 = 7.5 \times 10^{-6}$ M) produced gradual enhancement of the fluorescence intensity of **1**, accompanied by a hypsochromic shift of λ_{em} (Figure 3a). This pattern is analogous to the optical changes of **1** observed at varying pH[3] and hence may be rationalized in terms of the ligand ionization via NH-proton replacement by the metal ion.

Cs^+ complexation by **1** was characterized quantitatively in two ways: in a single-wavelength mode, by the metal-induced increase of the fluorescence intensity at the emission wavelength of the anion **1**$^-$, and in a dual-wavelength mode, by the ratio of the fluorescence intensities at the wavelengths of the ionized and neutral ligand. The graphs of ΔI_{495} versus C_{Cs} and I_{495}/I_{541} versus C_{Cs} (Figure 3, panels b and c, respectively) have similar shapes. The initial segments of both of these curves are linear, and either of those may be used as a calibration plot for determination of microconcentrations of Cs^+. Under the given conditions of solvent and pH and $C_1 = 7.5 \times 10^{-6}$ M, the detection limit for Cs^+, defined as 3 times the signal-to-noise ratio, was 4×10^{-7} M or 53 μg/L.

The selectivity of Cs^+ recognition by **1** in the presence of other relevant metal ions was tested in competitive complexation experiments. Tricomponent mixtures (**1**/Cs^+/M^{n+}) were prepared with 100-fold excess of the competing metal ions over the ligand and Cs^+ ($C_1 = C_{Cs} = 7.5 \times 10^{-6}$ M). The magnitude of I_{495}/I_{541} ratio in the absence and in the presence of M^{n+} was compared. As shown in Figure 3d, only insignificant changes in the fluorescence of **1**–Cs^+ complex were produced by almost all of the tested metal cations (of which Na^+ and K^+ are the most important potential interferences).

Stoichiometry and Formation Constants of Tl^+ and Cs^+ Complexes with 1. As mentioned above, **1** has a potential for

coordinating either one or two metal ions per ligand molecule, similarly to CBC6, which forms cesium complexes with both 1:1 and 2:1 metal-to-ligand stoichiometry.[6] However, it was noted[6] that the 2:1 complexes usually were observed in nonaqueous solutions and in the solid state, but not during solvent extraction or other complexation processes involving aqueous medium. In agreement, we found no indication of formation of the dicationic complex species in our previous studies of Cs^+ extraction with nonfluorogenic mono-ionizable prototypes of **1**, ligands **2**.[4]

To study complexation stoichiometry of Tl^+ and Cs^+ with **1**, MALDI-TOF mass spectrometry was employed.[7] Solutions containing **1** and varying concentrations of Tl^+ or Cs^+ in the metal-to-ligand ratio of 1:1, 2:1, 5:1, 10:1, and 100:1 in $MeCN-H_2O$ at the appropriate pH were prepared analogously to those used in the fluorescence studies described above. MALDI-TOF mass spectra of the samples were measured with the methyl ester of α-cyano-4-hydroxycinnamic acid as a matrix. This low-acidity compound with relatively weak metal chelating ability was utilized to minimize any possible matrix competition with **1** in binding of Tl^+ and Cs^+.

In the positive-ion mode, MALDI-TOF MS revealed analogous trends for the two M^+-**1** systems. (The original spectra are provided as Supporting Information, Figures S1–S10). In the mass spectra for all of the Tl-containing samples, peaks of the protonated and sodiated complexes, $[Tl^+$**1**$^- + H]^+$ (*m/z* calcd 1309.82) and $[Tl^+$**1**$^- + Na]^+$ (*m/z* calcd 1331.75), respectively, were observed along with signals for the sodiated ligand. Similarly, all of the mass spectra for **1** in the presence of Cs^+ at varying concentrations contained peaks for $[Cs^+$**1**$^- + H]^+$ (*m/z* calcd 1237.69), and some of them contained peaks for $[Cs^+$**1**$^- + Na]^+$ (*m/z* calcd 1259.69). For both Tl^+ and Cs^+ in the solutions with $C_M/C_1 < 10$, the measurements showed no indication of formation of complexes with metal-to-ligand stoichiometry other than 1:1. At $C_M/C_1 = 10$, a weak peak for a 2:1 complex appeared in the MALDI spectrum for the Tl-containing solution but not for the Cs-containing one. Only in the mass spectra of the samples with 100-fold excess of the metal ions over the ligand were noticeable peaks attributed to the ions $[Tl^+$**1**$^- + Tl]^+$ (*m/z* calcd 1513.81) and $[Cs^+$**1**$^- + Cs]^+$ (*m/z* calcd 1369.19) observed, along with intense peaks for the corresponding monothallium and monocesium species mentioned above. It is unclear, however, whether the second $Tl^+(Cs^+)$ cation was indeed encapsulated by the calixbiscrown during the complexation process (eq 2) or whether it was added to the corresponding 1:1 complex at the stage of its ionization, assisted by the matrix spiked with a large concentration of such metal cations. The confirmation for the dominance of the $[M^+$**1**$^-]$ complex type for both Tl^+ and Cs^+ was obtained from the following fluorescence studies.

As mentioned above, in complexation of Cs^+, **1** was utilized in its neutral form, while recognition of Tl^+ was conducted with predominantly ionized ligand, **1**$^-$ (the corresponding equilibria are presented by eqs 1a and 1b, respectively). Nevertheless, since

both of these reactions took place at constant pH, they may be characterized by the same general expression for the apparent complex formation constant, K_f^{app}:

$$K_f^{app} = \frac{[M\mathbf{1}]}{[M][\mathbf{1}]} \tag{3}$$

where [M**1**], [M], and [**1**] are the equilibrium concentrations of the complex, metal ion, and ligand, respectively. In the case of 1:1 complex formation, changes in the ligand fluorescence as a function of concentration of the metal ion added are described by[8]

$$\frac{I_0}{(I - I_0)} = \frac{a}{K_f[M]} + a \tag{4}$$

where a is a constant incorporating the factors of molar absorptivities and fluorescence quantum yields for the free ligand and complex. Under the conditions of $C_M \gg C_1$ and hence, $[M] \approx C_M$, a plot of $I_0/(I - I_0)$ versus $1/C_M$ is linear, and K_f is found as a ratio of the intercept at the OY axis and the slope.

To verify the complexation stoichiometry and determine K_f^{app} for the complexes $[Tl^+$**1**$^-]$ and $[Cs^+$**1**$^-]$ in Me**1**$^-CN-H_2O$ (1:1) at pH 5.5 and 3.5, respectively, the ligand fluorescence was studied at varied C_M under the conditions of large metal excess over **1**. As shown in Figure 4, the plots of $I_0/|(I - I_0)|$ versus $1/C_M$ for the complexation of **1** with Tl^+ and Cs^+ are linear in the range of C_M/C_1 from 5 to 600, which is indicative of the 1:1 complex dominance within this concentration interval. The K_f^{app} values for the complexes $[Tl^+$**1**$^-]$ and $[Cs^+$**1**$^-]$ are 1.6×10^5 and 2.3×10^3, respectively.
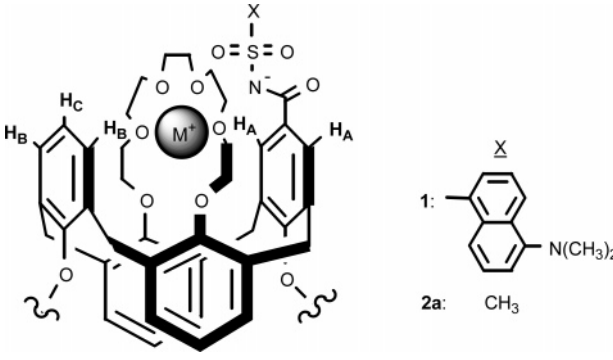
¹H NMR Study of [Tl⁺1⁻] and [Cs⁺1⁻]. The fluorescence studies demonstrated strong preference of **1** for Tl^+ and Cs^+ over many other soft and hard metal ions. It was interesting to compare the coordination modes of these two dissimilar cations with ionized **1**. The coordination arrangement of $[Cs^+$**1**$^-]$ in general features is predictable from the structural information available for the closest analogues, $[Cs^+(CBC6)NO_3^-]^6$ and $[Cs^+$**2**$^-]$.[4] Specifically, Cs^+ is expected to reside in the crown ether loop neighboring the ionized side arm, slightly above the two adjacent aromatic rings of the *1,3-alternate* calixarene skeleton, and interact with terminal arene carbons as well as negatively charged dansyl group and ether oxygens. Although $[Tl^+$**1**$^-]$ has no direct structural prototypes allowing projection of this complex geometry, one may anticipate that Tl^+, as a soft electron acceptor possessing strong affinity toward the π-basic calix[4]arene cavity,[9] will approach it more closely than the harder and larger Cs^+. Therefore, we were primarily interested in comparison of the metal ion positioning

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(7) Complex stability was not evaluated by MALDI-TOF MS, in agreement with opinion existing in the literature about limited applicability of this method to quantification. For example, see Shimada, K.; Nagahata, R.; Kawabata, S.; Matsuyama, S.; Saito, T.; Kinugasa, S. *J. Mass Spectrom.* **2003**, *38*, 948–954.

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		calixarene					side arm
		H$_A$ (s, 2H)		H$_B$ (d, 2H)		H$_C$ (t, 1H)	CH$_3$ (s)
ligand	cation	δ, ppm	$\Delta\delta$, ppm	δ, ppm	$\Delta\delta$, ppm	δ, ppm	δ, ppm
1		7.38		7.07		6.90	2.88 (6H)
1	Cs$^+$	7.88	0.50	7.20	0.13	6.97	2.83
1	Rb$^+$	7.77	0.39	7.21	0.14	6.98	2.83
1	Tl$^{+\ b}$	7.20	−0.18	7.63	0.56	6.98	2.83
2^a		7.55		7.10		6.83	3.42 (3H)
2^a	Cs$^+$	7.92	0.37	7.12	0.02	6.93	3.24
2^a	Rb$^+$	7.80	0.25	7.16	0.06	6.89	3.22
2^a	Tl$^+$	7.20	−0.35	7.78	0.68	6.95	3.21

^{a} Measured at 400 MHz and 298 K except as noted. ^{b} Measured at 600 MHz.

about the potential binding sites (i e., calixarene moiety, side arm, and crown ether loops) in [Cs$^+$**1**$^-$] and [Tl$^+$**1**$^-$]. To probe for any difference in the coordination modes of Tl$^+$ and Cs$^+$ with **1**, the corresponding complexes were prepared and studied by ^{1}H NMR in CDCl$_3$ (see Experimental Section for details). Herein we present only a brief description of the obtained data and main conclusions; a more extensive discussion is provided in the Supporting Information.

Conversion of neutral **1** into its Cs$^+$ and Tl$^+$ salts produced considerable overall changes in the ^{1}H NMR spectrum of the ligand. (Selected data for **1**, [Cs$^+$**1**$^-$], and [Tl$^+$**1**$^-$] are listed in Table 1; original spectra are presented in Figures S11–S19, Supporting Information.) However, only for the signals of calixarene aromatic protons does the pattern of these changes vary dramatically upon going from [Cs$^+$**1**$^-$] to [Tl$^+$**1**$^-$]. Hence, the principal structural dissimilarities between the two complexes must originate from different location of Cs$^+$ and Tl$^+$ about the calixarene moiety. (On the contrary, signals for the side-arm *N*-CH$_3$ and naphthalene protons in [Cs$^+$**1**$^-$] and [Tl$^+$**1**$^-$] exhibited almost the same magnitude downfield shifts relative to the corresponding signals of free **1**. Since spectral changes for these groups of protons are associated with ligand ionization, their invariance with the metal ion identity signifies equivalent interaction of Cs$^+$ and Tl$^+$ with the negatively charged side arm in **1**$^-$).

Systematic analysis of the NMR spectra for [Cs$^+$**1**$^-$] and [Tl$^+$**1**$^-$] in the region of aromatic protons revealed surprising disparity in both magnitude and direction of the complexation-induced changes in chemical shifts ($\Delta\delta$) for a singlet from the two protons in ortho positions to the site of the side-arm attachment (protons H$_A$), a doublet for the corresponding two protons (H$_B$) on the opposite arene unit of the *1,3-alternate* calixarene skeleton, and a triplet for the neighboring proton H$_c$. Some of these differences are rationalized in terms of cation−π interactions. Thus, appreciably larger downfield shift of the signal from H$_B$ in [Tl$^+$**1**$^-$] relative to that for [Cs$^+$**1**$^-$] is consistent with stronger π-coordination of Tl$^+$ with the corresponding arene ring. This suggests also that Tl$^+$ is positioned closer to the calixarene aromatics than Cs$^+$. However, neither a unique upfield shift of the H$_A$ singlet nor atypical disproportion in the magnitude of downfield $\Delta\delta$ observed for the signals of adjacent protons H$_B$ and H$_C$ in the spectrum of [Tl$^+$**1**$^-$] may be justified solely in terms of cation−π interactions. Such a divergent magnetic environment of H$_A$, H$_B$, and H$_C$ in [Tl$^+$**1**$^-$] and [Cs$^+$**1**$^-$] is likely to arise from dissimilar calixarene conformation, in particular, different mutual spatial orientation of the two opposite magneto-anisotropic arene units in these two complexes. To explore the effects of the cation electron density and presence of the side-arm dansyl group as other potential causative reasons for the contrasting NMR response of the ligand aromatics to coordination of Tl$^+$ and Cs$^+$, complex [Rb$^+$**1**$^-$] and metal salts of methylsulfonyl-containing calixbiscrown **2a**, respectively, were included in this study. As follows from the results presented in Table 1, neither of these two factors could be responsible for the observed phenomenon. For both **1** and **2a**, spectra of the Rb$^+$ complexes followed the same trend as the Cs$^+$ complexes and showed the same striking contrast with the spectra of Tl$^+$ complexes.

With the above considerations taken into account, the following explanation for distinctive NMR behavior of the aromatic protons in [Tl$^+$**1**$^-$] and [Cs$^+$**1**$^-$] may be proposed. Tl$^+$, which favors π interactions over binding with hard crown ether oxygens, is situated deeper in the π-basic calixarene cavity than Cs$^+$. This makes the coordinated side arm in [Tl$^+$**1**$^-$] approach the calixarene moiety more closely than in the analogous Cs complex. To enable such side-arm position, the supporting arene unit must turn appropriately. As a result, the mutual spatial orientation and, accordingly, mutual effect of magnetic fields of these two opposite aromatic rings in [Tl$^+$**1**$^-$] is different from that in [Cs$^+$**1**$^-$]. Thus, the observed diverse chemical shifts of protons H$_A$, H$_B$, and H$_C$ in the Tl and Cs complexes are a summary effect from the electronic (cation−π coordination) and geometric (ligand conformation) factors.

CONCLUSIONS

Fluorogenic *1,3-alternate* calix[4]arenebis(crown-6 ether) **1** is an example of a multipurpose optical chemosensor that, under different experimental conditions, allows for determination of Tl$^+$ and Cs$^+$ at parts per billion concentration levels. The ligand possesses very high selectivity for Tl$^+$ over many hard and soft metal ions and provides selective recognition of Cs$^+$ in

the presence of Na$^+$, K$^+$, and other relevant metal cations. Complexes [Cs$^+$**1**$^-$] and [Tl$^+$**1**$^-$] have different coordination arrangements.

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SUPPORTING INFORMATION AVAILABLE

MALDI-TOF MS spectra, ^{1}H NMR spectra, and discussion of the NMR studies. This material is available free of charge via the Internet at http://pubs.acs.org.