Synthesis and Properties of Diazacrown Ethers Carrying Two Tropone Chromophores

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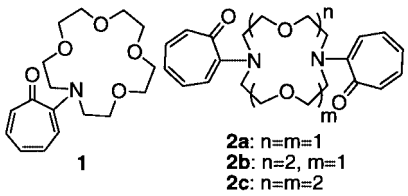
N,N'-Bis(tropon-2-yl)diazacrown ethers (**2**) were found to display unique absorption spectral changes in the presence of guest cations. X-ray crystallographic analysis indicated that **2a**·zinc and **2c**·calcium thiocyanate complexes consist of an ion pair with zinc tetrathiocyanate anion and **2a**·zinc cation, and with calcium hexathiocyanate anion and **2c**·H_2O·calcium cation, respectively. Complexation gave rise to deconjugation between the tropone ring and the lone pair electrons of the nitrogen atom to cause spectral changes.

Recently, we have prepared several ionophore derivatives having a tropone pendant.[1] *N*-(Tropon-2-yl)-1,4,7,10-tetraoxa-13-azacyclopentadecane (**1**) was found to display unique absorption spectral changes in the presence of guest cations.[2] By addition of guest thiocyanates to **1**, the two original absorption bands of **1** disappeared and a new absorption band appeared at lower wavelength. The complexes (**1**·$Ca(NCS)_2$ and [**1**·$Ba(NCS)_2]_2$) have been investigated by an X-ray crystallographic analysis[3,4] but the structure of the free host (**1**) has not been elucidated because of non-crystals at room temperature. In order to reveal the detailed structural changes of the troponoid azacrown ethers, we extended to the diazacrown ethers (**2**) having two tropon-2-yl groups.



N,N'-Bis(tropon-2-yl)diazacrown ethers (**2**) were prepared by the condensation of the corresponding diazacrown ethers and 2-(*p*-toluenesulfonyloxy)tropone.[5] The diazacrown ethers (**2**) also showed the spectral changes in the presence of guest cations. For example, addition of $Zn(SCN)_2$ to **2a** caused to disappear two original absorption bands at 360 and 420 nm of **2a** and a new absorption band around 330 nm appeared as shown in Figure 1. From the association constants of **2** for guest cations, the selectivity of **2a**, **2b**, and **2c** was Zn^{2+}, Ca^{2+}, and Ba^{2+}, respectively.

The crystal structures of free hosts (**2a** and **2c**), **2a**-zinc thiocyanate complex, and **2c**-calcium thiocyanate complex were elucidated by X-ray analyses.[6]

Compounds **2a** and **2c** are centrosymmetric and the two tropone units have an *anti* orientation to the crown ether ring (Figure 2). In the free hosts (**2a** and **2c**), the bond lengths[7] of the tropone ring except for the C1–C2 bond are close to 1.39 Å and the N1–C2 bond lengths [1.364 (2) for **2a** and 1.356 (2) Å for **2c**] are close to that of the typical $C(sp^2)$–$N(sp^2)$ bonds.[8] This result means that the aminotropone moiety of **2a** forms a conjugated 10 electron system.

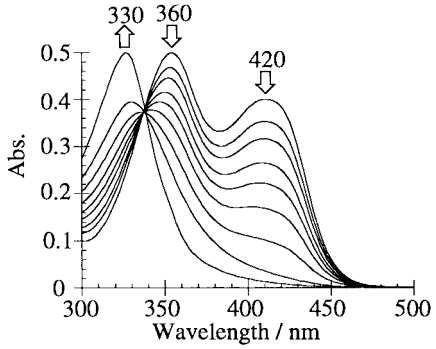


Figure 1. Absorption spectra of **2a** (2.0×10^{-5} M) with $Zn(SCN)_2$ (0–1.0×10^{-4} M) in CH_3CN.

Zinc thiocyanate complex of **2a** consists of an ion pair, $[Zn(NCS)_4]^{2-}$ and **2a**·Zn^{2+}, as shown in Figure 3. The zinc ion for $[Zn(NCS)_4]^{2-}$ is a tetrahedral coordination and that for **2a**·Zn^{2+} has six coordination involving two diazacrown nitrogen

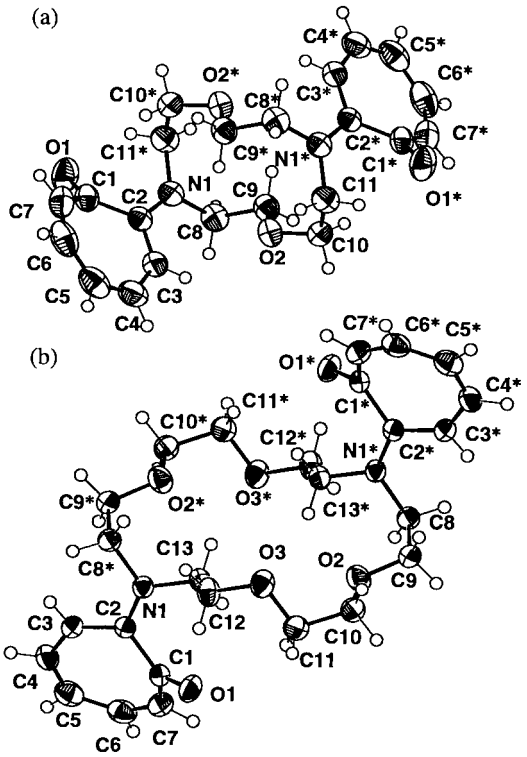


Figure 2. Molecular structures of (a) **2a** (*: symmetry codes: -x, -y, -z) and (b) **2c** (*: 1-x, 1-y, 1-z).

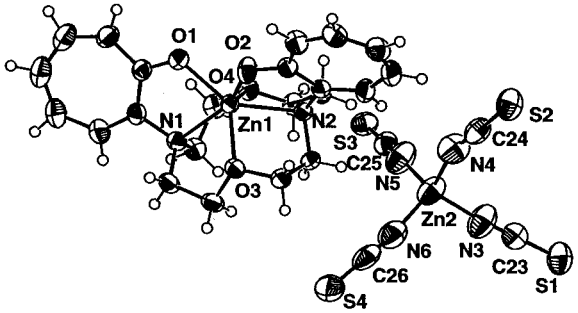


Figure 3. Molecular structure of $[\mathbf{2a}\cdot Zn^{2+}][Zn(NCS)_4]^{2-}$.

atoms, two ether oxygen atoms, and two tropone oxygen atoms. The structure of $[\mathbf{2a}\cdot Zn][Zn(NCS)_4]$ is smilar to those of $[Zn([9]aneN_2S)_2][ZnCl_4]$[9] and $(HTen)_2[Zn(NCS)_4]$.[10]

Interestingly, **2c**-calcium thiocyanate complex also consists of an ion pair with $[Ca(NCS)_6]^{4-}$ and $\mathbf{2c}\cdot Ca^{2+}\cdot H_2O$ (Figure 4). The calcium hexathiocyanate anion ($[Ca(NCS)_6]^{4-}$) has never been found. The calcium ion for $[Ca(NCS)_6]^{2-}$ is an octahedral coordination and that for $\mathbf{2c}\cdot Ca^{2+}\cdot H_2O$ has a nine coordination involving two diazacrown N atoms, four ether O atoms, and two tropone O atoms, and one O atom of water molecule.

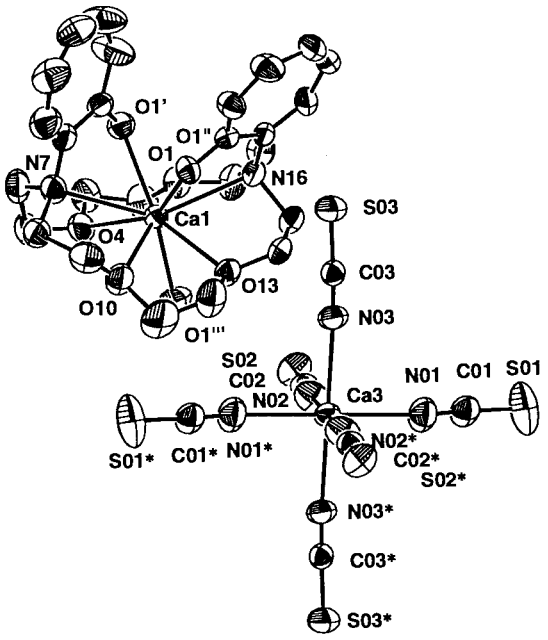


Figure 4. Molecular structure of $[\mathbf{2c}\cdot Ca^{2+}\cdot H_2O]\cdot 0.5[Ca(NCS)_6]^{4-}$ of $[\mathbf{2c}\cdot Ca^{2+}\cdot H_2O]\cdot 0.5[Ca(NCS)_6]^{4-}\cdot 0.5[Ca(NCS)_6]^{4-}\cdot H_2O\cdot CH_3CN$ (*: 2–x, –y, 1–z).

The tropone moieties[7] of the complexes ($\mathbf{2a}\cdot Zn^{2+}$ and $\mathbf{2c}\cdot Ca^{2+}\cdot H_2O$) showed pronounced bond alternation similar to those of tropone, [11] $\mathbf{1}\cdot Ca(NCS)_2$,[3] and $[\mathbf{1}\cdot Ba(NCS)_2]_2$[4]; the N1–C2 bond lengths [1.463 (3) for $\mathbf{2a}\cdot Zn^{2+}$ and 1.419 (10) Å for $\mathbf{2c}\cdot Ca^{2+}\cdot H_2O$] are longer than those of **2a** and **2c**. In conclusion, the complexation of **1** and **2** with guest cations caused deconjugation between the tropone ring and lone pair of electrons of the nitrogen atom. The difference in conjugation system of **2** and its complexes should be responsible for the absorption spectral changes.

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References and Notes

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5 Synthetic details and physical properties will be reported elsewhere.

6 Crystal data for **2a**: orange prisms, $C_{22}H_{26}N_2O_4$, orthorhombic, *Pbca*, a = 11.910 (2) Å, b = 10.347 (2) Å, c = 15.523 (4) Å, V = 1912.9 (7) Å^3, Z = 4, M_r = 382.44, D_x = 1.328 Mg m^{-3}, refinement on F^2 (SHELXL97),[12] $wR(F^2)$ = 0.1272. Crystal data for **2c**: orange prisms, $C_{26}H_{34}N_2O_6$, monoclinic, $P2_1/n$, a = 10.992 (1) Å, b = 14.152 (1) Å, c = 7.834 (1) Å, β = 101.495 (8)°, V = 1194.2 (2) Å^3, Z = 2, M_r = 470.56, D_x = 1.309 Mg m^{-3}, refinement on F^2 (SHELXL97),[12] $wR(F^2)$ = 0.1131. Crystal data for $[\mathbf{2a}\cdot Zn^{2+}][Zn(NCS)_4]^{2-}$: yellow prisms, $C_{26}H_{26}N_6O_4S_4Zn_2$, triclinic, $P\bar{1}$, a = 11.372 (1) Å, b = 14.152 (1) Å, c = 10.326 (1) Å, α = 93.438 (4)°, β = 94.482 (5)°, γ = 110.481 (4)°, V = 1545.2 (2) Å^3, Z = 2, M_r = 745.51, D_x = 1.602 Mg m^{-3}, refinement on F^2 (SHELXL97),[12] $wR(F^2)$ = 0.0841. Crystal data for $2[\mathbf{2c}\cdot Ca^{2+}\cdot H_2O]\cdot 0.5[Ca(NCS)_6]^{4-}\cdot 0.5[Ca(NCS)_6]^{4-}\cdot H_2O\cdot CH_3CN$: yellow prisms, $C_{60}H_{77}Ca_3N_{11}O_{15}S_6$, triclinic, $P\bar{1}$, a = 14.183 (3) Å, b = 21.225 (3) Å, c = 12.871 (2) Å, α = 91.504 (12)°, β = 98.355 (16)°, γ = 86.717 (15)°, V = 3826.6 (11) Å^3, Z = 2, M_r = 1504.93, D_x = 1.306 Mg m^{-3}, Refinement on F^2 (SHELXL97),[12] $wR(F^2)$ = 0.3451.

7 Selected bond lengths (Å) in **2a**: N1–C2, 1.364 (2); O1–C1, 1.234 (2); C1–C7, 1.438 (2); C1–C2, 1.489 (2); C2–C3, 1.380 (2); C3–C4, 1.401 (2); C4–C5, 1.353 (3); C5–C6, 1.394 (3); C6–C7, 1.361 (3). $[\mathbf{2a}\cdot Zn^{2+}][Zn(NCS)_4]^{2-}$: N1–C2, 1.463 (3); O1–C1, 1.265 (2); C1–C7, 1.438 (3); C1–C2, 1.442 (3); C2–C3, 1.364 (3); C3–C4, 1.421 (3); C4–C5, 1.343 (4); C5–C6, 1.402 (4); C6–C7, 1.357 (3).

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