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Synthesis, Complexation Behaviors, and Crystal Structures of Azamacrocycles Having Tropon-2-yl Groups

Emi Yamamoto, Kanji Kubo,*,† and Akira Mori*,†

Graduate School of Engineering Sciences, 39, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816-8580

†Institute of Advanced Material Study, 86, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816-8580

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Azamacrocycles **1**–**3**, having one to three tropon-2-yl groups, were found to display unique absorption spectral changes in the presence of guest cations. Aza-15-crown-5 **1**, 1,7-diaza-12-crown-4 **2a**, 1,7-diaza-15-crown-5 **2b**, 1,10-diaza-18-crown-6 **2c**, and 1,5,9-triazacyclododecane **3** derivatives showed Ba^{2+}, Zn^{2+}, Ca^{2+}, Ba^{2+}, and Zn^{2+} selectivities, respectively. The crystal structures of free hosts **2a** and **2c**, the calcium thiocyanate complexes of **1** and **2c**, the barium thiocyanate complex of **1**, and the zinc thiocyanate complex of **2a** were elucidated by X-ray analysis. The **2a**·zinc and **2c**·calcium thiocyanate complexes consist of an ion pair with a zinc tetrathiocyanate anion and a **2a**·zinc cation and with a calcium hexathiocyanate anion and a **2c**·H_2O·calcium cation, respectively. The aminotropone moiety of **2a** and **2c** forms a conjugated 10-electron system. Complexation gave rise to deconjugation between the tropone ring and the nonbonding electron pair of the nitrogen atom to cause absorption spectral changes.

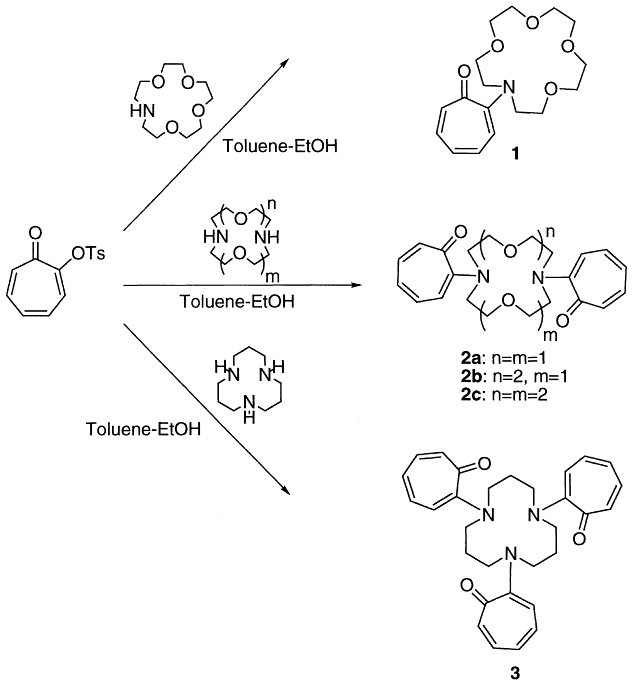
Synthetic chromoionophores,[1] which give rise to a specific absorption spectral change upon selective complexation with cations, have attracted considerable attention as spectrophotometric analytical reagents for the detection of particular metal cations.

Recently, we prepared several thiocrown ether derivatives having a tropone pendant.[2,3] It is of particular interest to observe that the tropone part can be used as a chromophore. For example, 5,8,11,14-tetraoxa-2,17-dithiabicyclo[16.4.1]tricosa-1(22),18,20-trien-23-one is used as a chromoionophore for Ca^{2+}, Ba^{2+}, and Hg^{2+} ions and as a Hg^{2+} carrier through a liquid membrane, while azamacrocycles have been important building blocks for constructing host molecules in supramolecular chemistry.[4] In this paper, we report on the synthesis and complexation behaviors of azamacrocycles containing one to three chromophoric tropon-2-yl pendants to take advantage of the metal cation binding ability of both the tropone and azamacrocycle moieties.

Results and Discussion

Tropone-functionalized azamacrocycles **1**–**3** were prepared by condensation with the corresponding azamacrocycles and 2-(*p*-tolylsulfonyloxy)tropone in a toluene–ethanol mixture (Scheme 1). The structure and purity of azamacrocycles **1**–**3** were ascertained by NMR spectroscopy and elemental analysis.

The complexation behaviors of azamacrocycles **1**–**3** with various guest salts (LiSCN, NaSCN, KSCN, RbSCN, CsSCN, NH_4SCN, $Mg(SCN)_2$, $Ca(SCN)_2$, $Ba(SCN)_2$, $Zn(SCN)_2$, CdI_2, $Hg(SCN)_2$) were studied by UV-vis spectroscopy. By the addition of guest salts, the UV-vis spectra of azamacrocycles **1**–**3** changed dramatically in CH_3CN (Figs. 1–5).



Scheme 1.

For example, the addition of $Zn(SCN)_2$ to **2a** caused the disappearance of two original absorption bands at 354 and 411 nm of **2a** and a new absorption band similar to that of tropone, which appeared around 330 nm, as shown in Fig. 2. This means that the complexation gave rise to deconjugation between the tropone ring and the nonbonding electron pair of the nitrogen atom. The guest cation-induced absorption shifts ($\Delta\lambda = |\lambda_{\text{complex}} - \lambda_{\text{free}}|$/nm, where λ_{free} is a longer wavelengh of two absorption bands) decreased in the following order: **1**, Cd^{2+} (93 nm) > Mg^{2+} (92) > Li^+ (90) > Ca^{2+} (82) > Ba^{2+} (78) > Na^+ (68) > K^+, Zn^{2+} (66) > Rb^+, NH_4^+ (8) > Cs^+ (1) > Hg^{2+} (0); **2a**, Zn^{2+} (84) > Mg^{2+} (82) > Ca^{2+} (81) > Cd^{2+} (79) > Ba^{2+} (75) > Li^+ (65) > Na^+ (60) >

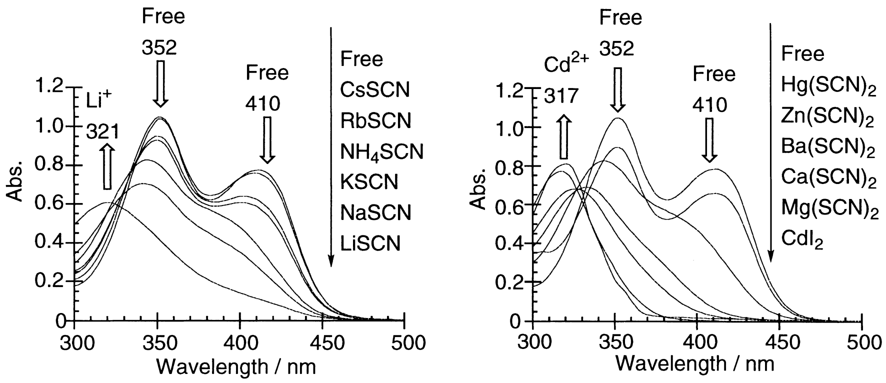


Fig. 1. Absorption spectra of **1** (1.0×10^{-4} M) with and without guest salts (1.0×10^{-2} M) in CH_3CN.

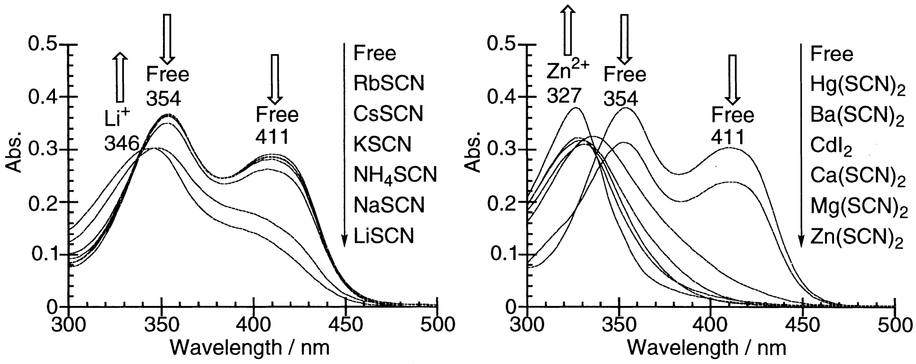


Fig. 2. Absorption spectra of **2a** (2.0×10^{-5} M) with and without guest salts (2.0×10^{-3} M) in CH_3CN.

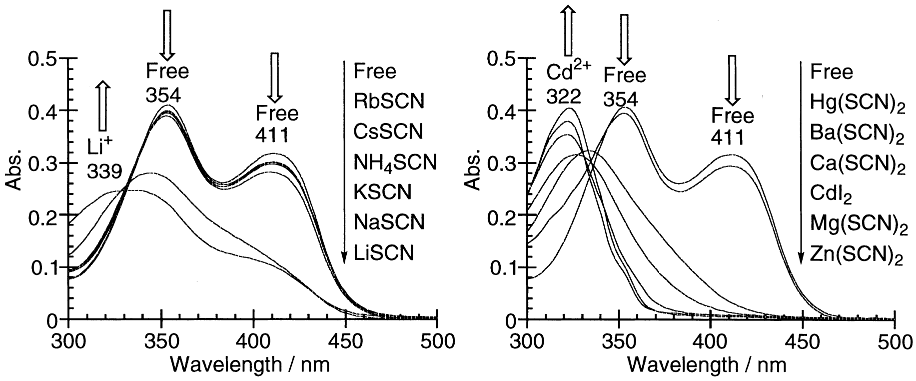


Fig. 3. Absorption spectra of **2b** (2.0×10^{-5} M) with and without guest salts (2.0×10^{-3} M) in CH_3CN.

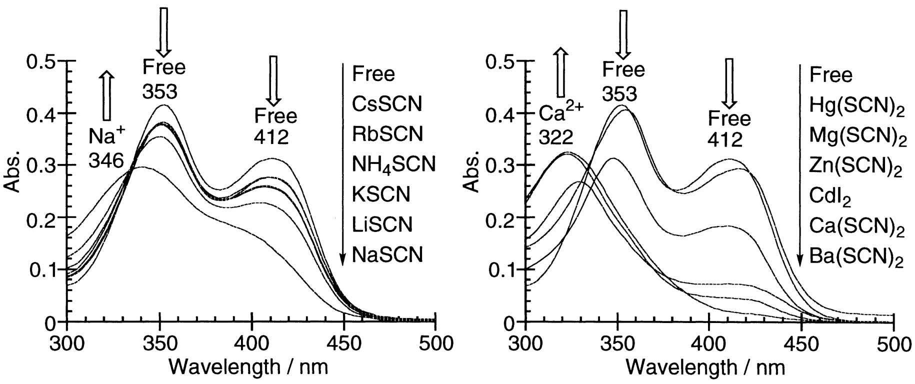


Fig. 4. Absorption spectra of **2c** (2.0×10^{-5} M) with and without guest salts (2.0×10^{-3} M) in CH_3CN.

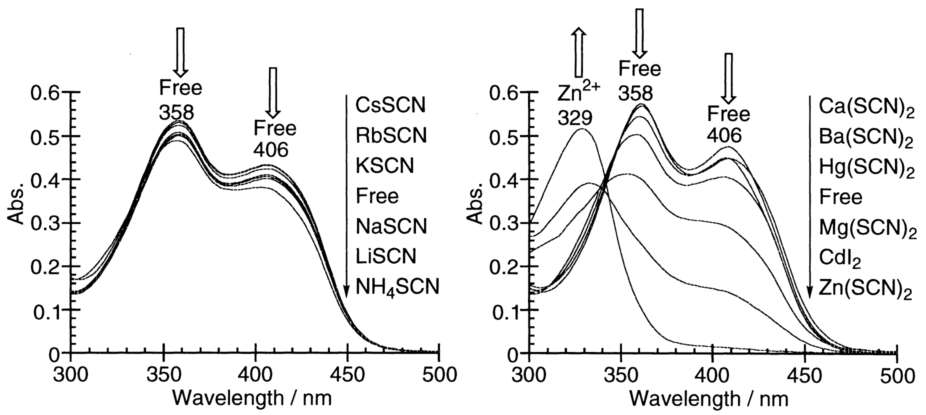


Fig. 5. Absorption spectra of **3** (2.0×10^{-5} M) with and without guest salts (2.0×10^{-3} M) in CH_3CN.

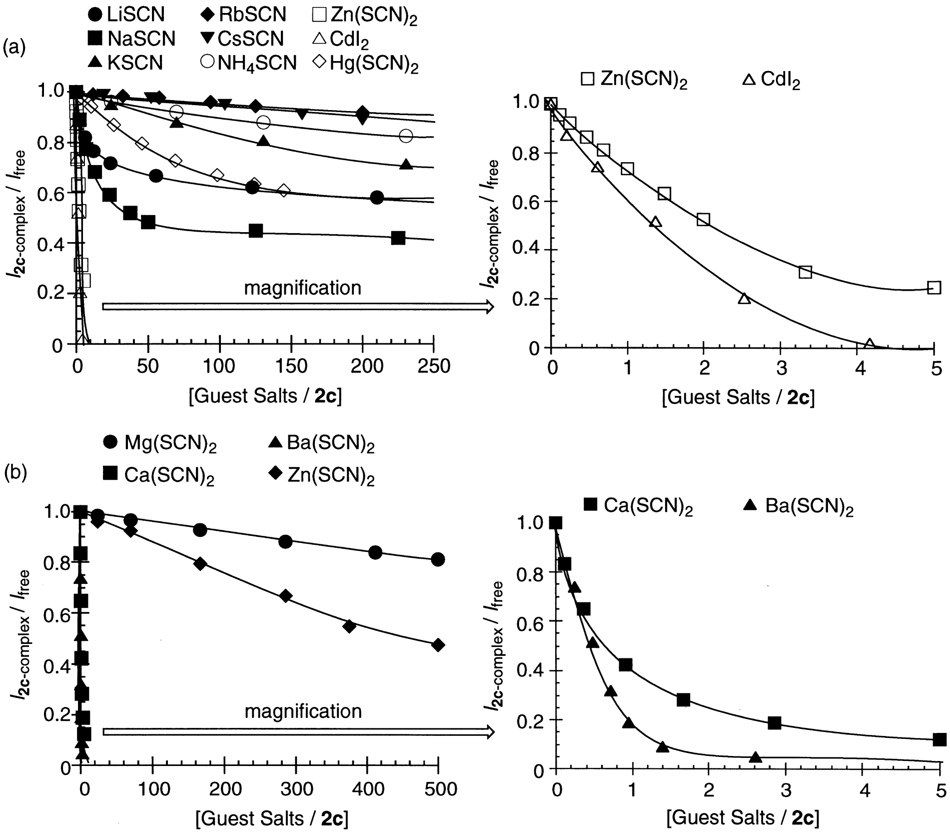


Fig. 6. Absorbance dependence of **2a** (2.0×10^{-5} M) on concentration of various guest salts in (a) CH_3CN and (b) $CHCl_3$–CH_3OH (9:1 v/v).

NH_4^+ (4) > K^+, Rb^+, Cs^+, Hg^{2+} (1); **2b**, Mg^{2+}, Zn^{2+} (89) > Ca^{2+} (85) > Ba^{2+} (75) > Li^+ (72) > Na^+ (66) > Cd^{2+} (59) > K^+, Rb^+, Cs^+, NH_4^+, Hg^{2+} (1); **2c**, Ca^{2+} (89) > Ba^{2+} (88) > Cd^{2+} (86) > Mg^{2+}, Zn^{2+} (82) > Na^+ (65) > Li^+ (10) > K^+, Rb^+, Cs^+, NH_4^+, Hg^{2+} (4); **3**, Zn^{2+} (77) > Cd^{2+} (74) > Mg^{2+} (46) > NH_4^+ (4) > Ca^{2+}, Ba^{2+}, Hg^{2+} (2) > Li^+, Na^+, K^+, Rb^+, Cs^+ (1). The absorption shifts for bivalent guest cations, except for Hg^{2+}, were larger than those for monovalent guest cations. The spectral changes depend on the concentration of guest salts, indicating that the tropon-2-yl group can be used as a chromophore.

Association Constants (*K*). The metal-ion concentration dependence of the absorbance (Fig. 6) allowed us to determine the association constants (*K*) by a nonlinear curve-fitting method[6] (Table 1).

Since the absorbance intensities in CH_3CN were out of range for alkaline earth metals, the solvent was changed to a mixture of CH_3OH and $CHCl_3$ (1:9 v/v). The azamacrocycles showed the following guest cation selectivity: (**1**: Ba^{2+} > Zn^{2+} > Cd^{2+} > Ca^{2+} > Mg^{2+} > Li^+ > Na^+ > K^+ > Cs^+ > NH_4^+ > Rb^+ > Hg^{2+}. **2a**: Zn^{2+} > Ca^{2+} > Ba^{2+} > Mg^{2+} > Cd^{2+} > Li^+ > Hg^{2+} > Na^+ > K^+ > Rb^+, Cs^+, NH_4^+. **2b**: Ca^{2+} > Ba^{2+} > Zn^{2+} > Cd^{2+} > Mg^{2+} > Li^+ > Na^+ > Hg^{2+} > Rb^+ > Cs^+ > NH_4^+ > K^+. **2c**: Ba^{2+} > Ca^{2+} > Zn^{2+} > Mg^{2+} > Cd^{2+} > Na^+ > Li^+ > Hg^{2+} > NH_4^+ > K^+ > Rb^+, Cs^+. **3**: Zn^{2+} > Cd^{2+} > Ca^{2+} >

Table 1. Association Constants (log K/M^{-1}) of **1**–**3** for Various Guest Salts in CH_3CN[a] and $CHCl_3$–CH_3OH (9:1 v/v)[b]

Guest Salts	**1**	**2a**	**2b**	**2c**	**3**
LiSCN	5.23 ± 0.03[a]	4.45 ± 0.06[a]	4.41 ± 0.01[a]	3.32 ± 0.09[a]	0.82 ± 0.32[a]
NaSCN	3.65 ± 0.02[a]	2.54 ± 0.02[a]	3.54 ± 0.01[a]	3.56 ± 0.01[a]	< 1[a]
KSCN	2.68 ± 0.01[a]	0.85 ± 0.25[a]	2.13 ± 0.04[a]	1.91 ± 0.05[a]	0.85 ± 0.25[a]
RbSCN	2.04 ± 0.01[a]	< 1[a]	2.40 ± 0.14[a]	< 1[a]	< 1[a]
CsSCN	2.32 ± 0.06[a]	< 1[a]	2.37 ± 0.16[a]	< 1[a]	< 1[a]
NH_4SCN	2.30 ± 0.01[a]	< 1[a]	2.23 ± 0.09[a]	1.94 ± 0.07[a]	2.59 ± 0.06[a]
$Mg(SCN)_2$	1.18 ± 0.10[b]	< 1[b]	< 1[b]	1.45 ± 0.05[b]	3.32 ± 0.04[a]
$Ca(SCN)_2$	3.40 ± 0.01[b]	2.45 ± 0.02[b]	3.95 ± 0.01[b]	5.23 ± 0.06[b]	3.65 ± 0.05[a]
$Ba(SCN)_2$	4.20 ± 0.01[b]	1.91 ± 0.03[b]	3.93 ± 0.02[b]	6.23 ± 0.05[b]	1.83 ± 0.04[a]
$Zn(SCN)_2$	3.82 ± 0.08[b]	3.20 ± 0.11[b]	3.59 ± 0.19[b]	1.80 ± 0.04[b] 4.37 ± 0.01[a]	2.34 ± 0.18[b]
CdI_2	3.51 ± 0.04[b]	4.51 ± 0.11[a]	3.18 ± 0.15[b]	4.39 ± 0.08[a]	4.36 ± 0.01[a]
$Hg(SCN)_2$	1.89 ± 0.09[a]	3.90 ± 0.08[a]	3.21 ± 0.05[a]	2.69 ± 0.02[a]	3.55 ± 0.14[a]

$Hg^{2+} > Mg^{2+} > NH_4^+ > Ba^{2+} > K^+ > Li^+ > Na^+, Rb^+, Cs^+$). It is known that with the series of crown ethers, Li^+, Na^+, and K^+ preferably form complexes with 12-crown-4, 15-crown-5, and 18-crown-6 derivatives, respectively.[6] The selectivity pattern of the azamacrocycles, **1** and **2**, is distinct from those of the crown ethers and *N*-substituted azamacrocycles, such as *N*,*N′*-dimethyl-diaza-18-crown-6 ($Ba^{2+} > Ca^{2+} > K^+ > Rb^+ > Na^+$)[6] and *N*,*N′*-bis(1-naphthylmethyl)diazacrown ethers (diaza-12-crown-4: $Zn^{2+} > Ca^{2+} > Li^+ > Ba^{2+} > Mg^{2+} > Na^+ > K^+ > Rb^+ > Cs^+ > NH_4^+$, diaza-15-crown-5: $Mg^{2+} > NH_4^+ > Ca^{2+} > Zn^{2+} > Ba^{2+} > Na^+$, diaza-18-crown-6: $Mg^{2+} > K^+ > NH_4^+ > Ba^{2+} > Rb^+ > Zn^{2+} > Na^+ > Cs^+ > Ca^{2+} > Li^+$).[7] The UV-vis spectral behaviors of azamacrocycles **1**–**3** indicated a change of conformation by complexation. Since the oxygen and nitrogen atoms of the tropone carbonyl group and azamacrocycles constitute the coordination form, the effective size of the crown cavity become smaller than the parent crown ether to decrease the mutual conjugation between the host system and the tropone moiety.

Crystal Structures of Azamacrocycles and Their Complexes. The crystal structures of the free hosts, **2a** and **2c**, the calcium thiocyanate complexes of **1** and **2c**, the barium thiocyanate complex of **1**, and the zinc thiocyanate complex of **2a** were elucidated by an X-ray analysis, as shown in Fig. 7.

Crystal Structures of Free Hosts: The structure of the free hosts **1** was not elucidated because of a failure of crystallization at room temperature. However, the diazacrown derivatives **2a**, **2c** crystallized nicely. ORTEP drawings of **2a** and **2c** are shown in Figs. 7a and b. Compounds **2a** and **2c** are centrosymmetric and the two tropone units have an *anti* orientation to the crown ether ring. The dihedral angles between the least-squares diazacrown plane (defined by N1–C8–C9–O2–C10–C11–$N1^i$–$C8^i$–$O2^i$–$C10^i$–$C11^i$ (i: symmetry codes: $-x$, $-y$, $-z$) for **2a**, N1–C8–C9–O2–C10–C11–O3–C12–C13–$N1^{ii}$–$C8^{ii}$–$C9^{ii}$–$C10^{ii}$–$C11^{ii}$–$C12^{ii}$–$C13^{ii}$ (ii: $1 - x$, $1 - y$, $1 - z$) for **2c**) and the tropone ring, defined by C1–C2–C3–C4–C5–C6–C7–O1, are 52.7(1)° and 90.6(1)°, respectively. The conformations of the ethereal moiety of **2a** and **2c** are: N1–C8–C9–O2–C10–C11 and C1–C2–C3–C4–C5–C6–C7–O1, respectively. On the other hand, the angles between the least-squares plane, defined by C1, C2, and C7, and the plane, defined by C2, C3, C6, and C7, are 30.3(2)° for **2a** and 30.5(1)° for **2c**, respectively, which are bigger than that of tropone. This result suggested that the diazacrown parts let the planarity of the seven-membered ring of **2a** and **2c** to decrease. The bond lengths 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.[10] This result means that the aminotropone moiety of **2a** and **2c** forms a conjugated 10-electron system.

Calcium and Barium Thiocyanate Complexes of 1:[8,9] As shown in Fig. 7c, the Ca^{2+} cation of **1**·$Ca(NCS)_2$ has an irregular eight coordination, which includes ether the O1, O7, O10 and O13 atoms, the carbonyl O1′ atom of tropone, the N4 atom of azacrown ether and the N01 and N02 atoms from thiocyanate anions. This geometry is similar to those observed in 15-crown-5·$Ca(NCS)_2$·H_2O,[11] benzo-15-crown-5·$Ca(NCS)_2$·H_2O,[12] benzo-15-crown-5·$Ca(NCS)_2$·CH_3OH,[13] and 2,5,8,11,14-pentaoxapentadecane·$Ca(NCS)_2$·H_2O.[14,15] Instead of an O atom from the solvents, such as methanol and water, the carbonyl O1′ atom of tropone coordinates to the Ca^{2+} cation. The four Ca1–O ether distances are in the range of 2.474(2)–2.583(2) Å, but the average value (2.51(5)°) is similar to those observed in other complexes of crown ethers[11,13] and to the sum of the ionic and van der Waals radii (2.52 Å = 1.12 + 1.40 Å).[10,16] The Ca1–O1′ distance (2.437(2) Å) is significantly shorter than the Ca1–O ether distances. The Ca1–N4 distance (2.749(2) Å) is longer than that of the sum of the ionic and van der Waals radii (2.67 Å = 1.12 + 1.55 Å),[10,16] indicating weak coordination of the 2-aminotropone moiety to the Ca^{2+} cation.

The barium thiocyanate complex of **1** has 2:2 stoichiometry with C_i symmetry, as shown in Fig. 7d. The structure is distinct from those of 2,5,8,11,14-pentaoxapentadecane·$Ba(NCS)_2$·$2H_2O$,[17] 1,4,7,10,13,16-hexaoxacyclooctadecane·$Ba(NCS)_2$·H_2O,[18] and 10-methyl-9-[2-methyl-4-(1,4,7,10-tetraoxa-13-aza-13-cyclopentadecyl)phenyl]acridinium·$Ba(ClO_4)_2$·CH_3CN.[19] Each Ba^{2+} ion of complex **1** has a nine coordination, which includes four ether O atoms (O1, O2, O3, and O4), one N1 atom of azacrown, two N atoms (N2 and N3) of thiocyanate, one O atom (O5) of a tropone, and one O atom ($O5^{iii}$) (iii: $2 - x$, $-y$, $1 - z$) of the other tropone; instead of the coordination of the perchlorate ion or water, the tropone O atom coordinates with the Ba^{2+} cation. One N1 atom and four O atoms (O1, O2, O3, and O4) of the azacrown are coordinated on one side of Ba1, and the two thiocyanate N atoms (N2 and N3) and the two tropone O atoms (O5 and $O5^{iii}$) on the opposite side. The dihedral angle between the least-squares azacrown plane, defined by O1–O2–O3–O4–N1, and the tropone ring, defined by C11–C12–C13–C14–C15–C16–C17–O5, is

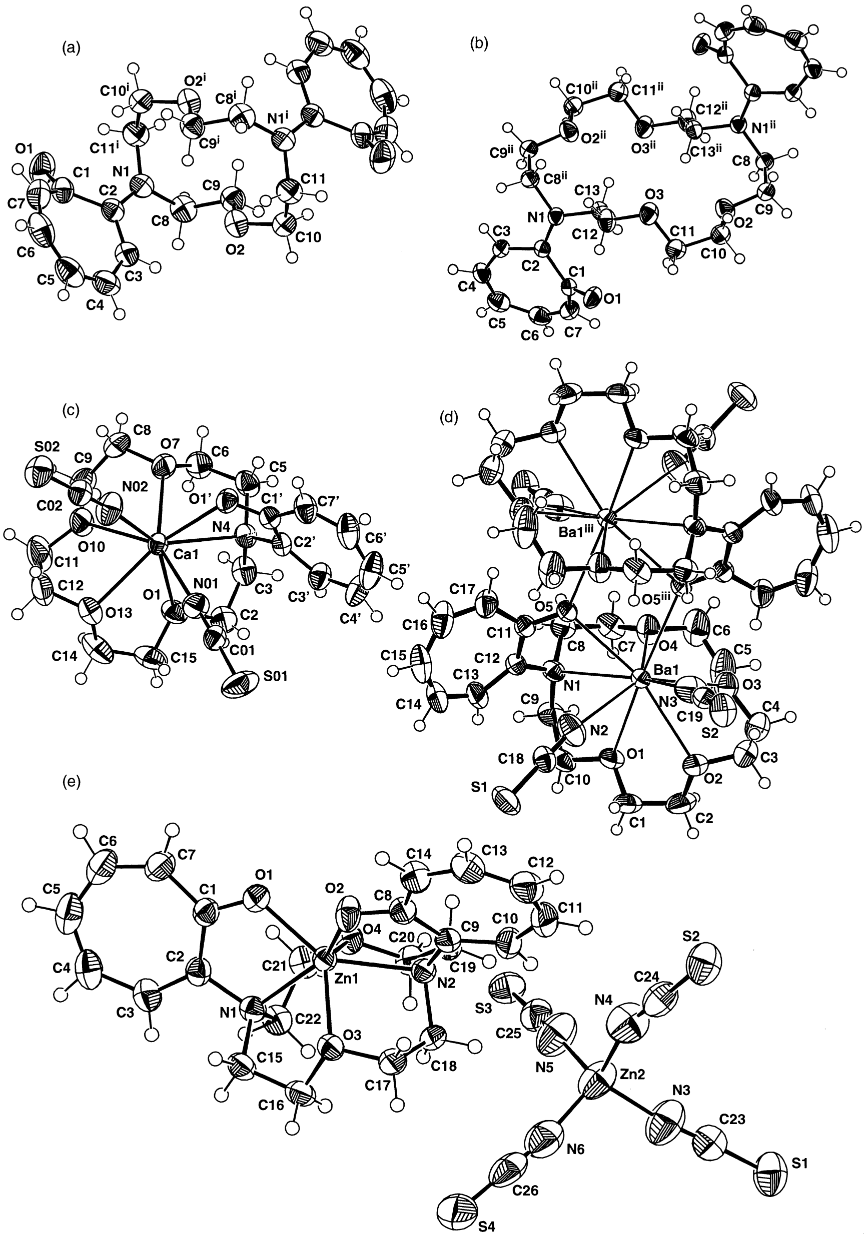


Fig. 7. Molecular structures of (a) **2a**, (b) **2c**, (c) **1**·Ca(NCS)$_2$, (d) [**1**·Ba(NCS)$_2$]$_2$, (e) [**2a**·Zn^{2+}][Zn(NCS)$_4$]$^{2-}$.

116.1(1)°, while the two BaNCS planes intersect at 76.5(5)° and 50.6(2)° to the azacrown plane, respectively.

Zinc Thiocyanate Complex of 2a:[3] A zinc thiocyanate complex of **2a** consists of an ion pair with [Zn(NCS)$_4$]$^{2-}$ and **2a**·Zn^{2+}, as shown in Fig. 7e. The zinc ion of [Zn(NCS)$_4$]$^{2-}$ has a tetrahedral coordination and that of **2a**·Zn^{2+} has a six coordination involving two diazacrown nitrogen atoms, two ether oxygen atoms, and two tropone oxygen atoms. The structure of [**2a**·Zn][Zn(NCS)$_4$] is similar to those of [Zn([9]aneN$_2$S)$_2$][ZnCl$_4$][20] and (HTen)$_2$[Zn(NCS)$_4$].[21] The two tropone rings of **2a**·Zn^{2+} adopt a *syn* conformation with respect to each other, and provide coordination from the same side to Zn^{2+}. The dihedral angles between the least-squares diazacrown plane, defined by N1–C15–C16–O3–C17–C18–N2–C19–C20–O4–C21–C22 and the tropone ring (defined by C1–C2–C3–C4–C5–C6–C7–O1 and C8–C9–C10–C11–C12–C13–C14–O2) are 70.1(1)° and 72.2(1)°, respectively. The average values of two Zn–O and Zn–N ether distances are similar to that of the sum of the ionic and van der Waals radii (for Zn–O, 2.14 Å = 0.74 + 1.40, and for Zn–N, 2.24 Å = 0.74 + 1.5).[10,16] The complex anion, [Zn(NCS)$_4$]$^{2-}$, has a distorted tetrahedral structure, and the four Zn–N bond lengths are 1.951–1.960 Å, which are similar to that of (HTen)$_2$[Zn(NCS)$_4$].[21]

The tropone moiety of the complex [**2a**·Zn]$^{2+}$ showed pronounced bond alternation similar to those of tropone,[22] **1**·Ca(NCS)$_2$,[8] and [**1**·Ba(NCS)$_2$]$_2$.[9] The tropone ring system of **2a** deviates from the plane: the angles of the intersection between the least-squares planes A [defined by C1, C2, and C7] and B [defined by C2, C3, C6, and C7] and between the least-squares planes C [defined by C8, C9, and C14] and D [defined by C9, C10, C13, and C14] are 1.8(3)° and 2.5(2)°, respectively. The planarity of the tropone ring of **2a** [30.3(2)°] is lower than those of [**2a**·Zn]$^{2+}$ [1.8(3)° and 2.5(2)°], since the carbonyl and amino groups donate electrons to the guest cation to form a tropylium ion, which contributes to increase the planarity of the seven-membered ring of the complex.

Calcium Thiocyanate Complex of 2c:[3] Interestingly, the **2c**-calcium thiocyanate complex also consists of an ion pair with $[Ca(NCS)_6]^{4-}$ and **2c**$\cdot Ca^{2+}\cdot H_2O$ (Fig. 8). The complex has the stoichiometry $(\mathbf{2c}\cdot Ca^{2+}\cdot H_2O)_2\cdot 0.5[Ca(NCS)_6]^{4-}\cdot 0.5[Ca(NCS)_6]^{4-}\cdot H_2O\cdot CH_3CN$. The calcium hexathiocyanate anion ($[Ca(NCS)_6]^{4-}$) has never been found. The calcium ion for $[Ca(NCS)_6]^{2-}$ as an octahedral coordination, and that for **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 a water molecule. An ORTEP diagram shows that the two tropone rings adopt a *syn* conformation with respect to one another across the crown ether ring; the two tropone groups provide coordination from the same side, while the water oxygen atom provides coordination from the opposite sides. The four dihedral angles between the least-squares diazacrown plane and the tropone ring of the two molecules are 82.4(1)°, 61.0(1)°, 84.7(2)°, and 67.1(2)°, respectively. The average value [2.48(5) Å] of four Ca–O ether distances is similar to that of the sum of the ionic and van der Waals radii (2.52 Å = 1.12 + 1.40 Å)[10,16] and to that of **1**$\cdot Ca(NCS)_2$. The average value [Ca1–O1′: 2.408(5) Å] of two Ca–O distances of the tropone carbonyl groups is shorter than that of **1**$\cdot Ca(NCS)_2$. The average value [2.773(6) Å] of two Ca–N distances of the diazacrown ether is larger than that of the sum of the ionic and van der Waals radii (Ca-N: 2.67 Å = 1.12 + 1.55 Å)[10,16] and to that of **1**$\cdot Ca(NCS)_2$. All of the six Ca–N bond lengths of $[Ca(NCS)_6]^{4-}$ are 2.433–2.465 Å, smaller than that of $Ca(NCS)_2$ and that of the sum of the ionic and van der Waals radii (Ca–N: 2.67 Å).[10,16]

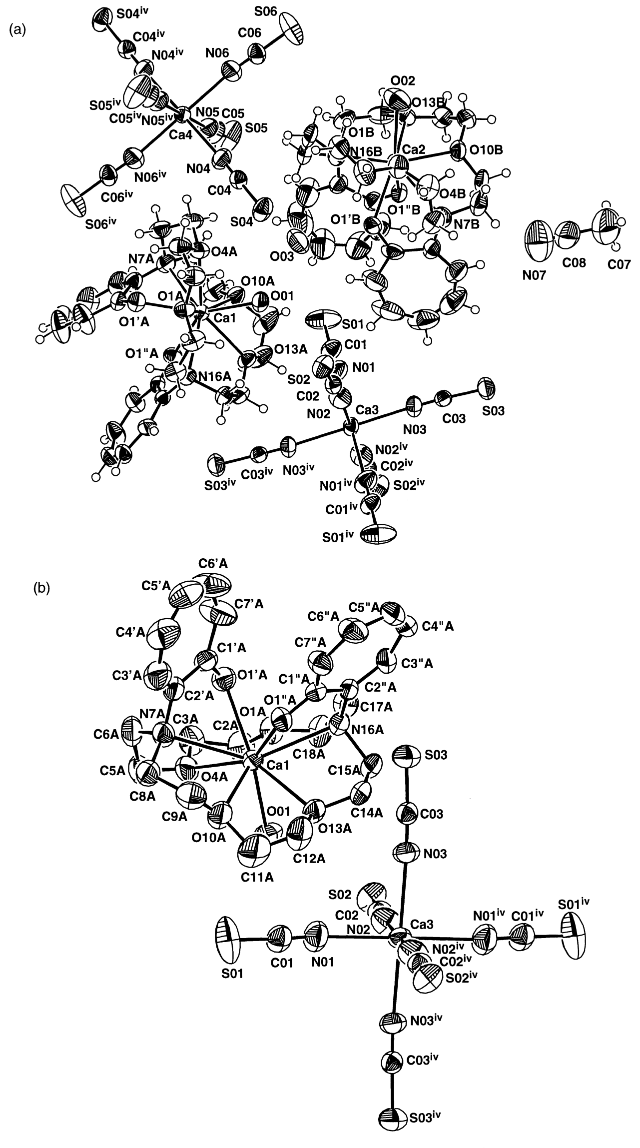


Fig. 8. Molecular structure of (a) $(\mathbf{2c}\cdot Ca^{2+}\cdot H_2O)_2\cdot 0.5[Ca(NCS)_6]^{4-}\cdot 0.5[Ca(NCS)_6]^{4-}\cdot H_2O\cdot CH_3CN$ and (b) **2c**$\cdot Ca^{2+}\cdot H_2O\cdot 0.5[Ca(NCS)_6]^{4-}$(iv: $2-x$, $-y$, $1-z$).

The tropone moieties of the complexes (**2c**$\cdot Ca^{2+}\cdot H_2O$) showed a pronounced bond alternation similar to those of tropone,[22] **1**$\cdot Ca(NCS)_2$,[8] [**1**$\cdot Ba(NCS)_2]_2$,[9] and [**2a**$\cdot$Zn][$Zn(NCS)_4$]. The N1-C2 bond length [1.419(10) Å] of **2c**$\cdot Ca^{2+}\cdot H_2O$ is longer than those of **2c**. The tropone ring system of **2c** deviates from the plane; the four angles of the intersection between the least-squares planes A [defined by C1, C2, and C7] and B [defined by C2, C3, C6, and C7] of the two tropones are 7.9(9)°, 0.9(5)°, 11.7(10)°, and 4.4(10)°, respectively. The angles of the tropone ring of the calcium complexes are smaller than that of the free host (**2c**).

In conclusion, the complexation of troponoid azamacrocycles **1**–**3** with guest cations caused deconjugation between the tropone ring and the nonbonding electron pair of the nitrogen atom, as shown in Fig. 9. The difference in the conjugation system of azamacrocycles **1**–**3** and its complexes should be responsible for the absorption spectral changes.

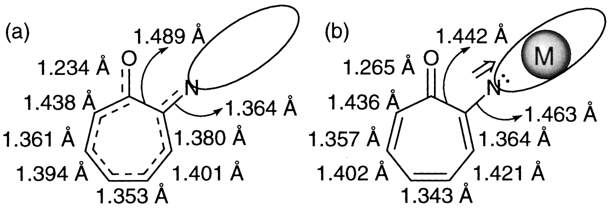


Fig. 9. (a) Conjugated 10 electron system of **2a** and (b) deconjugation between the tropone ring and nonbonding electron pair of the nitrogen atom of $[\mathbf{2a}\cdot Zn^{2+}][Zn(NCS)_4]^{2-}$.

Experimental

Instruments. The melting points were measured with a Yanagimoto Micro Melting Point Apparatus and are uncorrected. The NMR spectra were measured by means of JEOL Lambda-400 Model and Lambda-600 Model spectrometers in $CDCl_3$; the chemical shifts are expressed in units of δ. The mass spectra were measured with a JEOL JMS-01SG-2 spectrometer, except for FAB-MS measurements of high-resolution molecular weight determinations, which were performed by the JEOL JMS SX 102A model spectrometer being controlled by a JEOL DA-7000 Data System (Tokyo), of the Pharmaceutical School of Kyushu University. The IR spectra were taken as KBr disks for crystalline compounds, or as liquid films inserted between NaCl plates for oily compounds, using a JASCO IR-700 spectrometer. The UV spectra were measured using a Hitachi U-3410 spectrophotometer. The stationary phase for column chromatography was a Wakogel C-300 and the eluent was a mixture of ethyl acetate and hexane.

Synthesis of *N*,*N*′-Di(tropon-2-yl)-diazacrown ethers (2) and *N*,*N*′,*N*″-tri(tropon-2-yl)-triazacrown (3). A toluene-ethanol solution (6 cm^3, 1:1 v/v) of 1,7-diaza-12-crown-4 (0.042 g, 0.24 mmol), triethylamine (0.5 cm^3), and 2-(*p*-tolylsulfonyloxy)-tropone (0.153 g, 0.56 mmol) was refluxed for 8 h, and gave *N*,*N*′-di(tropon-2-yl)-1,7-dioxa-4,10-diazacyclododecane (**2a**) (0.082 g, 89%). The solvent was evaporated and the residue was purified by column chromatography over silica gel using ethyl acetate and hexane as the eluent. Recrystallization from chloroform. The physical and spectral data are given below.

***N*,*N′*-Di(tropon-2-yl)-1,7-dioxa-4,10-diazacyclododecane (2a):** Yield 89%, Yellow prisms, mp 169–170 °C; ^{1}H NMR (CDCl$_3$) δ 3.69–3.75 (16H, m), 6.56 (2H, dd, J = 9.4, 8.9 Hz), 6.78 (2H, d, J = 10.6 Hz), 6.89 (2H, d, J = 11.6 Hz), 6.96 (2H, ddd, J = 10.6, 8.9, 1.2 Hz), 7.05 (2H, ddd, J = 11.6, 9.4, 1.2 Hz); ^{13}C NMR (CDCl$_3$) δ 53.8 (4C), 69.5 (4C), 116.2 (2C), 123.7 (2C), 132.9 (2C), 133.9 (2C), 135.3 (2C), 157.4 (2C), 182.0 (2C). IR (KBr) 2928, 1604, 1559, 1442, 1413, 1372, 1349, 1271, 1250, 1171, 1132, 1068, 1050, 887, 862, 758, 701 cm^{-1}. UV (CH$_3$OH) 225.6 (ε 18600, sh), 254.4 (33000), 356.2 (20100), 404.5 (16600, sh), 417.6 nm (17800). MS *m*/*z* (%) 383 (25), (M$^+$, 382 (100)), 351 (28), 178 (70), 161 (49), 147 (86), 132 (77), 105 (44), 77 (44). Found: C 69.08; H 6.87; N 7.32%. Calcd for $C_{22}H_{26}N_2O_4$: C 69.09; H 6.85; N 7.32%.

***N*,*N′*-Di(tropon-2-yl)-1,4,10-trioxa-7,13-diazacyclopentadecane (2b):** Yield 72%, Yellow oil, ^{1}H NMR (CDCl$_3$) δ 3.58 (4H, s), 3.73–3.80 (16H, m), 6.55 (2H, dd, J = 9.4, 8.9 Hz), 6.68 (2H, d, J = 10.6 Hz), 6.88 (2H, d, J = 11.8 Hz), 6.95–7.07 (4H, m); ^{13}C NMR (CDCl$_3$) δ 52.8 (2C), 53.5 (2C), 68.6 (2C), 70.7 (2C), 71.0 (2C), 114.2 (2C), 123.3 (2C), 132.4 (2C), 133.8 (2C), 135.2 (2C), 157.8 (2C), 181.9 (2C). IR (NaCl) 2864, 1608, 1562, 1545, 1468, 1420, 1344, 1285, 1250, 1199, 1179, 1116, 1068, 990, 934, 873, 762, 705 cm^{-1}. UV (CH$_3$OH) 227.2 (ε 14200, sh), 253.9 (24000), 355.2 (14900), 404.5 (11400, sh), 416.5 nm (12400). HR MS (FAB) *m*/*z* 427.2233. Calcd for $C_{24}H_{30}N_2O_5$: M + H, 427.2225.

***N*,*N′*-Di(tropon-2-yl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (2c):** Yield 75%, Yellow prism, mp 108–109 °C, ^{1}H NMR (CDCl$_3$) δ 3.61 (8H, s), 3.76–3.83 (16H, m), 6.53 (2H, dd, J = 9.4, 9.2 Hz), 6.62 (2H, d, J = 10.6 Hz), 6.81 (2H, d, J = 10.6 Hz), and 6.85–7.07 (4H, m); ^{13}C NMR (CDCl$_3$) δ 52.8 (4C), 69.4 (4C), 70.7 (4C), 113.4 (2C), 122.9 (2C), 132.0 (2C), 133.7 (2C), 135.1 (2C), 157.4 (2C), 181.3 (2C). IR (KBr) 2926, 2860, 1599, 1549, 1494, 1465, 1426, 1381, 1346, 1293, 1244, 1119, 1095, 1071, 1028, 929, 853, 758, 692 cm^{-1}. UV (CH$_3$OH) 225.6 (ε 16800, sh), 254.2 (32700), 354.1 (20400), 404.8 (15200, sh), 417.8 nm (16400). MS (FAB) *m*/*z* 471 (M + H). Found: C, 66.26; H, 7.28; N, 5.88%. Calcd for $C_{26}H_{34}N_2O_6$: C, 66.36; H, 7.28; N, 5.95%.

***N*,*N′*,*N″*-Tri(tropon-2-yl)-1,5,9-triazacyclododecane (3):** Yield 60%, Yellow crystals, mp 219–221 °C, ^{1}H NMR (CDCl$_3$) δ 2.12 (6H, qui, J = 6.4 Hz), 3.51 (12H, t, J = 6.4 Hz), 6.62 (3H, dd, J = 9.4, 9.2 Hz), 6.68 (3H, d, J = 10.3 Hz), 6.92–6.99 (6H, m), 7.07 (3H, ddd, J = 12.1, 9.4, 1.5 Hz); ^{13}C NMR (CDCl$_3$) δ 24.7 (3C), 48.0 (6C), 118.5 (3C), 125.1 (3C), 133.4 (3C), 134.4 (2C), 135.3 (3C), 159.1 (3C), 182.8 (3C). IR (KBr) 2924, 1605, 1555, 1485, 1432, 1366, 1317, 1293, 1254, 1192, 1162, 1047, 773, 710 cm^{-1}. UV (CH$_3$CN) 229.8 (ε 22200), 254.1 (24300), 357.8 (17800), 398.4 (14700), 423.7 nm (11800, sh). HR MS (FAB) Found: *m*/*z* 484.2603. Calcd for $C_{30}H_{33}N_3O_3$: M + H, 484.2600.

Determination of Association Constants (*K*). The titrations were conducted by adding a crown-ether solution (1.0×10^{-4} M for **1**, 2.0×10^{-5} M for **2** and **3** in acetonitrile or methanol–chloroform (1:9, v/v)) progressively containing excess metal salts, using a 250 cm^3 syringe, to a cuvette containing 2 cm^3 of the crown-ether solution (1.0×10^{-4} M for **1**, 2.0×10^{-5} M for **2** and **3** in acetonitrile or methanol–chloroform (1:9, v/v)). The solutions were homogenized by ultrasonic waves for 5 min. The spectrum was recorded after each addition. The added equivalents of the cation were then plotted against the absorption-intensity change around 420 nm, as shown Fig. 6. Even though the solvent takes part in the association interaction, the solvent concentration is virtually unaffected. A self-written nonlinear curve-fitting computer program was used to fit the experimental titration curves.[5] The association constants were determined from the absorption-intensity changes around 420 nm using the equation given in Table 1.

X-ray Crystallographic Studies. All single crystals of **2a**, **2c**, **1**·Ca(NCS)$_2$, [**1**·Ba(NCS)$_2$]$_2$, [**2a**·Zn^{2+}][Zn(NCS)$_4$]$^{2-}$, and 2[**2c**·Ca^{2+}·H$_2$O]·0.5[Ca(NCS)$_6$]$^{4-}$·0.5[Ca(NCS)$_6$]$^{4-}$·H$_2$O·CH$_3$CN for the X-ray analysis were grown in a chloroform and acetonitrile solution at room temperature. Two orange crystals of free hosts and four yellow crystals of complexes having approximate dimensions of 0.40 × 0.40 × 0.37 mm for **2a**, 0.60 × 0.60 × 0.20 mm for **2c**, 0.57 × 0.33 × 0.30 mm for **1**·Ca(NCS)$_2$, 0.30 × 0.27 × 0.23 mm for [**1**·Ba(NCS)$_2$]$_2$, 0.53 × 0.47 × 0.37 mm for [**2a**·Zn^{2+}][Zn(NCS)$_4$]$^{2-}$, and 0.33 × 0.30 × 0.20 mm for 2[**2c**·Ca^{2+}·H$_2$O]·0.5[Ca(NCS)$_6$]$^{4-}$·0.5[Ca(NCS)$_6$]$^{4-}$·H$_2$O·CH$_3$CN were mounted on a glass fiber in a random orientation, respectively. A preliminary examination and data collection were performed with Cu Kα radiation (λ = 1.54184 Å) for **2a**, **1**·Ca(NCS)$_2$, and [**2c**·Ca^{2+}·H$_2$O]$_2$·0.5[Ca(NCS)$_6$]$^{4-}$·0.5[Ca(NCS)$_6$]$^{4-}$·H$_2$O·CH$_3$CN and Mo Kα radiation (λ = 0.71069 Å) for **2c**, [**1**·Ba(NCS)$_2$]$_2$, and [**2a**·Zn^{2+}][Zn(NCS)$_4$]$^{2-}$ on a Enraf-Nonius FR590 diffractometer. Data collection and cell refinement: CAD-4 Software. Data reduction: *MolEN* Structure solution: *SIR97*.[23] Refinement: *SHELXL97*.[24] Molecular graphics: *Xtal GX*. All H atoms were fixed at ideal positions and restrained with U_{iso} held fixed to $1.2U_{\mathrm{eq}}$ of the parent atoms. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and deposition numbers 166410 for **2a**, 166411 for **2c**, 166413 for [**2a**·Zn^{2+}][Zn(NCS)$_4$]$^{2-}$ and 166412 for [**2c**·Ca^{2+}·H$_2$O]$_2$·0.5[Ca(NCS)$_6$]$^{4-}$·0.5[Ca(NCS)$_6$]$^{4-}$·H$_2$O·CH$_3$CN, respectively. The data also were deposited as Document No. OB1014 for **1**·Ca(NCS)$_2$ and QA0361 for [**1**·Ba(NCS)$_2$]$_2$, respectively at the International Union of Crystallography.

Crystal data for **2a**: $C_{22}H_{26}N_2O_4$, Orthorhombic, P_{bca}, 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}, μ = 0.744 mm^{-1}, T = 296(2) K, refinement on F^2 (*SHELXL97*),[24] $R[F^2 > 2\sigma(F^2)]$ = 0.0437, $wR(F^2)$ = 0.1272, S = 1.094.

Crystal data for **2c**: $C_{26}H_{34}N_2O_6$, 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}, μ = 0.093 mm^{-1}, T = 296(2) K, refinement on F^2 (*SHELXL97*),[24] $R[F^2 > 2\sigma(F^2)]$ = 0.0409, $wR(F^2)$ = 0.1131, S = 1.044.

Crystal data for **1**·Ca(NCS)$_2$: $C_{19}H_{25}CaN_3O_5S_2$, Orthorhombic, P_{bca}, a = 13.356(5) Å, b = 23.060(5) Å, c = 14.719(5) Å, V = 4533(2) Å^3, Z = 8, M_{r} = 479.62, D_x = 1.405 Mg m^{-3}, μ = 4.412 mm^{-1}, T = 296(2) K, refinement on F^2 (*SHELXL97*),[24] $R[F^2 > 2\sigma(F^2)]$ = 0.0403, $wR(F^2)$ = 0.1174, S = 1.039.

Crystal data for [**1**·Ba(NCS)$_2$]$_2$: $C_{19}H_{25}BaN_3O_5S_2$, triclinic, $P\bar{1}$, a = 11.668(5) Å, b = 12.445(2) Å, c = 8.918(5) Å, α = 96.697(5)°, β = 106.143(5)°, γ = 106.720(5)°, V = 1163.8(9) Å^3, Z = 2, M_{r} = 576.88, D_x = 1.646 Mg m^{-3}, μ = 1.919 mm^{-1}, T = 296(2) K, refinement on F^2 (*SHELXL97*),[24] $R[F^2 > 2\sigma(F^2)]$ = 0.026, $wR(F^2)$ = 0.070, S = 1.147.

Crystal data for [**2a**$\cdot$Zn^{2+}][Zn(NCS)$_4$]$^{2-}$: $C_{26}H_{26}N_6O_4S_4Zn_2$, 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}, μ = 1.865 mm^{-1}, T = 296(2) K, refinement on F^2 (*SHELXL97*),[24] $R[F^2 > 2\sigma(F^2)]$ = 0.0304, $wR(F^2)$ = 0.0841, S = 1.054.

Crystal data for 2[**2c**$\cdot$Ca$^{2+}\cdot$H$_2$O]$\cdot$0.5[Ca(NCS)$_6$]$^{4-}\cdot$0.5[Ca(NCS)$_6$]$^{4-}\cdot$H$_2$O$\cdot$CH$_3$CN: $C_{60}H_{77}Ca_3N_{11}O_{15}S_6$, 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}, μ = 5.056 mm^{-1}, T = 296(2) K, refinement on F^2 (*SHELXL97*),[24] $R[F^2 > 2\sigma(F^2)]$ = 0.0904, $wR(F^2)$ = 0.3451, S = 1.145.

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