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Structural characterization for metal-ion complexation and isomerization of crowned bis(spirobenzopyran)s

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ABSTRACT

Metal ion complexes of crown ether derivatives bearing two spirobenzopyran moieties were synthesized and their structural features were studied by X-ray crystallography and NMR spectroscopy. The resulting X-ray crystal structure for the Ca^{2+} complex of diaza-12-crown-4-bis(spirobenzopyran) showed that both of two spirobenzopyran moieties were isomerized from their spiropyran forms to the corresponding merocyanine forms and their phenolate anions interacted with Ca^{2+} bound to its crown ether moiety. The crystal structure also revealed its *syn* conformation whose two spirobenzopyran moieties oriented on the same side of the crown ether moiety. Furthermore, density functional theories (DFT) calculations were carried out in order to predict energetically stable conformation of diaza-18-crown-6-bis(spirobenzopyran).

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1. Introduction

Crown compounds, whose metal-ion complexing abilities were controlled by the external stimulus, have been synthesized and their application abilities on the fields of analytical and materials chemistry have been examined [1–4]. Light is one of the most effective and energy-saving external stimuli for changing the performance of crown compounds. We have therefore designed and synthesized crown ether derivatives bearing spirobenzopyran moieties as photoresponsive unit, and it was found that a metal-ion complexing and extracting abilities and selectivities of these compounds were converted by UV or visible-light irradiations [5–9]. In a previous paper, we reported that the metal ion complexes of diazacrown ether derivatives with two spirobenzopyran moieties, what we called crowned bis(spirobenzopyran)s (Fig. 1), had extraordinarily high stability constants under dark conditions, as compared to those of their corresponding crowned mono(spirobenzopyran)s and the parent diazacrown ethers [9]. It is noteworthy that the metal-ion complexing abilities of crowned bis(spirobenzopyran)s were comparable to those of their corresponding diazacrown ethers under visible-light irradiation conditions, that is, the values of $\log K$ for diaza-12-crown-4-bis(spirobenzopyran)-Ca^{2+} complex were 7.8 and 5.0 under dark and visible-light irradiation conditions, respectively [10]. Furthermore, it was found from the previous experiment using absorption spectroscopy that the complexation of the crowned spirobenzopyrans with metal ions causes the isomerization of the electrically-neutral spirobenzopyran form to its corresponding zwitterionic merocyanine form even under dark conditions, while visible-light irradiation induces the reverse isomerization from its merocyanine form to spirobenzopyran form [8,9]. These results show that the metal-ion complexing ability of the crowned spirobenzopyran is enhanced by the interaction between the phenolate anion of its merocyanine form and a metal ion. The fact that the stability constants of crowned spirobenzopyrans with divalent metal complexes are generally larger than those of monovalent metal complexes under dark conditions also supports this phenomenon. Thus, the significant finding for complexing, extracting and photochromic behavior of crowned spirobenzopyrans were obtained from our previous studies. In this study, we investigated the relationship between the stabilities and the structures of the metal complexes with crowned bis(spirobenzopyran)s.

2. Experimental

2.1. Synthesis of (diaza-12-crown-4)-bis(spirobenzopyran)-Ca^{2+} complex (**1**)

A 2-propanol solution (4 mL) of $Ca(SCN)_2{\cdot}4H_2O$ (0.1 mM) was added to a 1,2-dichloroethane solution (4 mL) containing (diaza-12-crown-4)-bis(spirobenzopyran) (0.1 mM). This solution was allowed to stand under an ambient atmosphere for several days, thus yielding a red X-ray quality crystal. Anal. Calc. for

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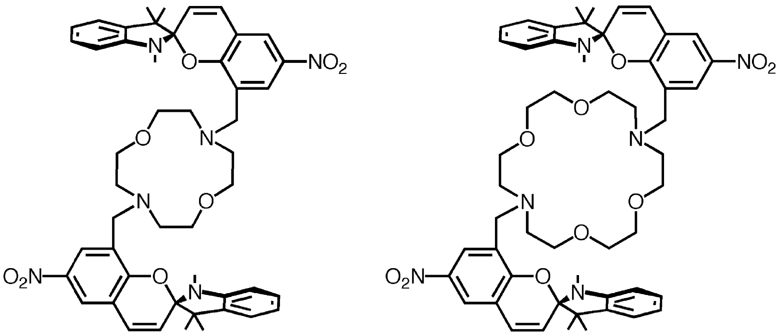

Fig. 1. Crowned bis(spirobenzopyran) used in this study.

$C_{50}H_{54}CaN_8O_8S_2{\cdot}1.3(C_2H_4Cl_2)$: C, 56.01; H, 5.29; N, 9.94; found: C, 56.08; H, 5.50; N, 9.90%

2.2. X-ray structure analysis of (diaza-12-crown-4)-bis (spirobenzopyran)/Ca^{2+} complex

A dark red block crystal of (diaza-12-crown-4)-bis(spirobenzopyran)/$Ca(SCN)_2$ complex having approximate dimensions of 0.50 mm × 0.40 mm × 0.20 mm was mounted on a glass fiber. All measurements were carried out using Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo-K_α radiation. The data were collected at $-100 \pm 1\,^\circ C$ to a maximum 2θ value of 55.0°. The 1200 oscillation images were collected. A first sweep of data was done using ω scans from −70.0 to 110.0° in 30.0° step, at $\chi = 45.0^\circ$ and $\phi = 90.0^\circ$. The exposure rate was 16.7 s/°. The detector swing angle was 20.1°. The crystal-to-detector distance was 44.76 mm. Among the collected 21,554 reflections, the 11,129 data were unique ($R_{int} = 0.040$); equivalent reflections were merged. The collected data were processed using the Crystal Clear program (Rigaku). The linear absorption coefficient μ for Mo–K_α radiation is 3.5 cm^{-1}. Asymmetry-related absorption correction using the program REQAB was applied, resulted in transmission factors ranging from 0.76 to 0.93. The data were corrected for Lorentz and polarization effects. The structure was solved by the direct method and expanded using Fourier techniques. Some non-hydrogen atoms were refined anisotropically, while the rest was refined isotropically. The final cycle of full-matrix least-square refinement was based on 11,129 reflections ($2\theta < 54.96$) and 897 variable parameters and was converged (largest parameter shift was 3.38 times its esd) with unweighted and agreement factors. The standard deviation of an observation of unit weight was 1.09. The weighting scheme was based on counting statistics and included a factor ($p = 0.200$) to downweight the intense reflections. Plots of $\sum \omega(F_0^2 - F_c^2)^2$ versus F_0^2, reflection order in data collection, $\sin\theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.89 and $-0.59\,e^{-1}/Å^3$, respectively. Neutral atom scattering factors were taken from Cromer and Weber [11]. Anomalous dispersion effects were included in Fcala [12]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [13]. The values for the mass attenuation coefficients are those of Creagh and McAuley [14]. All of calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.

2.3. Electronic structure calculations

Electronic structures of crowned bis(spirobenzopyran) complexes were calculated using Gaussian 03 (Gaussian Inc., USA) software. Initial geometries for the conformations of crowned bis(spirobenzopyran)s were obtained from molecular mechanics calculations and then their lowest-energy conformers were subjected to the higher level methods. Density functional theories (DFT, B3LYP) at 3-21G level were applied to two conformations, *syn* and *anti* conformations.

3. Results and discussion

3.1. X-ray structure analysis

As mentioned in experimental section in detail, gradual evaporation of diaza-12-crown-4-bis(spirobenzopyran) with calcium thiocyanate in 1,2-dichloroethane and 2-propanol mixed solution gave a dark red crystal of the Ca^{2+} complex **1**. Fig. 2 shows the structure of complex **1** obtained from X-ray structure analysis. In the structure of complex **1**, Ca^{2+} lies on the crown ether moiety and two right-handed spirobenzopyran moieties enwraps the metal ion from the same side on the crown ether moiety. To the best of our knowledge, this is the first example of X-ray structure for diaza-12-crown-4 derivative-Ca^{2+} complex. In the Cambridge structural database (CSD), only 12-membered ferrocene cryptand-Ca^{2+} complex has been so far reported as analogous complex of complex **1**. The crystal data of this complex is shown in Table 1. Complex **1** crystallizes in the $P2_1/c$ space group and is not chiral. The result indicates the complex contains a racemic mixture of two optical isomers, having right-handed and left-handed spiropyran moieties. Similar structures for metal ion complexes of crown ethers bearing lariat moiety, containing racemic mixture of enantiomers, were reported by Rodríguez-Blas and co-workers [15,16]. They showed that the crystal of *N,N'*-bis(2-salicylaldiminobenzyl)-4,13-diaza-18-crown-6-La^{3+} complex contains both right- and left-handed enantiomers of the lariat ether moieties. Thus, the surface appearance of this complex seems to be a common structure. The notable structural feature of complex **1** is that the two spirobenzopyran moieties of diaza-12-crown-4-bis(spirobenzopyran) isomerize from their electrically neutral spiropyran forms to their corresponding zwitterionic merocyanine forms. In our previous study,

Table 1
Crystal data for complex **1**

Empirical formula	$C_{52}H_{58}CaN_8O_8S_2Cl_2$
Formula weight	1098.18
Temperature	−100 °C
Crystal system	Monoclinic
Space group	$P2_1/c$
Lattice parameters	$a = 13.5916(9)$ Å
	$b = 14.1559(9)$ Å
	$c = 28.107(2)$ Å
	$\beta = 96.347(6)^\circ$
Volume	5374.6(6) Å^3
Z value	4
D_{calc}	1.357 g/cm^3

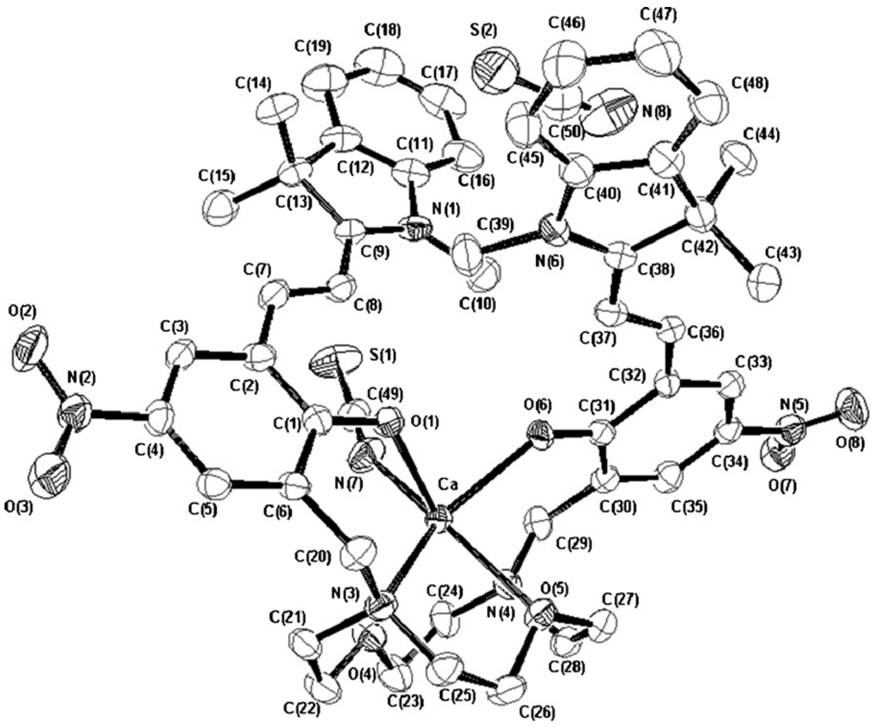

Fig. 2. X-ray crystal structure of complex **1** (disordered 1,2-dichloroethane molecule was omitted). CCDC number: 636945.

crowned spirobenzopyrans and crowned bis(spirobenzopyran)s were spectrophotometrically shown to be isomerized by their complexation with metal ions. That is to say, the complexation with Ca^{2+} could induce the isomerization of both spirobenzopyran moieties of diaza-12-crown-4-bis(spirobenzopyran) to their merocyanine forms. The crystal structure of complex **1** obtained in this study supports this phenomenon. We also found that the bond distances between Ca^{2+} and two phenolate anions of the merocyanine moieties are shorter than that between the Ca^{2+} and the crown ether oxygen and nitrogen atoms (Table 2). These results show that the interaction of a metal ion and two phenolate anions contribute to the complexation with metal ion more strongly than that of the Ca^{2+} and crown ether moiety.

3.2. ^{1}H NMR spectroscopy

In order to obtain more information about the isomerization behavior of diaza-12-crown-4-bis(spirobenzopyran) on the complexation with metal ions, ^{1}H NMR measurements were carried out using chloroform-*d*/acetone-d_6 (1:3) mixture as the solvent. The isomerization behavior of diaza-12-crown-4-bis(spirobenzopyran) is characterized from ^{1}H NMR spectra as shown in Fig. 3. On addition of equimolar $Ca(SCN)_2$ to diaza-12-crown-4-bis(spirobenzopyran), most of the proton signals of spirobenzopyran in the range between 6 and 7.5 ppm ($H_{a,b,e–h}$) almost disappeared while the proton signals for its merocyanine form appeared at the higher frequencies. It was found from the figure that both the spirobenzopyran moieties are isomerized to their corresponding merocyanine forms by the complexation with Ca^{2+}. On the other hand, in the Li^+ addition system of diaza-12-crown-4-bis(spirobenzopyran), the proton signals of the spirobenzopyran form in the range between 6 and 7.5 ppm ($H_{a,b,e–h}$) still remained unchanged, despite that most of the diaza-12-crown-4-bis(spirobenzopyran) molecules complex with Li^+ by the addition of excess LiSCN. (The value of log *K* for diaza-12-crown-4-bis(spirobenzopyran)-Li^+complex was 6.6 in methanol solution [10].) The existence ratio of spiropyran and merocyanine forms was estimated to be around 1: 1 by the signal integration value of ^{1}H NMR. These results suggest that only one of the two spiropyran moieties of diaza-12-crown-4-bis(spirobenzopyran) is isomerized to its merocyanine form on the complexation with Li^+, and the isomerization behavior of spiropyran moiety depends on the electrical charges of the complexed metal ion. The Li^+ and Ca^{2+} complexes of diaza-18-crown-6-bis(spirobenzopyran) also exhibited the same tendencies as those of diaza-12-crown-4-bis(spirobenzopyran) [17].

Table 2
Bond length (Å) for complex **1**

Atom	Atom	Distance
Ca	O(1)	2.270
Ca	O(4)	2.407
Ca	O(5)	2.450
Ca	O(6)	2.274
Ca	N(3)	2.593
Ca	N(4)	2.546
Ca	N(7)	2.447

3.3. Electronic structure calculations

As mentioned above, the structure of complex **1** is arranged in the *syn* conformation; two phenolate ions of the merocyanine moieties, which are formed by the isomerization of spirobenzopyran moieties, are orientated to Ca^{2+} from the same side of the diaza-12-crown-4. Of particular interest to us is that the doubly-armed lariat ether may form another possible structural isomers with *anti* conformation whose two nitrogen substituents are orientated on the opposite side of the crown ether moiety. The crystal structure of the Cu^{2+} complex of the 1,7-dioxa-4,10-diazacyclododecane-4,10-diacetate, which is only metal complex of diaza-12-crown-4 derivative listed in the CSD, shows the *syn* arrangement of their substituents [18]. On the other hand, the *anti* conformations are also reported in the systems of the diaza-12-crown-4 and its derivatives [19–22]. Firman et al. suggested that the *syn* and *anti*

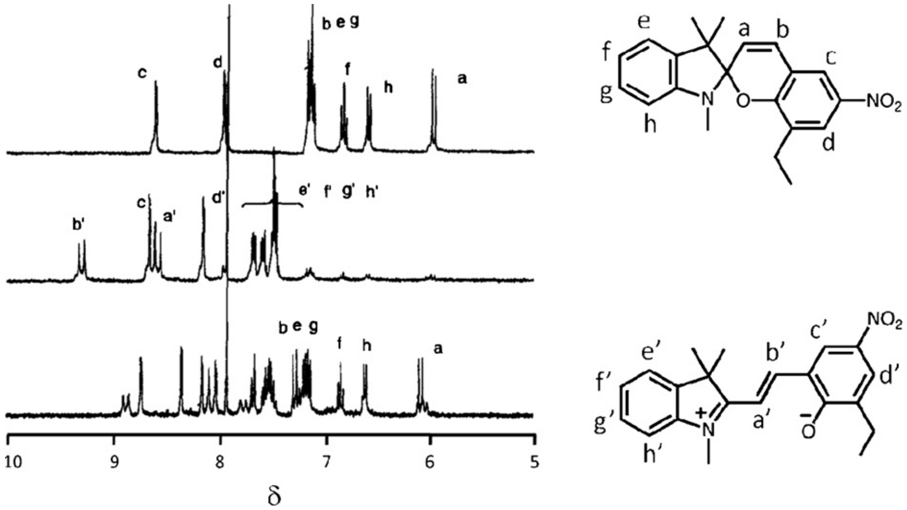

Fig. 3. ^{1}H NMR spectra for diaza-12-crown-4-bis(spirobenopyran) (5.0×10^{-3} M) without metal ion (a) and in the presence of Ca^{2+} (5.0×10^{-3} M) (b) and Li^+ (2.5×10^{-2} M) (c) in chloroform-*d*/acetone-d_6 (1:3).

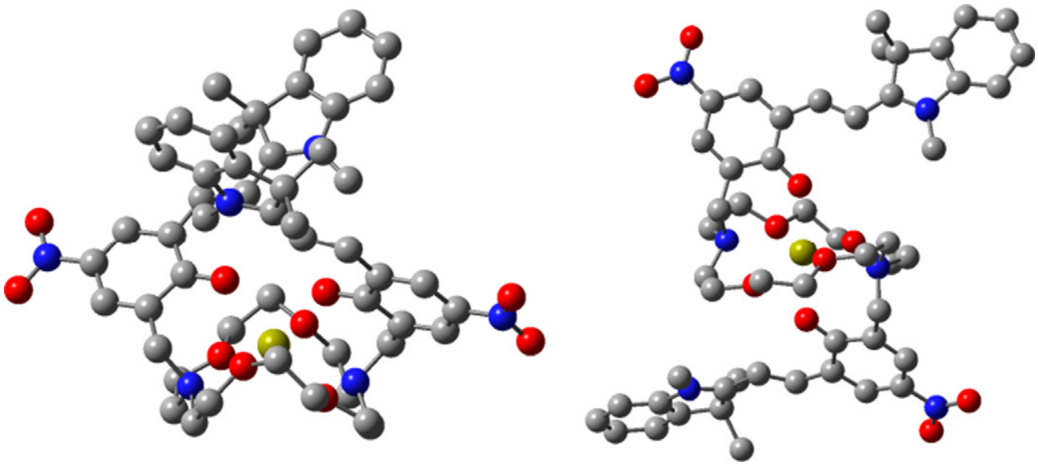

Fig. 4. The optimized structures of complex **2**: (a) *syn* conformer and (b) *anti* conformer.

configurations exist in equilibrium during the courses of ultrasonic and IR relaxation studies about the solutions of Ag^+ complexes of diaza-18-crown-6 [23]. Thus, one may expect that complex **1** also adopts both the *syn* and *anti* conformations in solution. If diaza-12-crown-4-bis(spirobenzopyran) complexes Ca^{2+} in an *anti* arrangement, Ca^{2+} should be oriented on the center of crown ether ring in order to provide two interactions of Ca^{2+} and phenolate anions in the equal distances. However, this complex is not able to adopt such a conformation because its crown ether moiety is much smaller than Ca^{2+} in size. Indeed, DFT calculation for anti conformation of Ca^{2+} complex of compound **1** failed, while that for *syn* conformation was successfully made. On the other hand, the metal complexes of diaza-18-crown-6 derivatives, which have a bigger cavity than diaza-12-crown-4, can make the planar arrangements. The Cd^{2+} and Pb^{2+} complexes of diaza-18-crown-6, and K^+ and Ca^{2+} complexes of diaza-18-crown-6 bearing two ethylphenol moieties are orientated in the planar arrangements, thus affording *anti* configurations [24–26]. In these complexes, the metal ion lies in the center of two nitrogen atoms on the crown ether ring, and the two substituents are orientated on the opposite side of the diaza-18-crown-6 moiety. It was assumed that diaza-18-crown-6-bis(spirobenzopyran) also complex with Ca^{2+} in the *anti* arrangement. Therefore, DFT calculations were done for the *syn* and *anti* conformations of the Ca^{2+} complexes of diaza-18-crown-6-bis(spirobenzopyran), complex **2**, in gas phase (Fig. 4). This theoretical study provided the stabilization energies of the optimized structure of **2** (Table 3). The energies were −2357176.71 and −2357173.05 kcal/mol for the *syn* and *anti* conformations, respectively, and their energy difference was 3.66 kcal/mol. Such a large energy difference between the *syn* and *anti* conformations of complex **2** shows a piece of evidence for the exclusive preference of the *syn* conformation for the Ca^{2+} complex of diaza-18-crown-6-bis(spirobenzopyran). The detailed mechanism, however, remains to be further elucidated.

Table 3
Stabilization energies of complex **2**

syn (kcal/mol)	*anti* (kcal/mol)	Δ*E* (kcal/mol)
−2357176.71	−2357173.05	3.66

4. Conclusion

In this paper, the structural features of crowned bis(spirobenzopyran) metal-ion complexes were discussed. The crystal structure of complex **1** shows that the complexation of diaza-12-crown-4-bis(spirobenzopyran) with Ca^{2+} induces the isomerization of both spirobenzopyran moieties from their spiropyran to the corresponding merocyanine forms and that two phenolate anions of the merocyanine moieties interact with Ca^{2+}. The only one of the two spirobenzopyran moieties of diaza-12-crown-4-bis(spirobenzopyran) is shown to be isomerized on the complexation with Li^+ by the ^1H NMR measurements. It should be concluded from these results that the stability of metal complex of crowned bis(spirobenzopyran)s depends on the electrical charges of metal ion. The progressing research in our group focuses on the synthesis of the crowned spirobenzopyran complex with lanthanide ion that has the high charge density and its feasibility as a photoresponsive contrast agent. The result of its researches will be reported in due course.

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