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Synthesis and cation-dependent photochromism of spironaphthoxazines obtained from crown-containing dihydroisoquinolines

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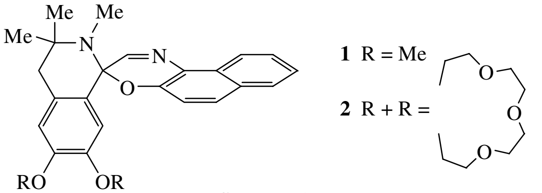
The formation of complexes between spirooxazines (SNOs) containing crown-ether and dihydroquinoline moieties and alkaline earth metal ions affects the spectral and kinetic properties of the SNO open form.

The introduction of crown ether moieties into photochromic molecules opened a new approach to controlling their properties. This approach is based on complexation with metal cations.[1,2] The binding of metal cations by an ionophore fragment could change such properties as photostability, sensitivity and the width of working spectral region. The addition of metal cations to the solutions changed the photochromic properties of spiropyrans[3–7] and spirooxazines.[8–14] For example, the introduction of the monoaza-12-crown-4 group into the 5′-position of a spironaphthoxazine (SNO) molecule and its complexation with the Li^+ ion stabilise the open form of SNO, increasing its lifetime by two orders of magnitude.[8]

This study is an extension of the study of complexation between crown-containing SNO and metal cations.[9–14] The test material is a new synthesised SNO having a crown-containing fragment in the dihydroquinoline part of the molecule (SNO **2** in Scheme 1). For comparison, crown-free SNO **1** was used (Scheme 1).[†] The spiro and merocyanine forms of SNO **1** and SNO **2** are referred to as S-**1**, S-**2**, M-**1** and M-**2**, respectively.

For complex formation, two alkaline earth metal cations (Mg^{2+} and Ba^{2+}) were chosen. The ionic radii of Mg^{2+} and Ba^{2+} are 0.72 and 1.36 Å, respectively.[15] The radius of a 15-crown-5-ether cavity is 0.85 Å.[16] Thus, the Mg^{2+} ion fits well the cavity of the ligand of SNO **2**, and the size of Ba^{2+} exceeds the size of the cavity.

As a source of Mg^{2+} and Ba^{2+}, corresponding perchlorates (Aldrich) were used. UV grade acetonitrile (Aldrich) was used as a solvent. UV spectra were recorded using an HP-8453 spectrophotometer (Hewlett-Packard) with the characteristic time of recording *ca.* 2 s. Experiments on laser flash photolysis were performed using a setup with excitation by a XeCl laser (308 nm).[17] Rate constants of the decay of the SNO open form with the characteristic lifetimes of several seconds were measured both by laser flash photolysis and under photostationary conditions. In the latter case, the sample was placed into the cuvette box of the HP-8453 spectrophotometer and irradiated by a high-pressure mercury lamp with a set of glass filters for the separation of a necessary wavelength. After interruption of the irradiation, the kinetic curves corresponding to the return of the photochromic system to the initial state were recorded.



Scheme 1

In the absence of irradiation, both SNO **1** and SNO **2** are in the spiro form. The UV absorption spectra of the spiro forms (S-**1**, S-**2**) are shown in Figure 1. For crown-containing SNO **2**, the spiro form binds both Mg^{2+} and Ba^{2+} cations. The spectral evidence of the complex formation is demonstrated in Figure 2(*a*). The existence of isosbestic points in the UV spectra [266 and 276 nm for (S-**2**)·Mg^{2+} system, Figure 2(*a*)] makes it possible to determine the composition of the complex and to estimate the equilibrium constants. It was performed under the assumption that the relative change in absorbance at the characteristic wavelength [295 nm for (S-**2**)·Mg^{2+}, Figure 2(*a*)] is proportional to the concentration of the complex in solution. By means of a molar equation method,[19] the composition of (S-**2**)·Mg^{2+} complex was found to be 1:1. It allows one to assume that the Mg^{2+} cation is located inside the crown ether ring. The proposed composition of the complex is shown in Scheme 2. For the Ba^{2+} cation, the [Ba^{2+}]/[SNO **2**] ratio was 1:2, which corresponds to

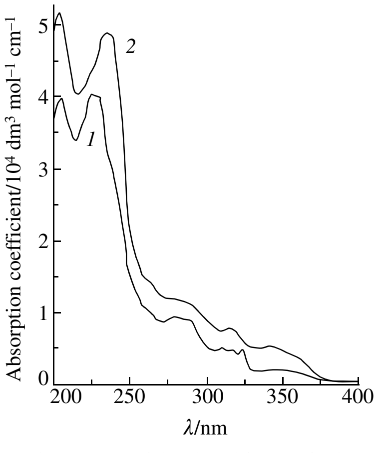
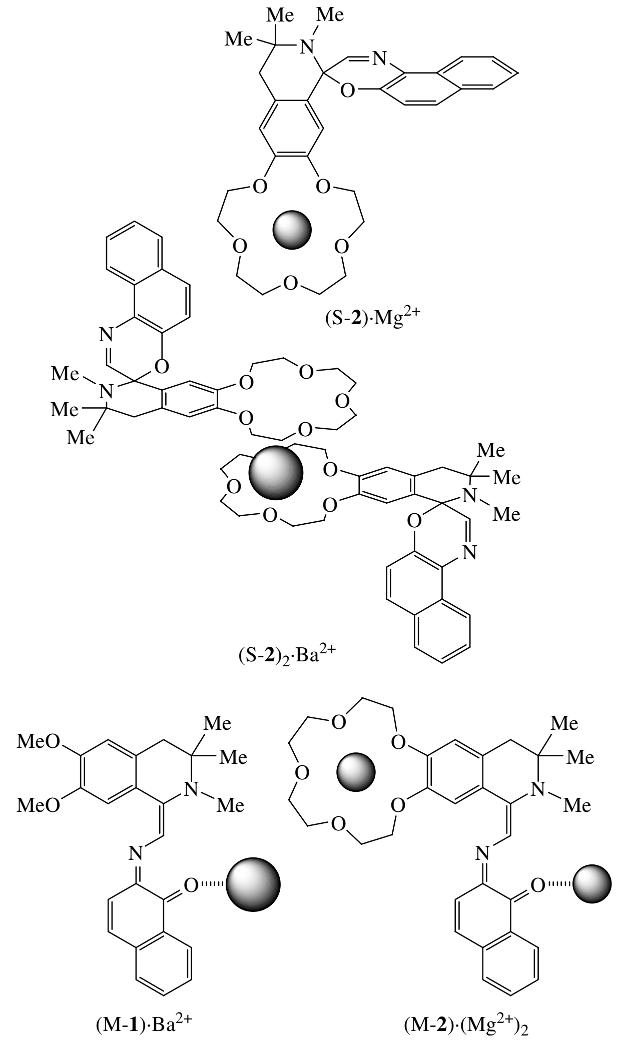


Figure 1 UV absorption spectra of the closed forms of spironaphthoxazines S-**1** (curve *1*) and S-**2** (curve *2*). Temperature, 298 K; solvent, acetonitrile.

[†] *3,4-Dihydro-2,3,3-trimethyl-6,7-dimethoxyspiro(isoquinolino-1,3′-[3*H*]-naphth[2,1-*b*][1,4]oxazine)* **1**: yellow oil. ^{1}H NMR ($CDCl_3$) δ: 1.26 (s, 3H, Me), 1.31 (s, 3H, Me), 2.22 (s, 3H, NMe), 2.58 (d, 1H, H-4a, *J* 15.6 Hz), 2.93 (d, 1H, H-4b, *J* 15.6 Hz), 3.65 (s, 3H, MeO), 3.89 (s, 3H, MeO), 6.56 (s, 1H, H-5), 6.62 (s, 1H, H-8), 7.06 (d, 1H, H-5′, *J* 8.9 Hz), 7.18 (s, 1H, H-2′) 7.38 (td, 1H, H-8′, *J* 8.2, 8.1 and 1.3 Hz), 7.57 (td, 1H, H-9′, *J* 8.2, 8.4 and 1.3 Hz), 7.71 (d, 1H, H-6′, *J* 8.9 Hz), 7.79 (d, 1H, H-7′, *J* 8.1 Hz), 8.59 (d, 1H, H-10′, *J* 8.4 Hz). Found (%): C, 74.72; H, 6.59; N, 6.89. Calc. for $C_{25}H_{26}N_2O_3$ (%): C, 74.60; H, 6.51; N, 6.96.

*3,4,7,8,10,11,13,14,16,17,-Decahydro-2,3,3-trimethylspiro{(6,9,12, 15,18)pentaoxacyclopentadecyno[2,3-g]isoquinolino-1,3′-[3*H*]naphth-[2,1-*b*][1,4]oxazine}* **2**, light-yellow oil. ^{1}H NMR ($CDCl_3$): 1.24 (s, 3H, Me), 1.29 (s, 3H, Me), 2.21 (s, 3H, NMe), 2.54 (d, 1H, H-4a, *J* 15.6 Hz), 2.90 (d, 1H, H-4b, *J* 15.6 Hz), 3.73 (m, 8H, 4OCH$_2$), 3.90 (m, 4H, 2OCH$_2$), 4.12 (m, 4H, 2OCH$_2$), 6.53 (m, 1H, H-5), 6.60 (s, 1H, H-8), 7.04 (d, 1H, H-5′, *J* 8.9 Hz), 7.16 (s, 1H, H-2′) 7.37 (td, 1H, H-8′, *J* 8.1, 8.1 and 1.1 Hz), 7.56 (td, 1H, H-9′, *J* 8.1, 8.2 and 1.1 Hz), 7.69 (d, 1H, H-6′, *J* 8.9 Hz), 7.75 (d, 1H, H-7′, *J* 8.1 Hz), 8.59 (d, 1H, H-10′, *J* 8.2 Hz). Found (%): C, 69.69; H, 6.89; N, 5.20. Calc. for $C_{31}H_{36}N_2O_6$ (%): C, 69.90; H, 6.81; N, 5.26.



Scheme 2

a sandwich structure of (S-**2**)$_2$·Ba^{2+} (Scheme 2). This structure is caused by impossibility for Ba^{2+} cation to be located inside the crown ether ring. The equilibrium constants of the complexes were estimated from the comparison of the experimental dependencies of the relative changes in the UV spectra at a characteristic wavelength and the calculated dependencies of complex percentage in solution *vs.* ratios of the reagents concentrations [Figure 2(*b*)]. The measured equilibrium constants are given in Table 1.

Irradiation of a spiro form of SNO at 308 nm leads to the formation of a merocyanine (M) form (Scheme 3), which absorbs at 600 nm. The characteristic times of the back M → S transitions at a room temperature are about several seconds.

The kinetic features of the SNO M-forms, including that in the presence of the metal cations, are listed in Table 2. The introduction of a crown ether fragment does almost not affect the spectrum and kinetic characteristics of the SNO M-form.

When metal cations are added in a ratio close to 1:1, the formation of (M-**2**)$_2$·Ba^{2+} and (M-**2**)·Mg^{2+} complexes decreases the stability of the M-form. The rate constants of M → S reactions for these complexes at room temperature are 4 and 16 times higher than that for free M-**2** (Table 2). The reason of destabilization is probably the Coulomb repulsion between the metal ion and a positive charge of the M-form (N$^{\delta+}$), which is partly located on the nitrogen atom of a dihydroquinoline fragment. For the Ba^{2+} ion, the effect of destabilization is less than that for Mg^{2+} located inside the crown ether cavity. It is possible that for a sandwich structure like (M-**2**)$_2$·Ba^{2+} the screening of the Coulomb interaction between the metal cation and N$^{\delta+}$ is more sufficient than for the (M-**2**)·Mg^{2+} structure.

The increase in the concentration of metal ions to the [Me^{2+}]/[SNO] ratio of 100:1 leads to the stabilization of the open forms for both SNO **1** and SNO **2**. As this takes place, the activation energy of the M → S reaction, in all the cases, is *ca.* 15–20 kcal mol^{-1}, which is typical of all of the SNOs.[18] For SNO **1**, the rate constant of the M → S reaction drops in an order of magnitude (Table 2). The stabilization of M-form is accompanied by a hypsochromic shift of the maxima of M-form absorption bands [Figure 3(*a*)]. The effect of stabilization could probably be explained by the formation of the (M-**1**)·Ba^{2+} type complex (Scheme 2). Under the assumption of the linear dependence of the relative shift of the M-form absorption band maximum on the fraction of bound M-**1**, it is possible to estimate the equilibrium constant of the (M-**1**)·Ba^{2+} complex [Figure 3(*b*) and Table 1].

For the crowned SNO **2** the great extent in metal cations concentration leads to the drop of the rate constant of the M → S transition in an order of magnitude in comparison with (M-**2**)·Mg^{2+} and (M-**2**)$_2$·Ba^{2+} complexes. For both Mg^{2+} and

Table 1 Equilibrium constants of SNO complexes with metal cations.

Complex	K_{eq}
(S-**2**)·Mg^{2+}	5×10^5 dm^3 mol^{-1}
(S-**2**)$_2$·Ba^{2+}	> 1×10^{12} dm^6 mol^{-2} [a]
(M-**1**)·Ba^{2+}	1.5×10^3 dm^3 mol^{-1}
(M-**2**)·(Mg^{2+})$_2$	3×10^3 dm^3 mol^{-1} [b]

[a] The lower limit of the equilibrium constant is estimated. [b] The equilibrium constant of the (M-**2**)·(Mg^{2+})$_2$ complex is determined as K_{eq} = [(M-**2**)(Mg^{2+})$_2$]/[Mg^{2+}][(M-**2**)Mg^{2+}].

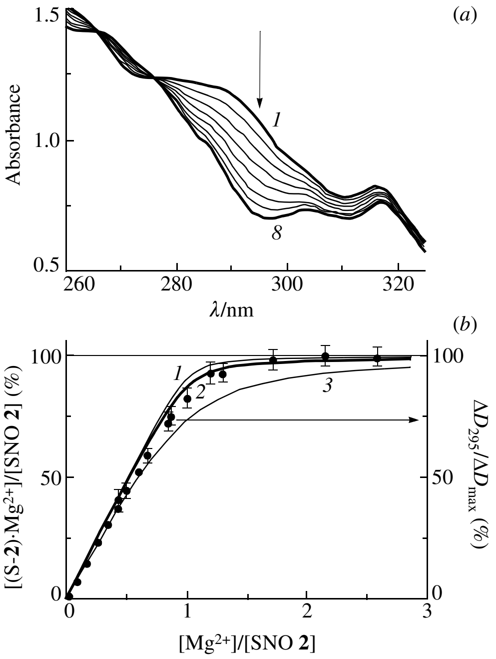
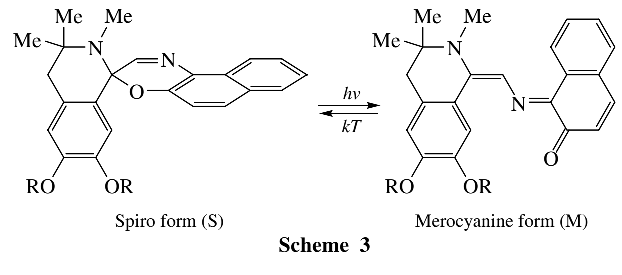


Figure 2 Complex formation of the SNO **2** spiro form with Mg^{2+} cations. (*a*) Changes in the UV spectrum of S-**2** in acetonitrile due to addition of Mg(ClO$_4$)$_2$. Temperature, 298 K; cuvette, 1 cm; initial concentration of SNO **2**, 1×10^{-4} M. Curves *1–8* correspond to the [Mg^{2+}]/[S-**2**] ratios equal to 0; 0.17; 0.33; 0.5; 0.66; 0.84; 1.0 and 1.2. (*b*) Estimation of the equilibrium constant. Dots (right axis) show relative changes in absorption at 295 nm. Solid lines (left axis) indicate the calculation of the percent content of the complex; curves *1–3* correspond to equilibrium constants of 1×10^6, 5×10^5 and 1×10^5 dm^3 mol^{-1}, respectively.



Scheme 3

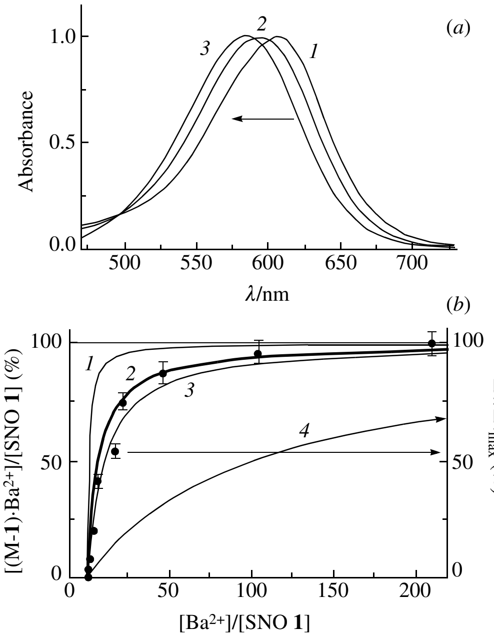


Figure 3 Complex formation between the M-form of SNO **1** and Ba^{2+} ions in MeCN. (*a*) Hypsochromic shift of the M-form absorption band caused by addition of Ba^{2+}. Curves *1–3* refer to $[Ba^{2+}]$/[SNO **1**] = 0; 17 and 104, respectively. Amplitudes of the bands are normalised to 1 in the maxima of M-form bands. (*b*) Determination of the equilibrium constants of the complex. Dots (right axis) show the dependence of the shift of M-form absorption band maxima on the relative initial concentration of Ba^{2+} [M-form was obtained by the photolysis (366 nm, 298 K) in the cuvette box of the HP 8453 spectrophotometer]. Solid lines (left axis) show the calculation of the percent content of the complex. Curves *1–4* correspond to equilibrium constants of 1×10^4; 1.5×10^3; 1×10^3 and 1×10^2 dm^3 mol^{-1}, respectively.

Ba^{2+}, the rate constant reaches the value which is 1.6 times lower than that in the absence of metal cations (Table 2). The stabilization effect of the great extent of metal cations could be explained by the same reason as in the case of SNO **1**, that is, by the addition of a metal ion to the oxygen atom of the (M-**2**)·Mg^{2+} complex. As a result, (M-**2**)-$(Mg^{2+})_2$ complex is formed (Scheme 2). The shift of the M-form absorption band maximum allows one to estimate the equilibrium constant of this complex (Table 1). For the Ba^{2+}–M-**2** system, the increase in the metal ions concentration could lead both to the conservation of the sandwich structure characteristic of (S-**2**)$_2$·Ba^{2+} complex and to the (S-**2**)·Mg^{2+} type structure. In the latter case, the Ba^{2+} cation would be located above the plane of the crown ether ring. Correspondingly, for the M-form one could assume the formation of either a (M-**2**)-$(Me^{2+})_2$ (as in the case of Mg^{2+}) complex or other structures.

In conclusion, we found the formation of different types of SNO complexes with metal cations. Complexation affects the spectral and kinetic properties of SNO, especially crown-containing one. And *vice versa*, conformation changes of SNO have a great effect on their ability to bind the metal cations. The crowned SNOs seem to be prospective systems for the production of photochromic materials, whose properties could be controlled by complex formation.

Table 2 Properties of the open form of SNO and their complexes with metal cations.

Complex (ligand-to-metal ratio)	λ^{M}_{max}/nm	$k_{M\to S}$ (298 K)/s^{-1}	E_{act}/kcal mol^{-1} [a]
Free M-**1**	607	0.26	21.4±1.2
(M-**1**)·Ba^{2+} (1:245)	581	0.037	17.2±1.6
Free M-**2**	607.5	0.28	20.7±1.4
(M-**2**)$_2$·Ba^{2+} (1:0.52)	607.5	0.99	—
(M-**2**)$_2$·Ba^{2+} (1:1.2)	607.5	1.2	—
(M-**2**)·$(Ba^{2+})_2$ (1:500)[b]	592	0.17	19.3±2.0
(M-**2**)·Mg^{2+} (1:1.22)	607.5	4.35	—
(M-**2**)·$(Mg^{2+})_2$ (1:157)	572	0.17	16.4±1.2

[a] The experimental error is taken as two standard deviations of the linear fit.
[b] For this complex another structures are also possible, see the text.

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