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Transformation of 6′-aminosubstituted spironaphthoxazines induced by Pb(II) and Eu(III) cations

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ABSTRACT: The transformation of spiroindolinonaphth[2,1-*b*][1,4]oxazines (SNOs) conjugated with aza-15(18)-crown-5(6) ether moieties or morpholine in the presence of Pb^{2+} or lanthanoid cations in MeCN solution was studied by UV–Vis, NMR and surface-enhanced resonance Raman scattering spectroscopy methods. The Pb^{2+} or Eu^{3+} cations induce the formation of the betaine merocyanine form of SNO. When the merocyanine complexes are kept in the dark, the corresponding oxazole derivatives are formed irreversibly and regioselectively. Copyright © 2005 John Wiley & Sons, Ltd.

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KEYWORDS: crown-containing spiroindolinonaphth[2,1-*b*][1,4]oxazine; synthesis; photochromic properties; metal ions; complexation; electrocyclic reaction

INTRODUCTION

Spiropyrans and spironaphthoxazines are members of a well-known class of photochromic compounds.[1–3] Practical applications of the compounds are based on their availability, photosensitivity, convenient thermal fade rates and good colour contrast, which makes them excellently perceived by the human eye.[4] There are various examples of the application of spiropyrans and spironaphthoxazines as photochromic elements for plastic ophthalmic sunglasses, optical memories, photocontrol units for polymeric materials, in bipolar membranes and in liquid crystalline solvents.[5–10]

The incorporation of an ionophore into a spiro compound affords a substance that responds optically to the presence of cations in solution. The study of the photochromic crown ethers is important with regard to the search for new types of materials whose spectral and photochromic properties are highly sensitive to the presence of metal cations in solution, and for which the metal–ligand binding constants of reversible photoconversions can be controlled effectively.[11–15]

In a previous paper[16] spironaphthoxazines (SNOs) conjugated with aza-15(18)-crown-5(6)-ether moieties at the 6′-position of a naphthalene fragment were synthesized and studied for the first time (Scheme 1, compounds **1a** and **1b**). The addition of Li^{+} and alkaline earth (Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}) metal cations to SNOs **1a** and **1b** solutions results in a hypochromic shift of the UV absorption band of the spiro form and a bathochromic shift of the absorption band of the merocyanine form in the visible region. In addition, the equilibrium is shifted towards the merocyanine form, and the lifetime of the photoinduced merocyanine form increases. Cation-induced formation of a merocyanine form was observed only in the presence of a large excess of Mg^{2+} cations. The successful combination of NMR, UV–Vis and surface-enhanced resonance Raman scattering (SERRS) spectroscopy allowed us to determine the structure of the complexes (Scheme 2).

In this paper we report on the transformation of SNOs **1a** and **1b** conjugated with the aza-15(18)-crown-5(6) ether moiety in the presence of Pb^{2+} and lanthanoid cations in MeCN. To explain the observed results, the model SNOs **2** and **3** were studied (Scheme 1). Synthesis of the compounds was reported earlier.[16,17]

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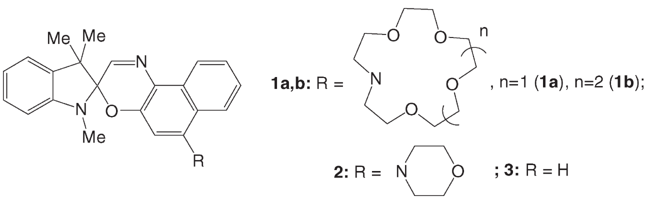


Scheme 1

RESULTS AND DISCUSSION

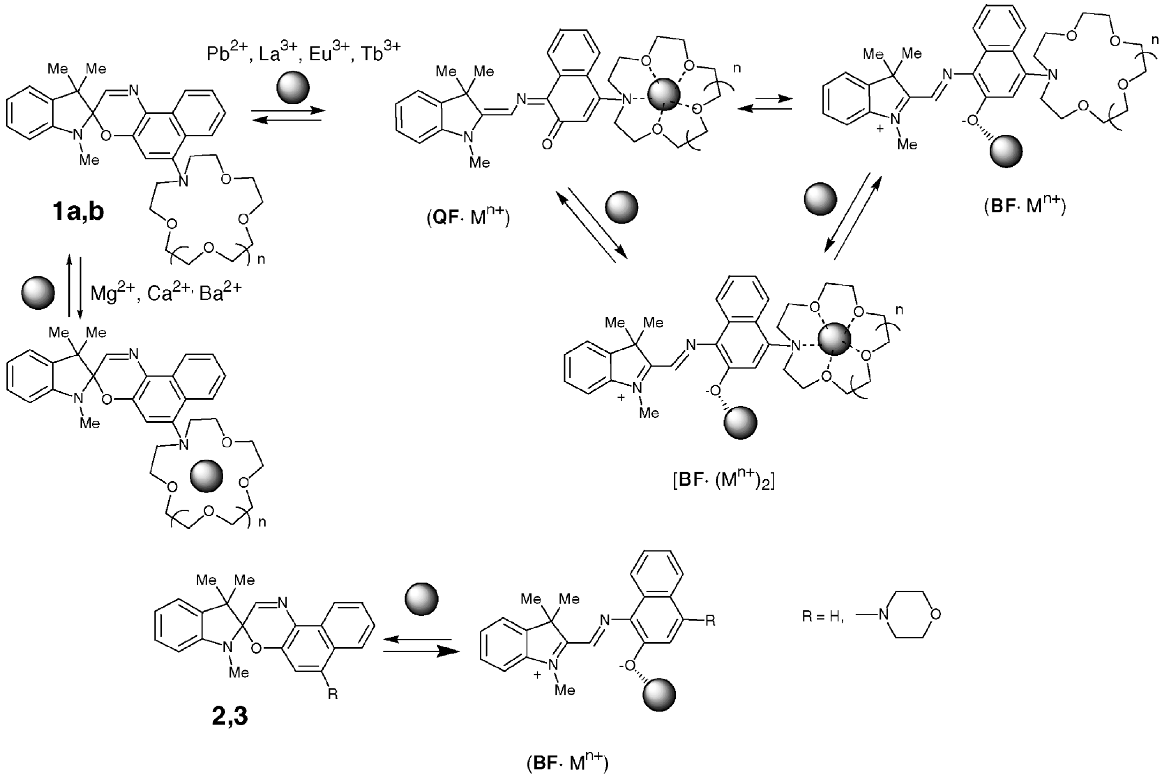
Effect of metal cations on the thermodynamic equilibrium between the spiro- and merocyanine forms

An addition of Pb^{2+} and lanthanoid perchlorates to solutions of **1a**, **1b**, **2** or **3** resulted in the cation-induced appearance of the merocyanine form (Fig. 1). The long-wavelength absorption band attributed to the merocyanine form appeared even at low concentrations of the studied metal cations. It is necessary to note that an addition of salt to amino-substituted SNOs **1a**, **1b** and **2** resulted in a more intense colouration compared with non-substituted SNO **3** at the same concentration of cations.

The spectrophotometric titration method combining ^1H NMR and SERRS spectroscopies was employed for analysis of the complexation processes. In the UV–Vis spectra, an addition of the salt to a solution of SNO **2** or SNO **3** was accompanied by an increase in the intensity of an absorption band of the merocyanine form, whereas an addition of the metal cations to a solution of SNO **1a** or **1b** led to both an intensity increase and a bathochromic shift of the long-wavelength absorption band. The optical effects of the complexation are related to the formation of complexes with different structures. Thus, the merocyanine form of compounds **2** and **3** is expected to form the complex with a metal cation via the oxygen atom of the betaine form ($BF{\cdot}M^{n+}$) (Scheme 2).[18] In the merocyanine form, crown-containing compounds **1a** and **1b** can form two types of complexes, being either in the betaine open form ($BF{\cdot}M^{n+}$) or the quinoid open form ($QF{\cdot}M^{n+}$) (Scheme 2). Both complexes have the same LM composition (L = ligand and M = metal cation). An equilibrium between these forms is determined by the relative ability of the crown ether fragment or the oxygen atom to bind the metal cation. An excess of metal cations in solution favours the formation of $[BF{\cdot}(M^{n+})_2]$ complex. The coordination of Pb^{2+} cations with the crown ether fragment is responsible for the bathochromic shift of the long-wavelength band in the UV–Vis spectra (Figure 1).

An addition of tenfold excess of Pb^{2+} cations to a solution of SNO **1a**, **2** or **3** in MeCN-d_3 led to changes in the ^1H NMR spectra of the compounds. The ^1H NMR spectra of both free and Pb^{2+}-complexed SNO **2** are shown in Fig. 2.

As follows from the spectra shown in Fig. 2, the presence of Pb^{2+} cations led to complete transformation of the closed spiro form into the open form. A similar



Scheme 2

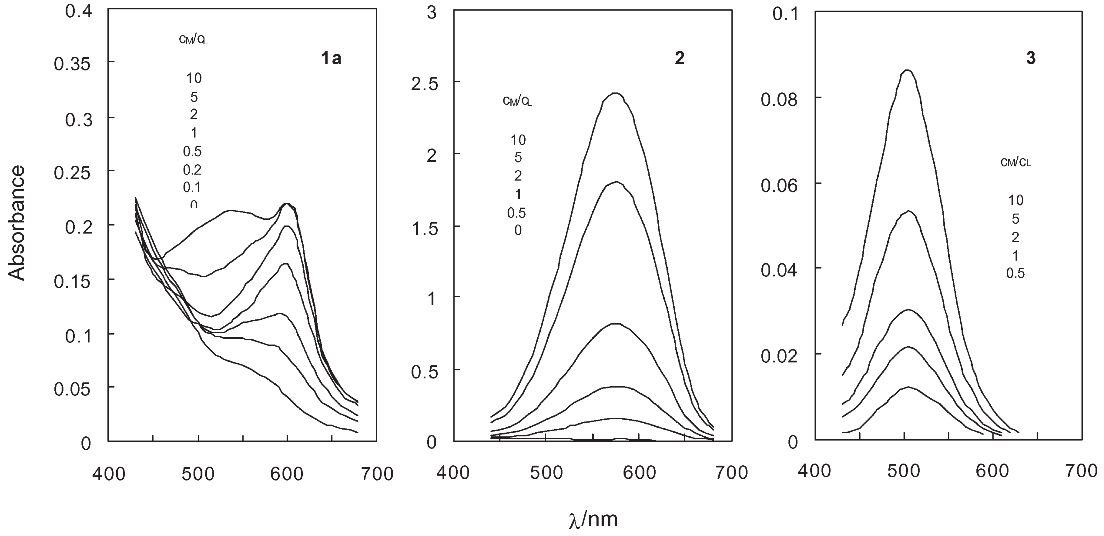


Figure 1. Absorption spectra of SNOs **1a**, **2** and **3** in the presence of Pb^{2+}cations ($C_{Pb}^{2+}/C_L = 0$–10; $C_L = 5 \times 10^{-5}$ mol l^{-1}) in MeCN at 25 °C

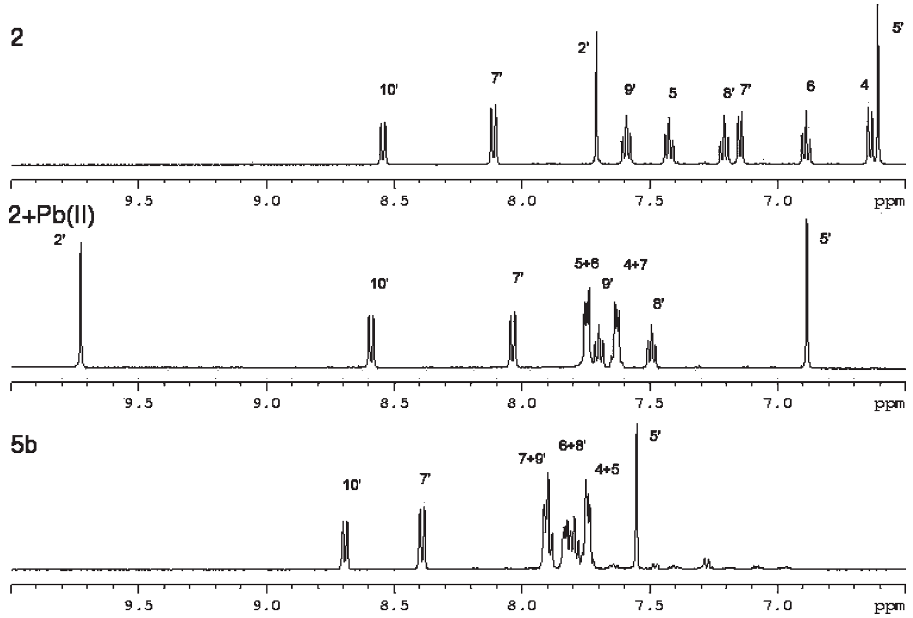


Figure 2. The ^{1}H NMR spectra of **2** ($C_L = 5 \times 10^{-3}$ mol l^{-1}), complex [**2**·Pb^{2+}] ($C_L = 5 \times 10^{-3}$ mol l^{-1}, $C_{Pb}^{2+} = 5 \times 10^{-2}$ mol l^{-1}) and product **5b** obtained after keeping complex [**2**·Pb^{2+}] for 168 h at 25° temperature ($C_{5b} = 5 \times 10^{-3}$ mol l^{-1}) in MeCN

complexation pattern was observed for SNOs **1a** and **1b** (see Experimental). A solution of SNO **3** in the presence of a tenfold excess of Pb^{2+} cations contains the equilibrium mixture of the initially closed spiro form and the open merocyanine form. Most probably, the presence of a donor substituent in SNOs **1a** and **2** is the reason for the higher electron density at the merocyanine oxygen atom, promoting its more efficient interaction with a metal cation.

Signals of the protons of the crown ether fragment in the ^{1}H NMR spectrum of the complex of SNO **1a** with Pb(ClO$_4$)$_2$ (see Table 1), compared with those of the free ligand, underwent a substantial downfield shift (~0.5–0.8 ppm) that indicated the formation of the complex via the crown ether fragment. On the contrary, signals of protons of the morpholine fragment of SNO **2** in the presence of Pb(ClO$_4$)$_2$ change their positions insignificantly (~0.1–0.3 ppm).

Signals of proton H-5′ of the naphthalene fragment in initial ligands **1a** and **2** were shifted upfield compared with the position of the signal of the identical proton in SNO **3** (Table 1). This fact is accounted for by the presence of the donor amino-substituent *ortho* to H-5′ in the naphthalene ring of **1a** or **2**. On the contrary, signals of proton H-5′ of the naphthalene nucleus in the complex of **1a** with Pb^{2+} cation is shifted downfield compared with those of SNOs **2** and **3** (Table 1). This fact is

Table 1. Position of the proton signals for SNOs **1a**, **2** and **3** and their complexes with Pb^{2+} cation in the ^1H NMR spectrum in MeCN-d_3 at 25 °C ($C_L = 5 \times 10^{-3}$ mol l^{-1}, $C_{Pb}^{2+} = 5 \times 10^{-2}$ mol l^{-1})

	$N(CH_2)_2$	$O(CH_2)_2$	$CH=N$	H-5′	H-6′	H-7′	H-8′	H-9′	H-10′
1a	3.40	3.51–3.59	7.72	6.9	—	8.30	7.42	7.59	8.54
[**1a**·Pb^{2+}]	**4.20**	**4.10**	9.89	**7.68**	—	8.33	7.68	7.82	8.70
2	3.05	3.88	7.71	6.61	—	8.15	7.45	7.59	8.51
[**2**·Pb^{2+}]	**3.37**	**3.98**	9.72	**6.89**	—	8.05	7.49	7.70	8.59
3	—	—	7.83	7.05		7.85	7.45	7.59	8.56
[**3**·Pb^{2+}]	—	—	9.90	**7.40**	7.93	8.02	7.54	7.73	8.55

additional evidence for the formation of a complex via the crown ether fragment of **1a**. It pointed out that the nitrogen atom of the crown ether moiety coordinates the metal cation, being unable to have a donor influence on the chromophore system.

Calculation of the stability constants for the described complexes (see Table 2) was carried out on the basis of the results of spectrophotometric titration. As follows from the titration curves and theoretical dependencies corresponding to the following complex formation model:

$$L + M \rightarrow LM(K_{11})$$

$$LM + M \rightarrow LM_2(K_{12})$$

The values of the stability constants for compound **1a** with Mg^{2+} and Pb^{2+} cations are higher than those determined for SNO **2**. The reason for the observed phenomenon is that in the complex with SNO **1a** the cation is located in a cavity of the crown ether moiety interacting with all the heteroatoms of the macrocycle. In contrast, in the complex of SNO **2** the cation coordinates only the single merocyanine oxygen atom.

Complexation of SNOs 1a and 2 with Eu^{3+} cations as probed by SERRS spectroscopy

The SERRS spectra of SNO **1a** and its complexes with Eu^{3+} are shown in Fig. 3. According to previous studies,[16,19] the Raman bands of the merocyanine form of SNO **1a** dominate in the SERRS spectra. The bands of both naphthalene and indolinic fragments are observed in the SNO **1a** spectrum (Fig. 3(c)), but assignment of the Raman vibrational modes to a particular molecular moiety is complicated.[19] Vibrations of the aza-crown ether moiety are out of resonance with the electronic transition and, accordingly, give no contribution to the SERRS spectrum.[19] There are two isomers of the merocyanine form of SNO **1a** in solution that differ in the configuration of =C—N=bridge. These are *trans-trans-cis* (*ttc*) and *cis-trans-cis* (*ctc*) isomers, which are characterized by the 1540 and 1558 cm^{-1} bands, respectively.[19] This conformation-sensitive band was assigned to the coupled double-bond stretching mode of the conjugated polyene-like chain of SNO **1a**.

Table 2. Stability constants of complexes **1a** and **2** with Mg^{2+} and Pb^{+2} in MeCN at 25 °C ($C_L = 2 \times 10^{-4}$ mol l^{-1}, $C_{Pb}{}^{2+}/C_L = 0$–10)

	[**2**·Mg^{2+}]	[**2**·Pb^{2+}]	[**1a**·Mg^{2+}]	[**1a**·Pb^{2+}]
$\log K_{11}$	0.6	2.8	2.5	4.0
$\log K_{12}$				4.4

Complexation of SNO **1a** with Eu^{3+} is accompanied by alterations in the relative intensity of the SERRS bands: the 474 cm^{-1} band is attenuated and the 650, 928, 1092, 1126 and 1558 cm^{-1} bands are enhanced (Figs 3(a)–3(c)). Moreover, the 924 cm^{-1} band undergoes a 4 cm^{-1} up-shift in the presence of Eu^{3+}. These spectral changes

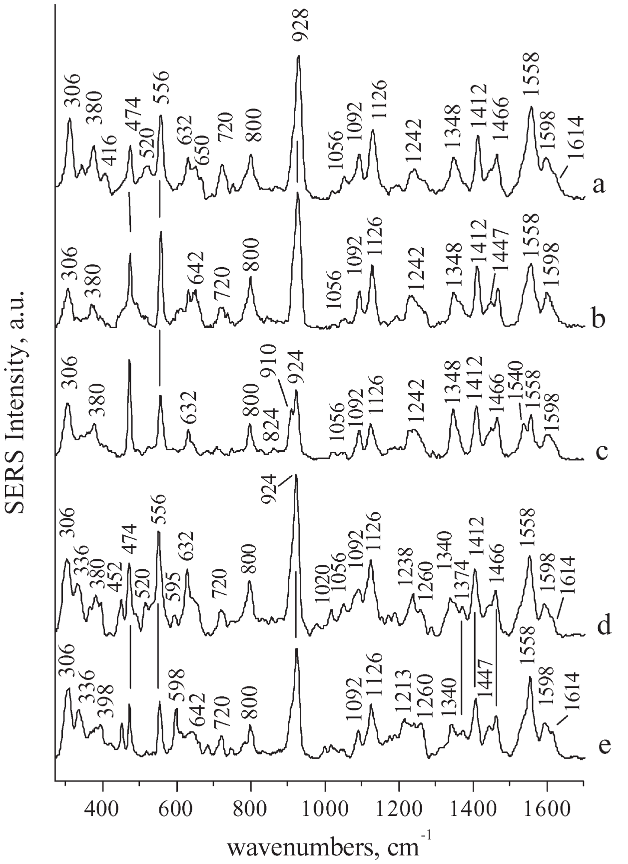


Figure 3. The SERRS spectra of SNO **1a** (c), complexes of SNO **1a** with Eu^{3+} (a, b), SNO **2** (e) and complexes of SNO **2** with Eu^{3+} (d): (a), $C_{Eu}{}^{3+}/C_L = 1$; (b) $C_{Eu}{}^{3+}/C_L = 10$; (d) $C_{Eu}{}^{3+}/C_L = 10$, $C_L = 0.2$ mmol l^{-1}

occur gradually in the range of C_M/C_L molar ratios of 1–10 (Figs 3(a)–3(c)). Further increase in the C_M/C_L ratio does not affect the SERRS spectrum. The same changes in the SERRS spectra were observed for the binding of Pb^{2+} with SNO **1a**. The relative enhancement of the 1558 cm^{-1} band indicates that the complexation of SNO **1a** with Eu^{3+} stabilizes the single *ctc* isomer of [(BF**1a**)·Eu^{3+}]. No evidence for a two-stage interaction between SNO **1a** and Eu^{3+} cations was revealed in the SERRS spectra, although the merocyanine form of SNO **1a** has two cation-binding sites (aza-crown ether unit and merocyanine oxygen).

This result differs from that obtained earlier[16] for Mg^{2+} cations, when a two-stage interaction of Mg^{2+} with the merocyanine form of SNO **1a** was detected distinctly. Initially, the Mg^{2+} cation formed a complex with the aza-crown moiety of SNO **1a**. This stage was distinguished at the low C_M/C_L ratio due to enhancement of the 1540 cm^{-1} band (i.e. the *ttc* isomer stabilization) and the appearance of new bands at 416, 642, 688, 776, 824 and 1146 cm^{-1}. No sign of such interaction is found in the [(BF**1a**)·Eu^{3+}] spectra (Figs 3(a) and 3(b)).

Interaction of the second Mg^{2+} cation with the merocyanine oxygen occurred upon increasing the C_M/C_L ratio, as revealed by gradual attenuation of the above-listed bands and alterations corresponding to the *ttc* to *ctc* isomerization. All the changes finished at a C_M/C_L ratio of 100 and resulted in a spectrum that was very similar to the [(BF**1a**)·Eu^{3+}] spectrum (Fig. 3(a)).

This similarity allows us to suppose that the interaction of Eu^{3+} and Pb^{2+} with the merocyanine oxygen of SNO **1a** occurs earlier or in parallel with complexation of the cations by the aza-crown moiety. This supposition was confirmed by experiment when the Eu^{3+} cations were added to the solution of SNO **2** (Figs 3(d) and 3(e)). A remarkable resemblance between the SERRS spectra of free SNOs **1a** and **2** and their spectral changes induced by Eu^{3+} cations is clearly seen (Fig. 3). Taking into account that the merocyanine oxygen is the only cation-binding site of SNO **2**, it is reasonable to conclude that the changes observed in the [(BF**1a**)·Eu^{3+}] spectra (Figs 3(a) and 3(b)) also originate from complexation of Eu^{3+} with the merocyanine oxygen of SNO **1a**.

As shown above, the interaction between Eu^{3+} and merocyanine oxygen begins at the low C_M/C_L ratio. Here, the SERRS data are in agreement with the results of the spectrophotometric titration. The triple charge of the cation seems to favour interaction with the oxygen of the betaine form, whereas the large size of Eu^{3+} diminishes its affinity to the aza-crown unit.

Irreversible processes with participation of complexes of the merocyanine form

The complexes of SNOs **1a**, **1b**, **2** and **3** with cations of lanthanoid and Pb^{2+} metals are characterized by a slow (several days) dark process that leads to the formation of a new product with absorption (~500 nm) shifted to shorter wavelengths with respect to that of the initial complexes.

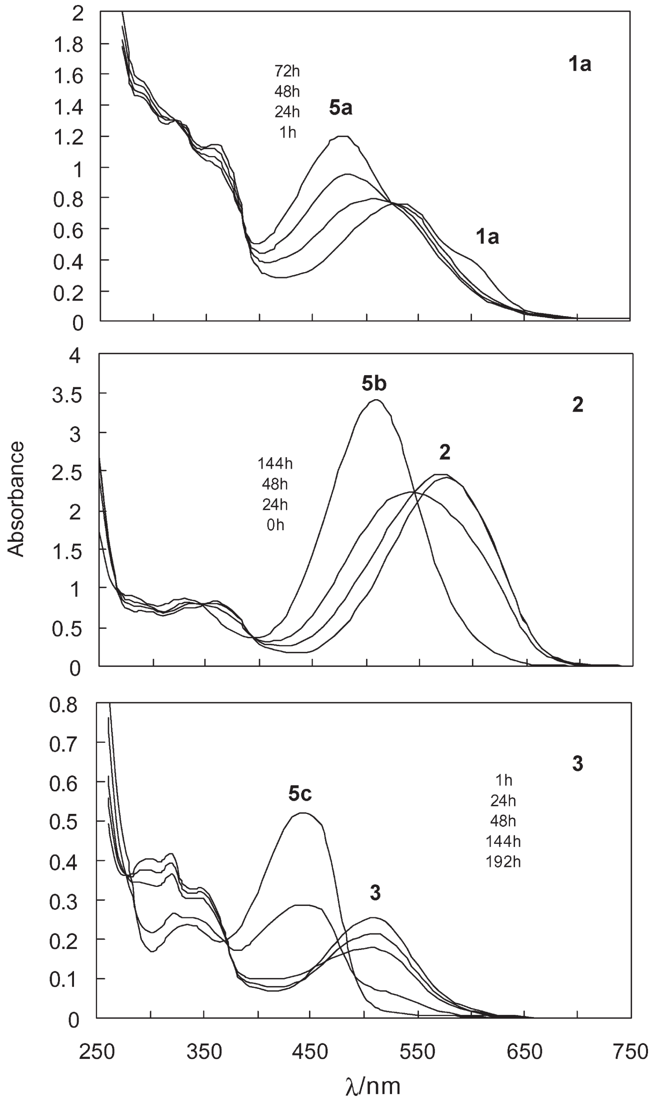


Figure 4. Changes in absorption spectra of SNOs **1a, 2** and **3** in MeCN kept in the dark at 25 °C in the presence of Pb^{2+} cations ($C_{Pb}^{2+}/C_L = 10$, $C_L = 5 \times 10^{-5}$ mol l^{-1}): SNO **1a**, 0–80 h; SNO **2**, 0–150 h; SNO **3**, 0–200 h

Figure 4 presents the time dependence of the absorption spectra of SNOs **1a**, **2** and **3** observed upon the addition of $Pb(ClO_4)_2$ to an acetonitrile solution of the SNO ([M]/[L] = 10). As can be seen, the complex of Pb^{2+} cations with the merocyanine form of SNOs **1a**, **2** and **3** disappears with subsequent transformation to a new product that absorps in a shorter wavelength region. Spectral properties of the final product do not depend on the nature of the metal cation, being the same in the presence of either lanthanoid or lead salts in solutions. The position of an absorption band of the product does not depend on the concentration of the metal salt in solution, whereas the kinetics of the formation of this product depends on the nature and concentration of the metal cations. Thus, disappearance of the complexes of **1a**, **2** and **3** with Pb^{2+} and the formation of the product occurs faster with europium salts (48 h for **1a**, 120 h for **2** and 144 h for **3**) than with those of lead (72 h for **1a**, 144 h for **2** and 198 h for **3**). Transformation of the SNO to the product is not defined by the initial concentration of complexes of the merocyanine form, which means that product formation is accompanied by the release of metal cations with their subsequent participation in the formation of new complexes of merocyanine form.

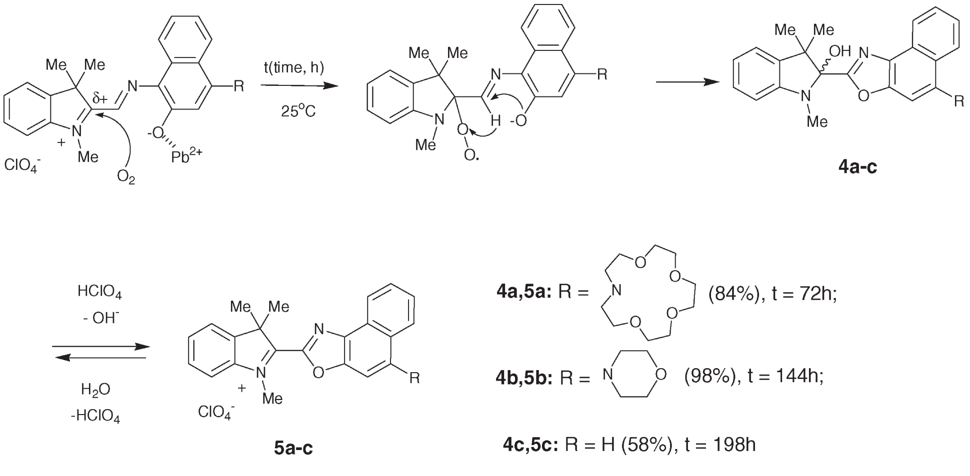
Structures of the transformation products were determined on the basis of data obtained by ^1H NMRs spectroscopy. The ^1H NMR spectrum of the complex of SNO **2** with Pb^{2+} cations after 168 h in the dark is shown in Fig. 2 (bottom). Analysis of the spectrum revealed the formation of an oxazole derivative. The possible mechanism of the dark process is presented in Scheme 3. We assume the initial interaction of an oxygen molecule with a complex of merocyanine form. Attachment of the oxygen is followed by an electrocyclic reaction by C-2′ and the formation of **4a**–**4c** and then **5a**–**5c** (Scheme 3). The role of dissolved oxygen in the above-described process was confirmed by the experimental results. Thus, keeping the complex of SNO **2** with Pb^{2+} under an inert atmosphere results in practically complete inhibition of transformation into the oxazole derivative.

Compounds **4a**–**4c** are easily converted to **5a**–**5c**, and vice versa. It was found that addition of water to a solution of compound **5a** resulted in the formation of **4a**, and the reverse reaction was observed upon acidification of the **4a** solution (see Experimental). The formation of compound **5c** and its derivatives was described in several recent papers.[18,20–24] In Ref. 20 it was noted that an irradiation of SNO **3** in presence of salts of copper, iron and chromium led to the appearance of a new fluorescent product. However, the structure of compound **5c** was not determined. Malatesta *et al.*[21,22] studied in detail the mechanism of thermal formation of methyl-substituted **5c** in the presence of an appropriate electron acceptor. In one of our recent papers[18] devoted to the study of benzothiazole SNOs we have extracted and characterized the crown-containing analogue of **5c**, and P. Uznanski *et al.*[23,24] have reported the thermal or photooxidation of SNO in the presence of gold or silver salts under deoxygenated conditions with the formation of a number of oxidation products, including **5c** (silver and gold are expected to be the oxidation agents in these cases).

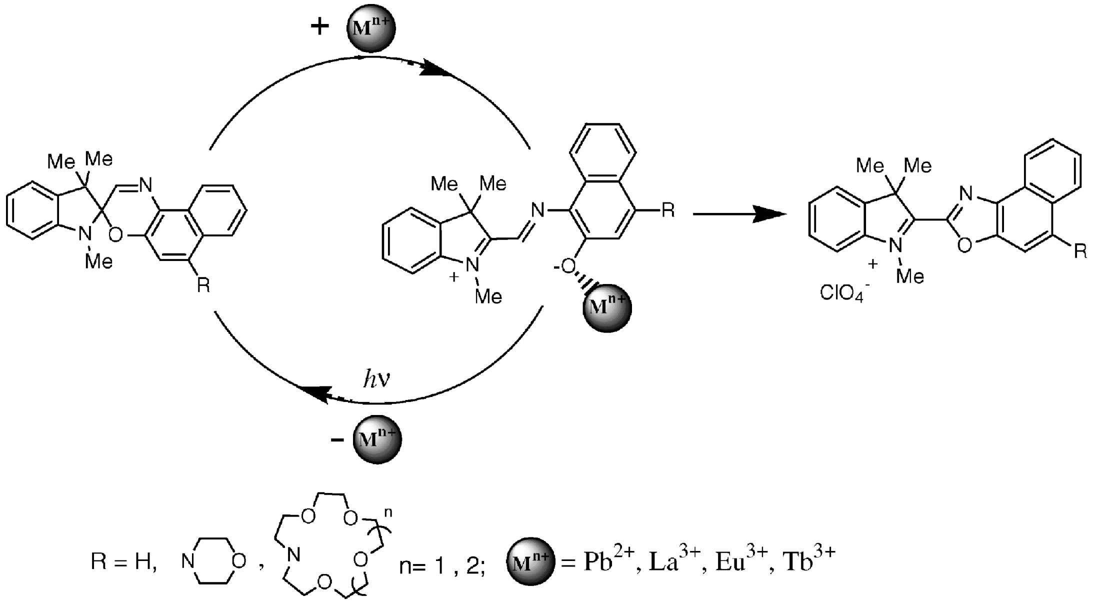
The discovered transformation of SNOs **1a**, **1b**, **2** and **3** has a number of analogies and discrepancies compared with previously known cases. We suppose that the presence of the betaine form of the spiro compound in solution is necessary for the formation of oxazole derivatives. As shown earlier,[18] the betaine form presents a different distribution of electronic density and bond lengths. Accordingly, in the betain form there is a site deficient in electronic density that is, able to be attacked by the dissolved oxygen.

The mechanism of formation of the oxazole derivatives in our case is similar to that described by Malatesta *et al.*[21,22] However, in the secited papers either irradiation or addition of electron acceptors was utilized to promote formation of the oxazole derivatives, whereas we have dealt with the dark process. Apparently, Pb^{2+} and lanthanoid cations promote the shift in equilibrium towards the betaine open form.

The H^1 NMR spectrum of the complex of **2** with Pb^{2+} cations after keeping in the dark for 7 days at room temperature is presented in Fig. 2 (bottom). In this case, only oxidation product **5b** was observed. An identical situation was discovered for **1a**, but the process ran out after 20 h. Hence, complexation via the crown ether fragment leads to acceleration of the formation of oxazole derivatives. In the case of non-substituted SNO **3** the oxidation process ran slowly (for 2 weeks) and was accompanied by partial degradation of the initial compound. As mentioned above, this is evidently related to the fact that cation-induced formation of the betaine open form is the most difficult to occur in the case of compound **3**.



Scheme 3



Scheme 4

CONCLUSION

To summarize, our investigations revealed that SNOs **1a**, **1b**, **2** and **3** in the presence of Pb^{2+} and lanthanoid cations tend towards cation-induced formation of the betaine open form of the compound, which can return to the initially closed non-coloured form by irradiation with light. Keeping the complexes in the dark leads to a regioselective process of high-yield formation of the oxazole derivatives (Scheme 4).

Because the presence of Pb^{2+} and lanthanoid cations in a solution of aminosubstituted SNO leads to the appearance of bright colouration, these compounds can be considered as candidates for the development of chemical sensors. Structural variation of the crown ether fragment of the molecule can be used for attaining selectivity of the colour reaction for the particular type of metal cation.

EXPERIMENTAL

Synthesis and NMR investigation

The ^1H NMR spectra were recorded on Bruker AMX-400 and Bruker DRX-500 spectrometers using tetramethylsilane (TMS) as the internal standard and CD_3CN as the solvent. The chemical shifts and the spin–spin coupling constants were determined with accuracies of 0.01 ppm and 0.1 Hz, respectively.

The SNOs **1a**, **1b**, **2** and **3** were synthesized as described in Refs 16 and 17.

Complex of 1,3,3-trimethyl-6-(1,4,7,10-tetraoxa-13-azacyclopentadec-13-yl)spiro{indolino-2,3′-[3*H*]naphtho[2,1-*b*]oxazine} (1a) with Pb^{2+}. To a solution of 0.005 mmol of **1a** in MeCN-d_3, 0.05 mmol of $Pb(ClO_4)_2$ was added. The solution was used for NMR analysis. ^1H NMR (MeCN-d_3, δ in ppm, J in Hz): **1a:** 1.34 (s, 6H, $2CH_3$); 2.74 (s, 3H, NCH_3); 3.41 (m, 4H, $2NCH_2$), 3.51 (m, 4H, $2OCH_2$); 3.59 (s, 12H, $6OCH_2$); 6.63 (d, 1H, H-4, $J = 7.7$); 6.88 (m, 2H, H-6, H-5′); 7.14 (d, 1H, H-7, $J = 7.1$); 7.20 (dd, 1H, H-5, $J = 7.5$, $J = 7.2$); 7.42 (dd, 1H, H-8′, $J = 7.1$, $J = 8.1$); 7.59 (dd, 1H, H-9′, $J = 7.3$, $J = 7.2$); 7.72 (s, 1H, H-2′); 8.30 (d, 1H, H-7′, $J = 8.5$); 8.54 (d, 1H, H-10′, $J = 8.3$); [**1a**·Pb^{2+}]: 1.36 (s, 6H, $2CH_3$); 3.60 (m, 4H, $2NCH_2$), 4.10 (m, 4H, $2OCH_2$); 4.20 (s, 12H, $6OCH_2$); 4.25 (s, 3H, NCH_3); 7.20 (d, 1H, H-4, $J = 7.5$); 7.68 (m, 3H, H-7, H-5′, H-8′); 7.82 (m, 3H, H-5, H-6, H-9′); 8.33 (d, 1H, H-7′, $J = 8.0$); 8.70 (d, 1H, H-10′, $J = 8.5$); 9.89 (s, 1H, H-2′).

Complex of 1,3,3-trimethyl-6-(4-morpholino)spiro-{indolino-2,3′-[3*H*]naphtho[2,1-b]oxazine} (2) with Pb^{2+}. This complex was prepared in a similar way from **2** and $Pb(ClO_4)_2$. ^1H NMR (MeCN-d_3, δ in ppm, J in Hz): **2:** 1.34 (s, 6H, $2CH_3$); 2.74 (s, 3H, NCH_3); 3.05 (m, 4H, $2NCH_2$), 3.88 (m, 4H, $4OCH_2$); 6.61 (s, 1H, H-5′); 6.63 (d, 1H, H-4, $J = 7.8$); 6.89 (dd, 1H, H-6, $J = 7.5$, $J = 6.9$); 7.15 (d, 1H, H-7, $J = 7.3$); 7.22 (dd, 1H, H-5, $J = 7.8$, $J = 7.6$); 7.45 (dd, 1H, H-8′, $J = 7.1$, $J = 8.1$); 7.59 (dd, 1H, H-9′, $J = 8.2$, $J = 7.2$); 7.71 (s, 1H, H-2′); 8.15 (d, 1H, H-7′, $J = 8.5$); 8.51 (d, 1H, H-10′, $J = 8.5$); [**2**·Pb^{2+}]: 1.93 (s, 6H, $2CH_3$); 3.37 (m, 4H, $2NCH_2$), 3.98 (m, 4H, $2OCH_2$); 4.12 (s, 3H, NCH_3); 6.89 (s, 1H, H-5′); 7.49 (dd, 1H, H-8′, $J = 7.1$, $J = 8.1$); 7.63 (m, 2H, H-4, H-7); 7.70 (dd, 1H, H-9′, $J = 8.4$, $J = 8.2$); 7.75 (m, 2H, H-5, H-6); 8.05 (d, 1H, H-7′, $J = 8.3$); 8.59 (d, 1H, H-10′, $J = 8.4$); 9.72 (s, 1H, H-2′).

Complex of 1,3,3-trimethylspiro(indolino-2,3′-[3*H*] naphtho[2,1-b]oxazine) (3) with Pb^{2+}. This complex was prepared in a similar way from **3** and $Pb(ClO_4)_2$. ^1H

NMR (MeCN-d_3, δ in ppm, J in Hz): **3:** 1.32 and 1.35 (2s, 6H, 2CH_3); 2.76 (s, 3H, NCH_3), 6.64 (d, 1H, H-4, $J = 7.8$); 7.03 (dd, 1H, H-6, $J = 7.4$, $J = 7.3$); 7.05 (d, 1H, H-5′, $J = 8.9$); 7.15 (d, 1H, H-7, $J = 7.6$); 7.22 (dd, 1H, H-5, $J = 8.5$, $J = 6.8$); 7.45 (dd, 1H, H-8′, $J = 7.0$, $J = 7.0$); 7.59 (dd, 1H, H-9′, $J = 7.2$, $J = 7.3$); 7.78 (d, 1H, H-6′, $J = 8.9$); 7.83 (s, 1H, H-2′); 7.85 (d, 1H, H-7′, $J = 7.7$); 8.56 (d, 1H, H-10′, $J = 8.5$); [**3**·Pb^{2+}]: 1.32 and 1.35 (2s, 6H, 2CH_3); 2.76 (s, 3H, NCH_3), 7.40 (d, 1H, H-5′, $J = 8.9$); 7.54 (dd, 1H, H-8′, $J = 7.10$, $J = 7.1$); 7.73 (m, 3H, H-5, H-6, H-9′); 7.84 (d, 1H, H-4, $J = 7.2$); 7.89 (d, 1H, H-7, $J = 7.4$); 7.93 (d, 1H, H-6′, $J = 8.0$); 8.02 (d, 1H, H-7′, $J = 9.0$); 8.55 (d, 1H, H-10′, $J = 8.5$); 9.90 (s, 1H, H-2′).

1,3,3-Trimethyl-2-[5′-(1,4,7,10-tetraoxa-13-azacyclopentadec-13-yl)naphtho[2,1-*d*]oxazol-2′-yl]-3*H*-indolinium perchlorate (5a). A solution of 0.012 g (0.005 mmol) of **1a** and 0.023 g (0.05 mmol) of $Pb(ClO_4)_2$ in 20 ml of MeCN was kept at ambient temperature for 20 h. The solvent was evaporated and the residue was recrystallized from MeOH. The yield of **5a** was 0.46 g (84%), m.p. 279–181 °C. ^{1}H NMR (MeCN-d_3, δ in ppm, J in Hz): 1.44 (s, 6H, 2CH_3); 3.65–4.20 (m, 20H, 2NCH_2 + 8OCH_2); 4.74 (s, 3H, NCH_3); 7.75 (m, 2H, H-4, H-5); 7.87 (m, 2H, H-6, H-8′); 7.88 (s, 1H, H-5′); 7.96 (m, 1H, H-7, H-9′), 8.60 (d, 1H, H-7′, $J = 8.2$); 8.80 (d, 1H, H-10′, $J = 7.3$). Found (%): C, 49.28; H, 5.15; N, 5.41. $C_{32}H_{38}ClN_3O_9 \cdot 2H_2O \cdot HClO_4$. Calculated (%): C, 49.19; H, 5.50; N, 5.38.

1,3,3-Trimethyl-2-[5′-(1,4,7,10-tetraoxa-13-azacyclopentadec-13-yl)naphtho[2,1-*d*]oxazol-2′-yl]-1*H*-indol-2-ol (4a). Heating of **5a** in distilled water results in full conversion to **4a**, m.p. 141–146 °C. ^{1}H NMR (MeCN-d_3, δ in ppm, J in Hz): 1.34 (s, 6H, 2CH_3); 2.74 (s, 3H, N- CH_3); 3.20–3.70 (m, 20H, 2NCH_2 + 8OCH_2); 6.63 (d, 1H, H-4, $J = 7.8$); 6.85 (dd, 1H, H-5, $J = 7.5$, $J = 7.5$); 7.05 (d, 2H, H-7, $J = 6.8$); 7.13 (dd, 1H, H-6, $J = 7.9$, $J = 7.7$); 7.58 (dd, 1H, H-8′, $J = 7.9$, $J = 7.2$); 7.68 (dd, 1H, H-9′, $J = 7.0$, $J = 7.9$); 7.81 (s, 1H, H-5′); 8.31 (d, 1H, H-7′, $J = 8.1$); 8.43 (d, 1H, H-10′, $J = 8.4$). Found (%): C, 66.17; H, 6.95; N, 6.97. $C_{32}H_{39}N_3O_6 \cdot H_2O$ Calculated (%): C, 66.30; H, 7.13; N, 7.25.

1,3,3-Trimethyl-2-[5′-(4-morpholino)naphtho[2, 1-*d*] oxazol-2′-yl]-3*H*-indolinium perchlorate (5b). This compound was prepared in a similar way as described for **5a** from **2** and $Pb(ClO_4)_2$ and the time of reaction is 168 h. The yield of **5b** was 98%, m.p. 228–230 °C. ^{1}H NMR (MeCN-d_3, δ in ppm, J in Hz): 2.10 (s, 6H, 2CH_3); 3.33 (m, 4H, 2NCH_2), 4.02 (m, 4H, 4OCH_2); 4.64 (s, 3H, NCH_3); 7.56 (s, 1H, H-5′); 7.75 (m, 2H, H-4, H-5); 7.83 (m, 2H, H-6, H-8′); 7.91 (m, 1H, H-7, H-9′), 8.40 (d, 1H, H-7′, $J = 8.4$); 8.60 (d, 1H, H-10′, $J = 8.4$). Found (%): C, 57.04; H, 5.46; N, 7.63. $C_{26}H_{27}ClN_3O_6 \cdot 2H_2O$. Calculated (%): C, 56.99; H, 5.52; N, 7.67.

1,3,3-Trimethyl-2-naphtho[2,1-*d*]oxazol-2-yl-3*H*-indolinium perchlorate (5c). This compound was prepared in a similar way as described for **5a** from **3** and $Pb(ClO_4)_2$ and the time of reaction is 320 h. The yield of **5c** was 58%, m.p. 164–167 °C.[23] ^{1}H NMR (MeCN-d_3, δ in ppm, J in Hz): 1.96 (m, 6H, 2CH_3); 4.73 (s, 3H, NCH_3); 7.82 (m, 3H, H-5, H-6, H-8′); 7.88 (d, 1H, H-4, $J = 7.0$); 7.94 (dd, 1H, H-9′, $J = 7.3$, $J = 7.8$), 7.98 (d, 1H, H-7, $J = 7.8$); 8.06 (d, 1H, H-5′, $J = 9.1$); 8.24 (d, 1H, H-7′, $J = 8.2$); 8.36 (d, 1H, H-6′, $J = 9.1$); 8.75 (d, 1H, H-10′, $J = 8.2$). Found (%): C, 45.71; H, 4.75; N, 4.84. $C_{22}H_{19}ClN_2O_5 \cdot 2H_2O \cdot HClO_4$. Calculated (%): C, 45.41; H, 4.47; N, 4.81.

UV–Vis spectroscopy

Electronic absorption spectra were measured on a Shimadzu UV-3100 spectrophotometer.

Acetonitrile (Aldrich, water content 0.005%) was used as solvent and analytical-grade magnesium, lead and europium perchlorates were used for the investigations without additional purification.

To mesure the stability constants, the procedure described in Ref. 16 was applied.

SERRS experiments

The SERRS spectra were measured using an electrochemically roughened silver electrode as a SERRS-active substrate, prepared for SERRS experiments as described elsewhere.[16]

The SERRS spectra were recorded with a Ramanor HG-2S spectrometer (Jobin Yvon, France) in the 200–1800 cm^{-1} range (1 cm^{-1} increment, 1 s integration time) and averaged over three scans. The excitation wavelength of the Krion laser (Spectra-Physics, Model 164-03) was 647.1 nm and the laser power was 20 mW.

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