

# Effect of complexation on the photochromism of 5'-(benzothiazol-2-yl)spiroindolinonaphthooxazines in polar solvents

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## Abstract

Complexation of Ni(II), Co(II) and Zn(II) with the photomerocyanines obtained under steady irradiation of spiroindolinonaphthooxazines containing benzothiazolyl substituent in the naphthooxazine moiety induces a slight hypsochromic shift of its visible absorption band and drastically slows down its thermal bleaching in the dark. As a result, the relaxation time at 20°C ranges from 2 to 42 min, the actual value depending on the metal ion and compound. High 'colourabilities' up to  $5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  ( $\epsilon = 6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) are calculated from the absorbance values obtained by extrapolation to  $t=0$  of the room temperature linearly descending kinetic curves  $\ln A/t$ . Complexation with Ni(II), Co(II) and Zn(II) allows the spiroindolinonaphthooxazines to isomerize to their open-coloured form even under dark conditions giving a complex spectroscopically identical to the photoinduced product and greatly increasing its lifetime to several days.

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**Keywords:** Photochromism; Spiroindolinonaphthooxazines; Complexation; Spectral properties; Kinetics

## 1. Introduction

There is technical interest in photochromic materials based on spiro-compounds [1–8], in which the coloured photomerocyanine once produced cannot revert back to the colourless spiroform, or at least the reversion rate is greatly retarded [9–11]. One way of achieving this is to try to trap the photomerocyanine in a metal-chelated form [12–22], by having suitable substituents in the spiro-compound and metal ions in the solution. This approach has been reported for spiropyranes [12–19] and in single cases for spirooxazines [20–22].

In this paper, we have studied the photochemical and kinetic behaviour of several spiro[indolinonaphthooxazines] (SO), recently synthesized in our laboratory, containing benzothiazolyl substituent in the naphthooxazine moiety as a potential chelating functional group [23] and their metal ion complexation ability in stabilizing the coloured merocyanine (MC) form.

Thermal equilibrium between the closed and opened form in Scheme 1 is also affected by the change in solvent polarity [23,24], since polar solvents promote the formation of the coloured form at room temperature in the absence of light. The equilibrium between both forms is strongly displaced upon irradiation to the side of open-chain coloured photomerocyanine and spontaneously converts to the colourless spiroform to reach thermal equilibrium immediately after removing the light [24]. Here, we report our results on the possibility to stabilize the coloured MC form towards thermal reversion by complexation with selected metal ions in appropriate solvents.

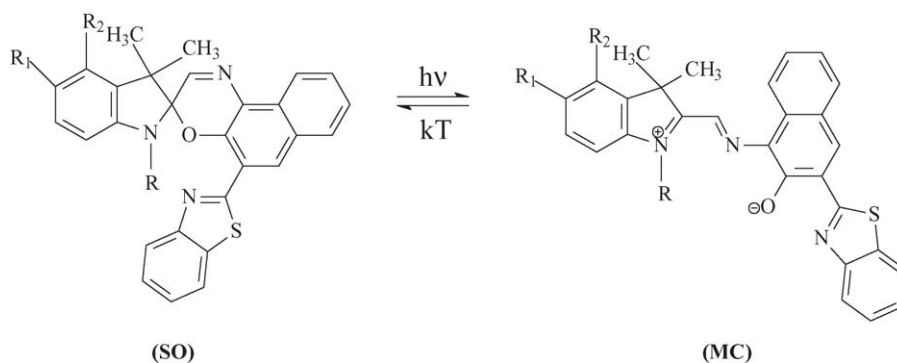
## 2. Experimental

### 2.1. Materials

The molecules under study were four spiro[indolinonaphthooxazines]: 1,3,3-trimethyl-5'-(2-benzothiazolyl)-spiro(indoline-2,3'-[3H]naphtho[2,1-b][1,4]oxazine) (**1**); 1-butyl-3,3-dimethyl-5'-(2-benzothiazolyl)-spiro(indoline-

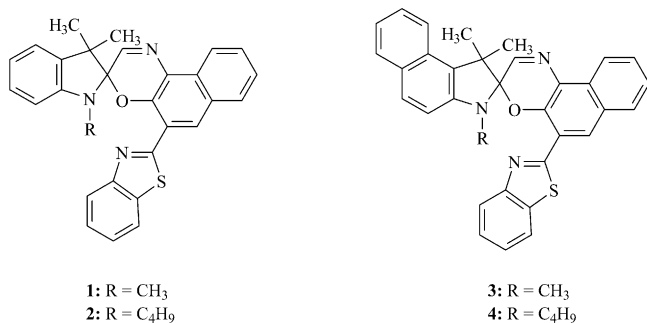
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Scheme 1.

2,3'-[3H]naphtho[2,1-b][1,4]oxazine] (2); 1,3,3-trimethyl-5'-(2-benzothiazolyl)-spironaphth(indoline-2,3'-[3H]naphtho[2,1-b][1,4]oxazine) (3) and 1-butyl-3,3-dimethyl-5'-(2-benzothiazolyl)-spironaphth(indoline-2,3'-[3H]naphtho[2,1-b][1,4]oxazine) (4).



The photochromic molecules were recently prepared and characterized in our laboratory [23,24]. The p.a. grade metal nitrates were obtained from Fluka and were used without further purification. The solvents were used after distillation.

## 2.2. Instruments

Visible absorption spectra were recorded on a SPECORD UV-vis (Carl Zeiss, Jena) spectrophotometer using the range of 350–750 nm. For absorption measurements at varying temperatures the reaction cell was enclosed in a thermostatic water jacket placed inside the spectrophotometer sample chamber. Continuous photolysis experiments were performed using a 250 W medium-pressure mercury lamp equipped with a shutter and housed in a light box. Photochemical reactions were carried out in the spectrophotometric quartz cell with a homogeneously spread light on the cell window to avoid stirring [25,26]. Measurements were made on aerated solutions.

## 2.3. Kinetics measurements

The effects of metal ions on the  $SO \rightleftharpoons MC$  process were studied in acetone and 1:1 hexane/acetone mixtures. The concentration of the spiroindolinonaphthooxazine was kept constant in the interval of  $1\text{--}5 \times 10^{-5}$  M and the ra-

tio between SO and the metal ions was varied from 1:1 to 1:250.

Kinetics of thermal ring opening of SO was measured in the presence of metal ions at different temperatures in the range of 20–50 °C, ca. 30 min after having set the temperature control in order to allow the initial solutions to reach the appropriate temperature in separate vessels. Absorbance was measured at  $\lambda_{\max}$  directly in the sample cell at 30 s intervals after the insertion of acetone solution of the metal ion in acetone or hexane solutions of 1–4. The activation energies of thermal ring opening were determined from Arrhenius plots.

In photocoloration experiment, the cuvette was irradiated for several seconds after thermal equilibration in the dark following the addition of acetone solution of the metal ion to acetone or hexane solution of SO. Trial and error experiments enabled the optimum exposure time to be determined for maximum build-up of the complex.

The ring-closure reaction after photocoloration was monitored directly after removal of the light, scanning at the wavelength of maximum absorption of the complex between the MC form and the metal ion ( $\lambda_{\text{compl}}$ ) at 15 s intervals over a period of 20 min at room temperature. First-order rate constants were obtained from the linear  $\ln A$  versus time descending curves. By extrapolation of the obtained  $\ln A/t$  plots to zero time the absorbance  $A_0$  of the complexes at  $t = 0$  was related to their 'colourabilities' [26–29] using the expression  $A_0/c_{SO}b$  in which  $c_{SO}$  was the initial concentration of SO and  $b$  was the optical path length. When measured in this way 'colourability' depended on the quantum yield  $\Phi_c$  of the colour-forming reaction and the  $\epsilon$ -value of the visible absorption band of the complex.

## 3. Results and discussion

The colourless spiro compounds gave no complex with the metal ions. However, their merocyanines appeared to form complexes readily with Ni(II), Co(II) and Zn(II) in polar solvents (acetone or 1:1 hexane/acetone). The opened MC form did not form complexes with Mn(II), Al(III) or Mg(II), and they did not affect the equilibrium between SO and MC in Scheme 1, while Cr(III), Cu(II) and Fe(III)

Table 1  
Experimental values of  $\lambda_{\max}$  (nm) and  $\epsilon$  ( $M^{-1}cm^{-1}$ ) of the visible absorption band of complexes of **1–4** with Ni(II), Co(II) and Zn(II) in acetone

SO	$\lambda_{\max}$ ( $\epsilon$ )		
	Ni(II)	Co(II)	Zn(II)
<b>1</b>	620 (48500)	610 (44500)	600 (36500)
<b>2</b>	625 (51500)	615 (48000)	605 (38500)
<b>3</b>	630 (59000)	620 (54000)	610 (41000)
<b>4</b>	640 (54000)	630 (53500)	620 (40500)

yielded irreversible photo-degradation with a broad visible absorption appearing at ca. 450 nm, previously reported as yellowing phenomenon and assigned to photooxidation [30].

### 3.1. Absorption spectra

Visible spectra of photomerocyanines, obtained by UV irradiation of **1–4** in acetone [24], are characterized by a strong absorption band in the range 640–660 nm. All bands remain unchanged upon UV-irradiation in the presence of Mn(II), Al(III) or Mg(II), while insertion of Ni(II), Co(II) or Zn(II) generates a new intense photo-reversible absorption band in the range 610–640 nm. According to the data of Table 1 the new absorption band obtained on addition of  $5 \times 10^{-5}$  M acetone solution of Ni(II), Co(II) or Zn(II) to equimolar acetone, hexane (or cyclohexane) solutions of **1–4** is slightly blue-shifted, ca. 25–45 nm for **3** in acetone and the same is observed at 10- to 250-fold molar excess of M(II). The intensity of this band increases upon UV irradiation and reverses back to its initial level after the light is removed. While  $\lambda_{\max}$  depends only moderately on the nature of the metal ion (15–45 nm), the time needed for re-establishing equilibria is sensitive to the metal ion and substantially prolonged compared to the non-complexed merocyanine.

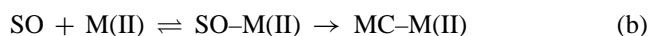
Photoirradiation of the parent unsubstituted spiroindolinonaphthooxazine (Scheme 2) in the presence of either metal salt [31] induces irreversible photo-degradation without any complexation, indicating that nitrogen atom at the 1' position in the naphthooxazine moiety takes no part in chelation.

On the other hand, replacing benzothiazol-2-yl at the 5' position in the naphthooxazine moiety with a hydroxyl substituent strongly changes the coordinating ability of spiroindolinonaphthooxazines and 5'-(hydroxy)spiroin-

dolinonaphthooxazines only give complexes with Al(III), Fe(II) and Cu(II) in acetone, ethanol or their 1:1 aqueous mixtures. However, the obtained complexes undergo thermal degradation within 1 h and are not suitable for photochromic systems.

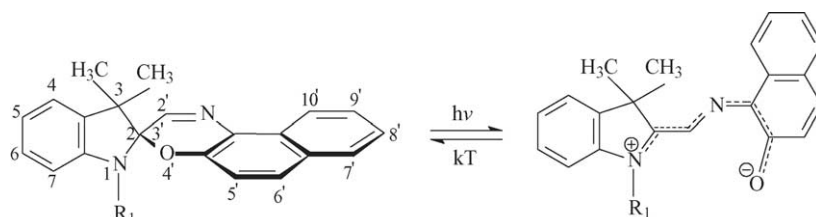
### 3.2. Chelation in the dark

Typical spectra obtained at different times after mixing of  $5 \times 10^{-5}$  M acetone solutions of Ni(II), Co(II) or Zn(II) with equimolar solutions of **1–4** in acetone (a) or hexane (b) are given in Fig. 1a and b. The obtained absorption band gradually increases in intensity on keeping the sample in the dark. The observed changes correspond to the thermal conversion of SO to a MC–M(II) complex, as indicated by the position of the visible absorption. The higher intensity of spectrum 1 in Fig. 1a compared to spectrum 1 in Fig. 1b is due to higher polarity of the medium and higher equilibrium concentration of the open MC form taking part in chelation in the dark. Chelation affects the thermal equilibrium and promotes the formation of the open form at room temperature in the absence of light according to one of the following pathways [15]:



To choose the reaction scheme of chelation, the process was studied at different metal ion concentrations. Fig. 2a shows typical kinetics runs at different concentrations of M(II). The corresponding rate plots for the first-order chelation given in Fig. 2b indicate that both the concentration and the nature of the metal ion have no effect on the rate of complex formation. It seems from these data that route (c) is the reaction pathway of chelation since for (a) and (b), the formation rates of the complex are proportional to the concentration of the metal ions. For (c), the coloured form MC reacts readily with metal ions as it is formed thermally from SO, and the formation process is the rate-determining step in the reaction sequence, with practically no effect of metal ion on the reaction rate.

The first-order build-up kinetics, i.e., the plots of the linear dependences ( $\rho > 0.99$ ) versus time of  $\ln A$  at  $\lambda_{\text{compl}}$  were analysed by the least-squares method to give the results of  $k_c$  ca.  $1 \times 10^{-3} s^{-1}$  for **1–4**. Plots of the obtained first-order



Scheme 2.

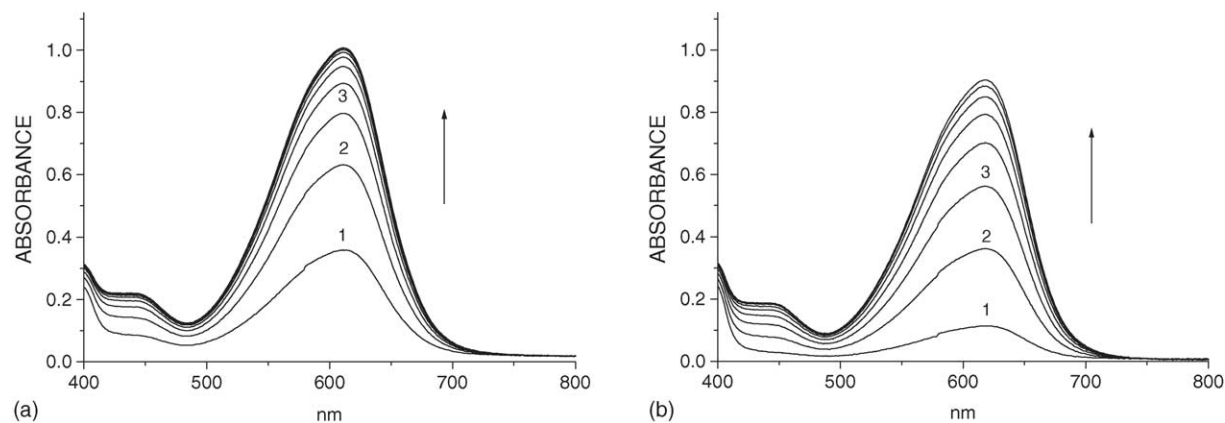


Fig. 1. Visible absorption spectra taken in the dark every minute after insertion of 1 equiv. of Zn(II) acetone solution in  $5 \times 10^{-5}$  M acetone (a) or hexane (b) to give 1:1 hexane/acetone solution of **4**.

rate constants of chelation ( $\log k_c$ ) versus  $1/T$  in the range 20–50 °C are shown in Fig. 3a,b for all complexes. Activation energies ( $E_a$ ) derived from the linear dependences in Fig. 3a are 27–29 kJ mol $^{-1}$  (25–26 kJ mol $^{-1}$  in Fig. 3b), with no effect of the metal ion as the process of thermal ring opening of the spiroform, is the rate limiting step of chelation.

Data of  $k_c$  were used to estimate the constant of thermal  $SO \rightleftharpoons MC$  equilibrium  $K_e = [\text{merocyanine}]/[\text{spirooxazine}]$  by the expression  $K_e = k_c/k$  in which  $k$  is the previously estimated rate constant of thermal ring closure of the photomerocyanines [24] and  $k_c$  is the rate constant of the forward reaction of thermal ring opening of the spiroform to give MC. The results of  $K_e$  are given in Table 2.

Table 2

Constants of thermal  $SO \rightleftharpoons MC$  equilibrium ( $K_e$ ) of **1–4** and of their complex formation ( $K_c$ ) with Ni(II), Co(II) or Zn(II), 20 °C

SO	Solvent	$pK_e$	$\log K_c$		
			Ni(II)	Co(II)	Zn(II)
<b>1</b>	Acetone	1.77	6.16	6.04	5.60
	Hexane/acetone	2.00	6.04	5.78	5.48
<b>2</b>	Acetone	1.71	6.28	6.05	5.70
	Hexane/acetone	1.95	6.15	5.90	5.60
<b>3</b>	Acetone	1.32	6.15	5.78	5.60
	Hexane/acetone	1.43	5.84	5.48	5.30
<b>4</b>	Acetone	1.21	6.08	5.78	5.57
	Hexane/acetone	1.30	5.78	5.60	5.48

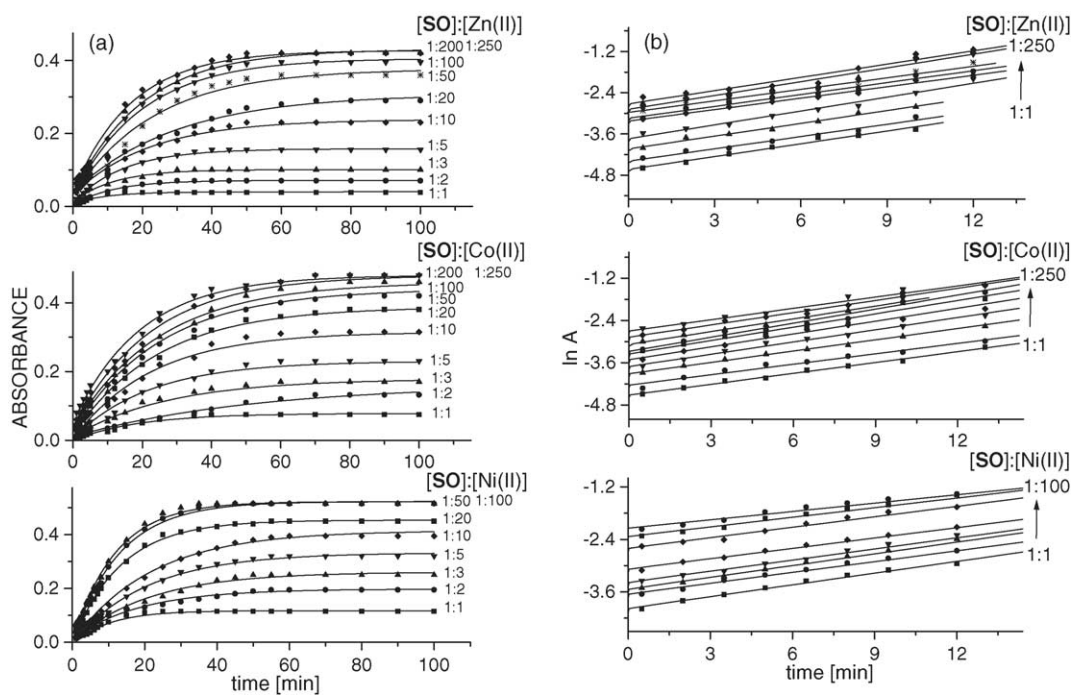


Fig. 2. Kinetic runs of chelation between  $1 \times 10^{-5}$  M solution of **2** and  $1 \times 10^{-5}$  to  $2.5 \times 10^{-3}$  M Zn(II) at 605 nm;  $1 \times 10^{-5}$  to  $2.5 \times 10^{-3}$  M Co(II) at 615 nm; and  $1 \times 10^{-5}$  to  $1 \times 10^{-3}$  M Ni(II) at 625 nm taken in the dark at 20 °C in acetone (a) and the corresponding rate plots for the first-order chelation (b).

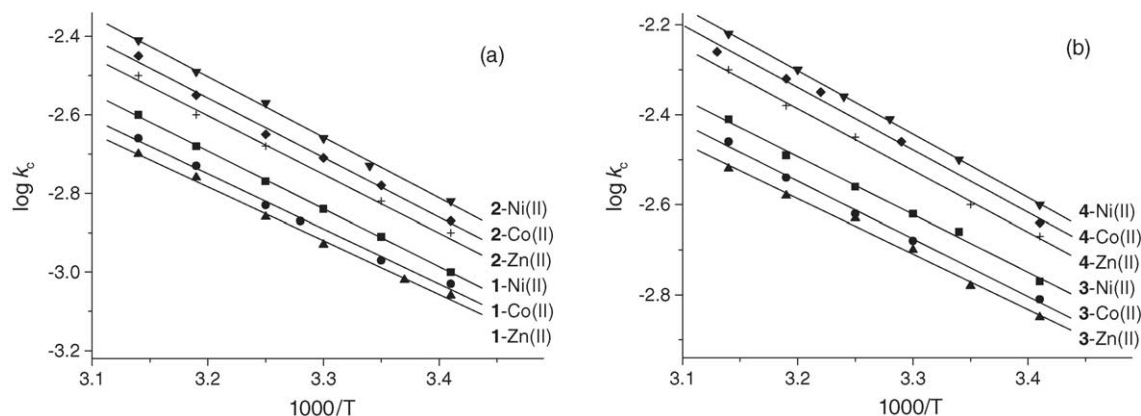


Fig. 3. Arrhenius plots in the range 20 °C–50 °C for thermally activated complex formation of: **1**, **2** (a) and **3**, **4** (b) with Zn(II), Co(II) and Ni(II).

Kinetic runs at reaction times larger than 40 min in Fig. 2a indicate complete stabilization of the MC form towards thermal decay and the obtained complexes persist for at least 3 days in the dark. According to the data in Fig. 2a, the complex concentration under equilibrium conditions increases with increasing metal ion excess. In fact, the amount of the obtained complex depends on SO, metal ion and  $[M(II)]/[SO]$  ratio. The molar absorptivity values ( $\epsilon$ ) of the visible absorption band of MC–M(II) in Table 1 are calculated from the absorbances at reaction times larger than 40 min and  $[SO]/[M(II)]$  ratio 1:100 for Ni(II), and 1:250 for Co(II) and Zn(II), assuming that SO is completely involved in the complex following route (c). To distinguish between complexation of metal nitrates with one or two merocyanine ligands, we suggest that for those cases where the metal ion concentration is higher than that of the SO form one merocyanine and four acetone molecules as ligands for M(II) in Scheme 3. The spectral and kinetic data (Figs. 1–5) also indicate this possibility for  $[SO] \sim [M(II)]$ . Job's [32], which is commonly used for determination of the stoichiometry, cannot be applied to our case, since the ligand MC concentration cannot be varied independently of  $[M(II)]$ .

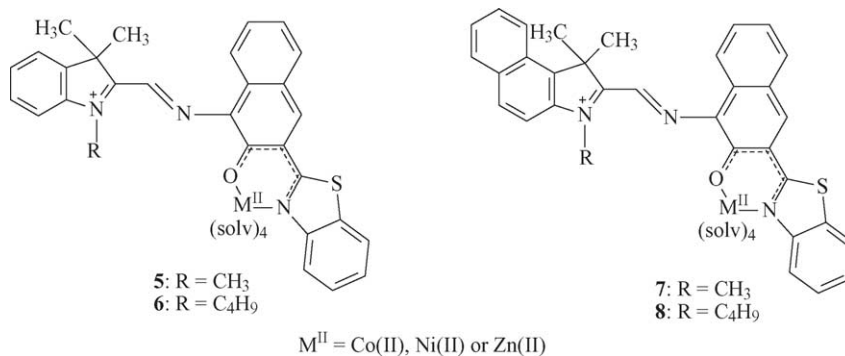
When thermal equilibrium is attained, we obtain the following expression for the equilibrium constant of complex

formation  $K_c$ :

$$K_c = \frac{[MC-M(II)]}{[M(II)][MC]}$$

The values of  $K_c$  at 20 °C (Table 2) are estimated by this expression in which the equilibrium concentration of the complex is derived from the equation  $[MC-M(II)] = A/\epsilon b$ , using the absorbances  $A$  at reaction times larger than 40 min and  $[SO]/[M(II)]$  ratios from 1:1 to 1:50 (see Fig. 2(a),  $\epsilon$  are the molar absorptivities given in Table 1 and  $b = 1$  cm. The equilibrium concentration of the ligand  $[MC]$  is obtained by the equation  $[MC] = [SO]K_e$ , in which the constant of thermal equilibrium  $K_e$  between merocyanine and spirooxazine has the values given in Table 2. The equilibrium concentration of SO is  $[SO] = c_{SO} - [MC-M(II)]$  where  $c_{SO}$  is the initial concentration of SO, and the equilibrium concentration of the metal ion is  $[M(II)] = c_M - [MC-M(II)]$ , where  $c_M$  is the analytical concentration of the metal ion.

According to the values of  $K_c$  in Table 2, the ability for complexation of the studied merocyanines decreases in the order from **1** to **4** and their formation constants in the order Ni(II) > Co(II) > Zn(II). Higher polarity of the medium, i.e., higher equilibrium concentration of MC favours complexation.



Scheme 3.

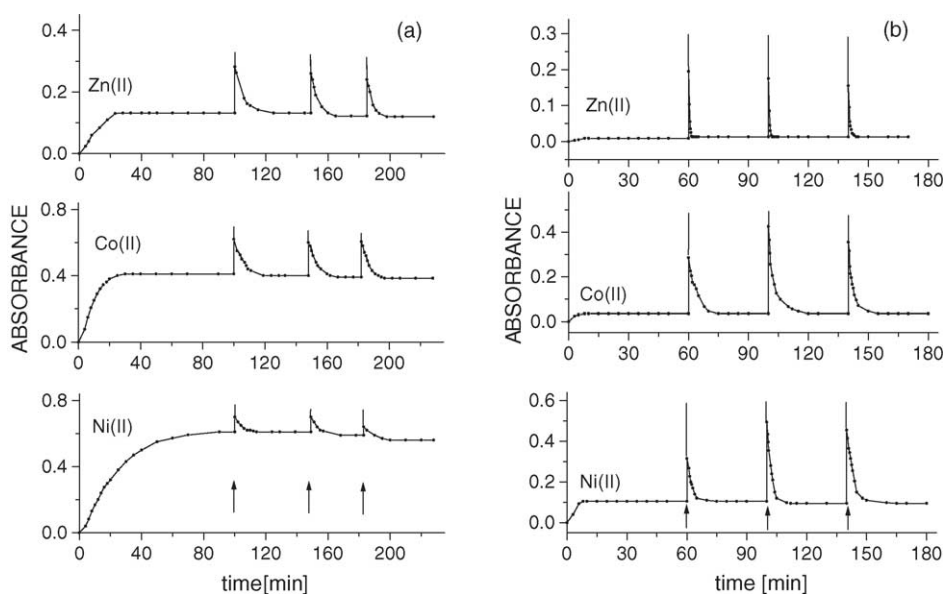


Fig. 4. Absorbance changes of hexane/acetone (1:1) solution of **2** in the presence of: 10 equiv. (a) and 1 equiv. (b) of Zn(II) at 605 nm; Co(II) at 615 nm and Ni(II) at 625 nm, following short UV illumination after the thermal equilibration in the dark. Upward arrows show 10 s UV irradiation;  $c_{SO} = 1.25 \times 10^{-5}$  (a) and  $1.0 \times 10^{-5}$  M (b). The solid lines correspond to exponential fits of the absorbance decay in the dark using the first-order rate constants  $k_r$  in Table 3.

### 3.3. Effect of chelation on the photochromism of spiroindolinonaphthooxazines

#### 3.3.1. Reversibility of photocoloration

The time dependence of absorbance changes at  $\lambda_{\text{compl}}$  was studied under alternative cycles of dark conditions and UV light irradiation after mixing of 10 equiv. of Ni(II), Co(II) or Zn(II) in acetone with hexane (Fig. 4a) or acetone (Fig. 5a) solutions of **1–4**. Fig. 4a depicts slowly increasing intensity of MC–Zn(II), MC–Co(II) and MC–Ni(II) absorption band of **2** getting a saturation for 40–100 min in 1:1 hexane/acetone solutions in the dark. Short UV-irradiation strongly accelerates the increase in intensity displacing the equilibrium  $SO \rightleftharpoons MC$  to the side of photomerocyanine, which promptly forms a chelate.

Kinetic runs in Fig. 4a followed at  $\lambda_{\text{compl}}$  immediately after irradiation indicate that the obtained complex undergoes spontaneous ring closure reaching the thermal equilibrium at 20 °C in the dark. Absorption is substantially increased again upon new short UV irradiation of the equilibrated solution and reverses back to its initial level after the light is removed. The obtained kinetic runs clearly indicate that the photocoloration is reversible. The behaviour is typical for all studied systems in 1:1 hexane/acetone solution. Absorbance changes at  $\lambda_{\text{compl}}$  are better pronounced when alternative cycles of dark conditions and UV light irradiation are carried out with 1 equiv. of metal ion (Fig. 4b), since complexation in the dark is not well revealed under these conditions (see Fig. 2a). Better results are obtained with Zn(II) and Co(II) because of the lower stability of their MC complexes. In acetone (Fig. 5a,b), thermal colouration follows the general properties described above, but thermal re-equilibration after short UV irradiations indicates a minor photodegradation.

From the other solvents used, acetonitrile, ethanol and toluene are not suitable for complexation, while cyclohexane/acetone mixture could also be used. In acetonitrile, photoirradiation of 5'-(benzothiazol-2-yl)spiroindolinonaphthooxazines induces irreversible photo-degradation (a yellowing process) in the presence of either metal salt. In ethanol, photoinduced complexation of 5'-(benzothiazol-2-yl)spiroindolinonaphthooxazines is strongly hindered probably because of the competitive effect of both solvation of M(II) and hydrogen bonding of MC [24]. Kinetic runs of dark chelation in 1:1 toluene/acetone, disprove stabilization of MC form towards degradation contrary to acetone (Fig. 2a) and thermally obtained in 1:1 toluene/acetone MC–M(II) complexes persist only a few hours.

#### 3.3.2. Thermal decoloration

In the absence of metal ions [24], the relaxation times of the photomerocyanines of **1–4** are about 2.5 s in hexane and vary from ~10 to ~25 s in acetone. In contrast to the lack of effect of Mn(II), Al(III) and Mg(II) on the ring closure of the free MC forms, their light-enhanced colouration disappears much slower after irradiation in the presence Ni(II), Co(II) or Zn(II). The thermal reverse reaction is first order in all cases and the slopes of the linearly descending  $\ln A/t$  curves give the first-order rate constants,  $k_r$  in Table 3. The relaxation times of the complexes ( $\tau_{\text{com-SO}}$ ) are obtained using the expression  $\tau_{\text{com-SO}} = 1/k_r$ . The observed lifetimes between 2 and 42 min summarized in Table 3 for the complexes **5–8** with Ni(II), Co(II) or Zn(II) demonstrate that the stabilization of the MC form to thermal reversion through complexation is metal-dependent following their  $K_c$  values in Table 2 and the  $[M(II)]/[SO]$  ratios. As for the influence of **1–4**, the stabilization of MC is rather related to the constant  $K_e$  of thermal

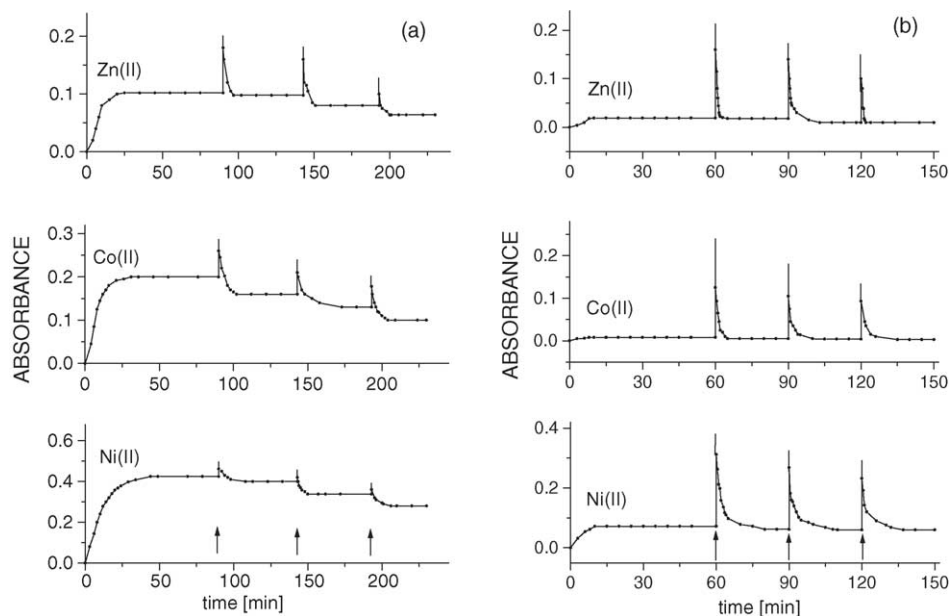


Fig. 5. Absorbance changes of acetone solution of **2** in the presence of 10 equiv. (a) and 1 equiv. (b) of Zn(II) at 605 nm; Co(II) at 615 nm and Ni(II) at 625 nm, following periodic ultraviolet illumination after the thermal equilibration in the dark. Upward arrows show 10 s UV irradiation;  $c_{\text{SO}} = 1.25 \times 10^{-5}$  (a) and  $1.0 \times 10^{-5}$  M (b). The solid lines correspond to exponential fits of the absorbance decay in the dark using the first order rate constants  $k_r$  in Table 3.

SO  $\rightleftharpoons$  MC equilibrium, than to its ability for complexation (see  $K_c$  values in Table 2). It is obvious that about twice the lower rate of reversion of **7–8** compared to **5–6** is obtained by replacing benzene in the indoline moiety by naphthalene because of the decreased rotational freedom upon cyclization. However, the rate of thermal relaxation is unaffected by changing the *N*-alkyl group on the indoline part of the molecule from  $-\text{CH}_3$  to  $-\text{C}_4\text{H}_9$  group.

From the absorbances  $A_0$  obtained by extrapolation to  $t = 0$  of the room temperature linearly descending kinetic curves

Table 3

Rate constant  $k_r$  ( $\times 10^3 \text{ s}^{-1}$ ) of thermal re-equilibration of complexes **5–8**, obtained by 15 s photoirradiation of **1–4** in the presence of Ni(II), Co(II) or Zn(II) and the lifetime  $\tau_{\text{coml-SO}}$  (min) of the coloured form

SO	Solvent	[SO]:[M(II)]	$k_r$ ( $\tau_{\text{coml-SO}}$ )		
			Ni(II)	Co(II)	Zn(II)
<b>1</b>	Acetone	1:1	1.4 (12)	1.9 (9)	6.8 (2)
		1:10	1.0 (17)	1.1 (15)	1.9 (9)
	Hexane/acetone	1:1	3.4 (5)	4.3 (4)	6.5 (3)
		1:10	0.7 (24)	0.9 (19)	3.0 (6)
<b>2</b>	Acetone	1:1	1.3 (13)	1.8 (9)	5.8 (3)
		1:10	0.8 (21)	1.1 (15)	1.8 (9)
	Hexane/acetone	1:1	2.9 (6)	4.0 (4)	5.6 (3)
		1:10	0.7 (24)	0.8 (21)	2.6 (6)
<b>3</b>	Acetone	1:1	1.2 (14)	1.6 (10)	3.9 (4)
		1:10	0.6 (28)	0.8 (21)	1.2 (14)
	Hexane/acetone	1:1	1.3 (13)	1.8 (9)	2.9 (6)
		1:10	0.4 (42)	0.5 (33)	1.0 (17)
<b>4</b>	Acetone	1:1	1.1 (15)	1.6 (10)	2.7 (6)
		1:10	0.6 (28)	0.8 (21)	1.1 (15)
	Hexane/acetone	1:1	1.2 (14)	1.6 (10)	2.4 (7)
		1:10	0.4 (42)	0.4 (42)	0.8 (21)

Table 4

'Colourability values' ( $\text{M}^{-1} \text{ cm}^{-1}$ ) of complexes **5–8**, obtained by 10 s photoirradiation of **1–4** in the presence of 10 equiv. of Ni(II), Co(II) or Zn(II) in acetone and the evaluated quantum yields  $\Phi_c$  (mol/Einstein) of the ring-opening reaction

SO	Colourability ( $\Phi_c$ )		
	Ni(II)	Co(II)	Zn(II)
<b>1</b>	36500 (0.75)	33500 (0.75)	27500 (0.75)
<b>2</b>	41000 (0.80)	38000 (0.80)	31000 (0.80)
<b>3</b>	50200 (0.85)	46000 (0.85)	35000 (0.85)
<b>4</b>	49000 (0.90)	48000 (0.90)	36500 (0.90)

$\ln A/t$  taken immediately after UV-irradiation were calculated high 'colourability' [26–29] values up to  $5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  ( $\epsilon = 6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) given in Table 4 together with the related quantum yields (0.75–0.90 mol/Einstein) of the ring-opening reaction of **1–4**.

#### 4. Conclusions

Coordination,  $\text{M} = \text{Ni(II)}$ ,  $\text{Co(II)}$  or  $\text{Zn(II)}$ , with the open MC form of four 5'-(benzothiazol-2-yl)spiroindolinonaphthooxazines takes place thermally (slowly) or photochemically in acetone and 1:1 hexane/acetone yielding a reversibly photochromic complex. Acetonitrile, ethanol or toluene are not suitable for complexation, while cyclohexane/acetone mixture could also be used. The thermal build-up reaction ( $\sim 10^{-3} \text{ s}^{-1}$ ) is independent of  $[\text{M(II)}]$ , which implies that the ring opening is the rate determining step. Chelation induces a 10–40 nm hypsochromic shift of the visible absorption band of the

photomerocyanine and drastically slows down its thermal bleaching in the dark. The rate constants for thermal re-equilibration of all compounds measured in different solvents are metal-dependent ranging from 0.4 to  $7 \times 10^{-3} \text{ s}^{-1}$ . The ability for complexation of the merocyanines decreases in the order from **1** to **4** and their formation constants in the order Ni(II) > Co(II) > Zn(II).

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