Photo- and thermochromic cation sensitive spiro[indoline-pyridobenzopyrans]

Anatoly V. Chernyshev,[1]* Anatoly V. Metelitsa,[1] Elena B. Gaeva,[1] Nikolai A. Voloshin,[2] Gennady S. Borodkin[1] and Vladimir I. Minkin[1]

[1]Institute of Physical and Organic Chemistry, Southern Federal University, 194/2 Stachka Av., Rostov on Don 344090, Russia
[2]Southern Scientific Center of Russian Academy of Science, 41 Chekhova Str., Rostov on Don 344006, Russia

ABSTRACT: The photo- and thermochromic behaviour of a series of spiro[indolinepyridobenzopyrans] **1–5** has been studied. The thermodynamic and kinetic parameters of the thermal equilibria between the ring-closed and ring-opened (merocyanine) isomeric forms of spiropyrans have been determined using UV–Vis absorption and ^{1}H NMR spectroscopies techniques. The most stable form of 1-(2-hydroxyethyl)-spiro[indoline-pyridobenzopyran] **4** is represented by its *trans*-(hydroxystyryl)oxazolidineindoline isomer coexisting in acetone solution with the ring-closed spiroform. In the presence in solution of metal salts, spiro[indoline-pyridobenzopyrans] exhibit strong ionochromic effect due to the formation of complexes with the merocyanine ligand. The composition of the complexes formed by Zn^{2+} and Ni^{2+} ions has been determined with the use of spectrophotometric and electrospray ionisation mass spectroscopy techniques. The stepwise stability constants and spectral properties of the most stable 1:1 and 1:2 metal/merocyanine complexes have been determined. Selectivity of the complexation reaction depends on the position of the thermochromic equilibrium. Copyright © 2007 John Wiley & Sons, Ltd.
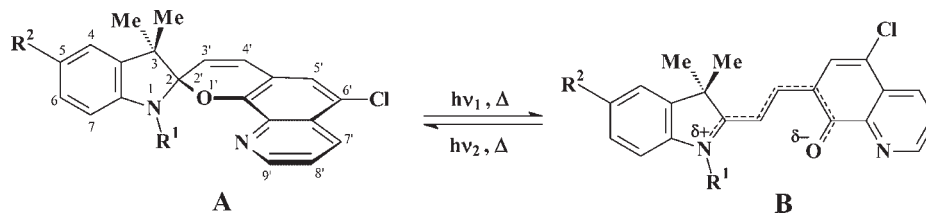*Supplementary electronic material for this paper is available in Wiley InterScience at http://www.mrw.interscience.wiley.com/suppmat/0894-3230/suppmat/*

KEYWORDS: spiropyran; photochromism; complex; binding constants

INTRODUCTION

Photo- and thermochromic behaviour of spiropyrans, as exemplified by the case of spiro[indoline-pyridobenzopyrans] **1–5**, is caused by the reversible heterolytic cleavage of the spiro C—O bond followed by *cis–trans* isomerisation of the formed metastable merocyanine form **B**.[1,2]

The negatively charged oxygen atom of the merocyanine **B** offers a good donor centre to coordinate metal ions[3–5] and to form molecular complexes with other electrophilic species.[6,7] In general, the formation of complexes leads to significant changes in their absorption and fluorescent characteristics as compared to the free ligands **B**. At the same time, the ring-closed isomers of spiropyrans (SPP) **A** do not possess strong donor ability, do not form stable metal or molecular complexes and their spectral properties are very slightly disturbed by metal ions. Switching between the two states sharply different in their spectral properties is effected under the action of light, which also controls the processes of formation and dissociation of complexes of **B**. Such spectral behaviour is at the origin of the use of photochromic spiropyrans, in particular spiro[indoline-pyridobenzopyrans], as sensitive photodynamic fluorescent chemosensors for metal ions.[8–14]

Scheme 1.

Herein, we report on photo- and thermochromic properties of new derivatives of spiro[indoline-pyridobenzopyrans] and present a study of their complexation with Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} metal ions.

*Correspondence to: Anatoly V. Chernyshev, Institute of Physical and Organic Chemistry, Southern Federal University, 194/2 Stachka Av., Rostov on Don 344090, Russia.
E-mail: anatoly@ipoc.rsu.ru

RESULTS

Thermal equilibrium and photochromism

In solutions of nonpolar solvents (hexane, toluene), SPP **1–5** exist in their colourless ring-closed form **A**, but their solutions in polar solvents are slightly coloured at room temperature due to the establishment of the thermal equilibrium (Scheme 1) and the appearance of small amounts of the merocyanine isomers **B**.[15]
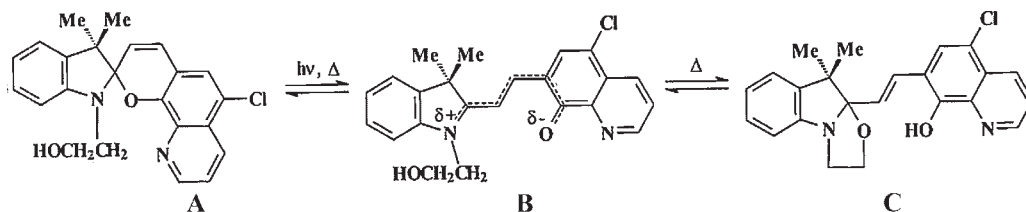
Position of the **A** ⇌ **B** equilibrium in acetone-d_6 solutions has been studied using ^{1}H NMR technique. Chemical shifts of *gem*-dimethyl and *N*-alkyl groups as well as protons at the $C^3=C^4$ double bond in the ring-closed **A** and ring-opened **B** isomeric forms of SPP significantly differ.[16,17] For SPP **1–3**, **5**, the AB-quartet signals of 3'-H and 4'-H protons of the ring-closed form **A** appear as two doublets at 5.97–5.99 and 7.19 ppm correspondingly ($J = 10.2$ Hz, 4'-H signal is superimposed with the 4-H and 6-H signals). The signals of the diastereotopic *gem*-dimethyl groups are found in the range of 1.19–1.26 and 1.34–1.38 ppm and those of the *N*-methyl group (for SPP **1–3**) in the range of 2.76–2.79 ppm.

In the case of SPP **4**, the equilibrium amount of the isomer **B** is negligible because it undergoes a further ring-chain tautomerisation step to convert into the oxazolidine-containing isomer **C** (Scheme 2). At 293 K, an acetone-d_6 solution of SPP **4** contains 69.2% of the form **C** in the equilibrium with **A**. The signals of protons of the vinyl group of **C** appear as an AB-quartet

with chemical shifts at 6.70 and 7.42 ppm and $J = 16.1$ Hz, similar to the spectral pattern observed for the analogous *trans*-(hydroxystyryl)oxazolidineindoline derivatives.[18] Signals of the *gem*-dimethyl group of SPP **4** are splitted into two singlets at 1.24 and 1.37 ppm (**A**) and at 1.23 and 1.51 ppm (**C**).

In acetone, the cyclic isomers **A** of spiropyrans **1–3**, **5** are characterised by long wavelength absorption bands with maxima at 341–343 nm and molar absorption coefficients (ε) 4400–4980 L · mol^{-1} · cm^{-1}. The position and the intensity of the absorption bands do not practically depend on the origin of the substituents R^1 and R^2 (Table 1). The longest wavelength absorption band of the SPP **4** oxazolidine isomer **C** has a maximum at 334 nm ($\varepsilon = 7440$ L · mol^{-1} · cm^{-1}).

The structured merocyanine absorption bands are observed in the region 522–620 nm (Fig. 1, Table 1). For SPP **1** and **3**, the equilibrium content (3 and 12%, respectively) of the merocyanine forms was estimated from the ^{1}H NMR data and the molar absorption coefficients (ε) of the ring-opened isomers were determined. The values $\varepsilon = 47900–57000$ L · mol^{-1} · cm^{-1} thus obtained are close to that found for SPP **1** in chloroform solution.[15] For SPP **2**, **4**, **5**, the equilibrium content of the ring-opened isomer **B** is very low for a reliable determination with the use of NMR technique. Hence, the equilibrium content of the **B** isomer was estimated spectrophotometrically. The spectral parameters of the merocyanine isomers **B** are relatively slightly affected by the substituents R^1, R^2, the most pronounced effect being exerted by an alkoxy group in position 5 of the indoline fragment (Fig. 1, Table 1).

Scheme 2.

Table 1. Spectral properties of isomeric forms of SPP **1–5** in acetone solution

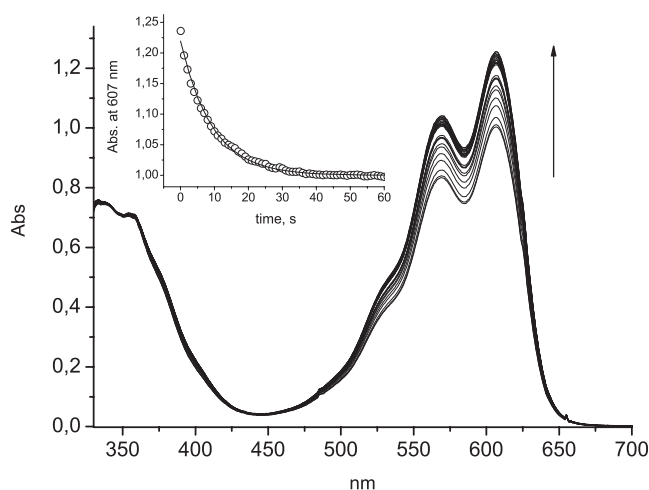| Compound	λ_{max}^{abs} (**A**), nm	ε (**A**), L · mol^{-1} · cm^{-1}	λ_{max}^{abs} (**B**), nm	ε (**B**), L · mol^{-1} · cm^{-1}
1	341	4400	562	53900
			599	51700
2	341	4880	562	—[b]
			599	—[b]
3	341	4490	568	47900
			607	57000
4	334[a]	7440[a]	561	—[b]
			600	—[b]
5	341	4980	563	—[b]
			598	—[b]

[a] Oxazolidine form.
[b] Merocyanine content < 2%.

Figure 1. Evolution of the absorption spectrum of SPP **3** in acetone ($T = 293$ K) upon irradiation at $\lambda_{irr} = 365$ nm. The spectra were recorded within 1 s interval. (Inset: thermal relaxation curve observed at 607 nm; dots are experimental points, continuous line is an approximation by monoexponential function)

The calculated constants and thermodynamic parameters of the tautomeric equilibrium $\mathbf{A} \rightleftarrows \mathbf{B}$ are listed in Table 2. The difference between the levels of the ground state estimated from ΔH° values has been found to range from 1.0 to 6.2 kJ $\cdot$ mol^{-1} depending on the SPP structure (as described in Supplementary Materials).

As shown in Fig. 1, irradiation of an acetone solution of SPP with UV light at the longest wavelength absorption band of the ring-closed form **A** leads to the rise in the absorption of the ring-opened merocyanine form **B**. The initial thermal equilibrium is gradually restored on extinguishing the irradiation. The thermal relaxation kinetic curves are sufficiently well fitted to the monoexponential function with lifetimes $\tau = 2.4$–6.0 s at 293 K. The activation energies of the thermal isomerisation processes range from 30.3 to 74.3 kJ $\cdot$ mol^{-1} (as described in Supplementary Materials).

Ionochromism

Upon addition of perchlorates of metal cations Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} to acetone solutions of SPP, the appearance of new intense absorption bands with maxima at 533–573 nm shifted
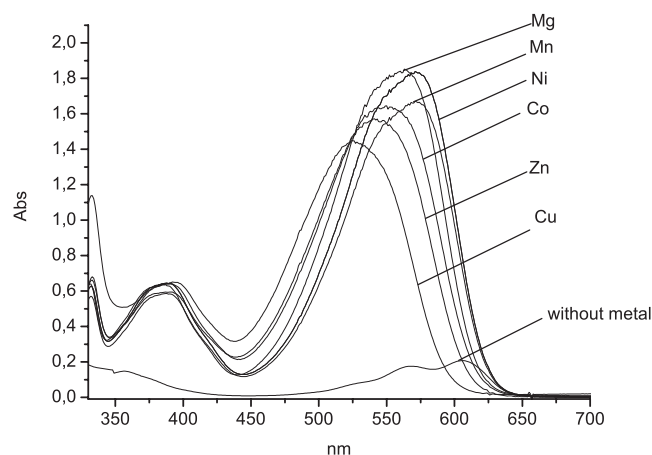

Figure 2. Absorption spectra of an acetone solution of SPP **3** containing metal (II) perchlorates. $C(\text{SPP}) = 3.45 \times 10^{-5}$ M, $C(\mathbf{M}) = 1 \times 10^{-4}$ M

hypsochromically with respect to those of the merocyanine isomers **B** has been observed (Fig. 2). Position of the absorption bands depends on the metal cation (Table 3). The solutions of SPP containing Mg^{2+}, Zn^{2+} ions exhibit fluorescence with maximum intensities at 610–625 nm. In ^{1}H NMR spectra of SPP measured in the presence of salts of metal ions, all the proton signals are shifted downfield with respect to their positions in solutions of free ligands. In an acetone solution containing equimolar amounts of SPP **1** and ZnCl$_2$, signals of protons of *gem*-dimethyl group appear as a six-proton singlet at 1.91 ppm, those of *N*-methyl protons at 4.14 ppm, protons 3'-H and 4'-H of the vinyl group at 8.79 and 8.17 ppm ($J = 15.8$ Hz), which are characteristics of the merocyanine form of the ligand (Scheme 3).

Stoichiometry and stability of complexes of SPP with metal ions

The composition of the complexes was determined spectrophotometrically by means of the isomolar solutions technique (Job method), which was successfully applied to analyse composition of various complexes of spiropyrans with metal ions.[19–21] The plot of the corrected absorbance values measured at the absorption maximum of a complex of SPP **1** with Zn^{2+} *versus* composition of isomolar solutions is featured in Fig. 3. The sharp

Table 2. Thermodynamic parameters of ring-chain tautomeric equilibrium in acetone at 293 K

Compound	$K_T \times 10^3$	ΔG°, kJ $\cdot$ mol^{-1}	ΔH°, kJ $\cdot$ mol^{-1}	$-\Delta S^\circ$, J $\cdot$ mol^{-1} K^{-1}
1	30.1	3.5	3.1 ± 0.5	18.7 ± 1.8
2	9.2	4.7	6.1 ± 0.6	18.1 ± 2.0
3	141.5	11.9	1.0 ± 0.2	12.8 ± 0.5
5	21.8	3.8	3.5 ± 0.3	20.3 ± 1.0

Table 3. Spectral properties of complexes of 6'-chlor-3,3'-dimethylspiro[indoline-2,2'-[3,2-*h*]pyrido-2*H*-1-benzopyrans] with metal cations in acetone solutions

SPP	Complex type	Mg λ_{max}^{abs}, nm	Mg λ_{max}^{flu}, nm	Mg ε, 10^{-4} L·mol^{-1}·cm^{-1}	Mn λ_{max}^{abs}, nm	Mn ε, 10^{-4} L·mol^{-1}·cm^{-1}	Co λ_{max}^{abs}, nm	Co ε, 10^{-4} L·mol^{-1}·cm^{-1}	Ni λ_{max}^{abs}, nm	Ni ε, 10^{-4} L·mol^{-1}·cm^{-1}	Zn λ_{max}^{abs}, nm	Zn λ_{max}^{flu}, nm	Zn ε, 10^{-4} L·mol^{-1}·cm^{-1}	Cu λ_{max}^{abs}, nm	Cu λ_{max}^{flu}, nm	Cu ε, 10^{-4} L·mol^{-1}·cm^{-1}
1	1:1	558	612	5.10	568	4.91	555	4.42	561	4.76	540	612	4.22	528	612	4.16
	1:2	567		10.10	573	10.95	578	12.83	583	11.58	564		11.40	549		13.95
2	1:1	567	620	5.21	576	5.01	565	4.51	571	4.87	553	620	4.65	538	620	4.19
	1:2	575		9.75	585	10.36	586	10.52	591	10.61	577		11.98	557		11.61
3	1:1	560	614	4.92	570	4.89	553	4.46	565	4.76	535	612	4.69	524	612	4.56
	1:2	574		10.98	581	13.96	587	12.85	590	10.50	576		11.90	556		11.05
4	1:1	561	616	4.98	570	4.92	558	4.32	567	4.68	551	620	4.40	534	620	3.33
	1:2	573		13.33	587	11.25	585	11.08	583	11.47	576		12.51	551		8.72
5	1:1	566	620	4.18	577	4.78	561	3.51	571	4.91	551	616	3.39	537	616	3.49
	1:2	582		7.11	587	11.36	590	8.36	592	11.39	578		11.62	560		10.80

maximum of the curve corresponds to the solution of composition 1:2 (metal/SPP). The analogous curves with maxima corresponding to the same composition were obtained when applying absorbances at other wavelengths. The 1:2 compositions were also found for the complexes of SPP with other M^{2+} ions studied in the present work and for the previously studied[22] complex of 6'-nitro-spiropyridobenzopyran with Zn^{2+} ion.

The results of the spectrophotometric determinations of the composition of the complexes of spiro[indoline-pyridobenzopyrans] with metal ions were corroborated by the data obtained with the use of electrospray-ionisation mass spectrometry (ESI-MS) method. Due to its unique characteristics involving 'soft' ionisation and low degree of defragmentation of a molecule, this method already became an effective tool for investigation of complexes in solution.[23] The ESI-MS technique has already been successfully employed to study complexes of crown containing spiropyrans with alkali and alkaline-earth metal ions.[24–26]
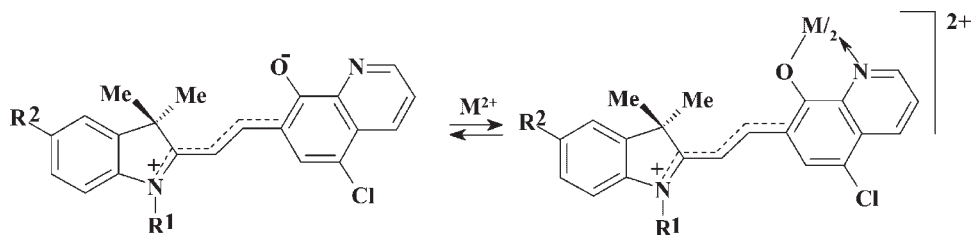
Mass spectrum of the positive polarisation of an acetonitrile solution containing equimolar amounts of SPP **2** and $ZnCl_2$ (Fig. 4) displays a peak of an ion $[Zn(SPP)Cl]^+$ at $m/z = 497$ and a peak of an ion $[Zn(SPP)_2Cl]^+$ at $m/z = 895$ originated from the 1:2 complex. The formation of the ions $\{[Zn(SPP)Cl]_2Cl\}^+$ at $m/z = 1030$ related to the dimer of the 1:1 complex has also been detected. A peak at $m/z = 1426$ corresponding to the ion $[Zn_2(SPP)_3Cl_3]^+$ should be assigned to the associate of the 1:1 and 1:2 complexes. No peaks were detected that might correspond to the protonated merocyanine or solvates of the SPP $\mathbf{2} \cdot ZnCl_2$ complex. The similar set of signals was observed in the ESI-MS spectrum of a SPP **2** solution containing $Ni(ClO_4)_2$ (as described in Supplementary Materials).

The investigation of the complex composition of the SPP with metal ions carried out with the aid of two different methods (UV–Vis absorption and ESI-MS spectroscopies) leads to the conclusion on the greater stability of 1:1 and 1:2 complexes.

Determination of stability constants

In a solution of a spiro[indolinepyridobenzopyran] containing metal salts, the following equilibria must be taken into account, where **A** and **B** stand for the ring-opened and ring-closed (merocyanine) isomers of SPP and **MB** and $\mathbf{MB_2}$ for 1:1 and 1:2 complexes of the merocyanine form with a metal ion (**M**).

$$\mathbf{A} \rightleftharpoons \mathbf{B}$$

$$\mathbf{B} + \mathbf{M} \rightleftharpoons \mathbf{MB}$$

$$\mathbf{B} + \mathbf{MB} \rightleftharpoons \mathbf{MB_2}$$

Scheme 3.

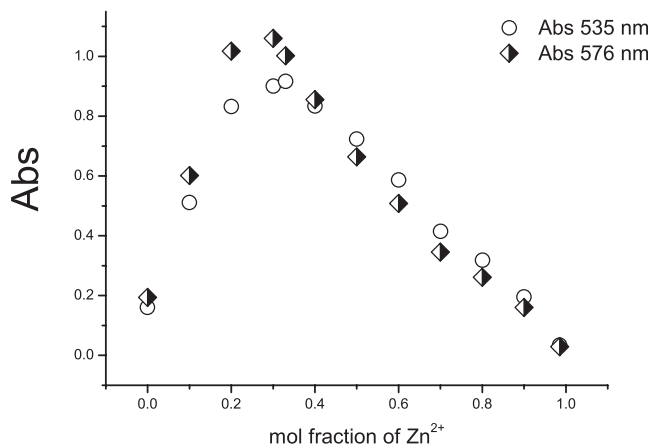**Figure 3.** Continuous variation plot of the SPP **1**:Zn ($C(\mathbf{1}) + C(\text{Zn}) = 3 \times 10^{-5}$ M) in acetone. $I = 0.01$ M (t-Bu$_4$NClO$_4$). $T = 293$ K

The corresponding equilibrium constants are given by the Eqns (1)–(3).

$$K_T = \frac{[\mathbf{B}]}{[\mathbf{A}]} \tag{1}$$

$$K_1 = \frac{[\mathbf{MB}]}{[\mathbf{B}][\mathbf{M}]} \tag{2}$$

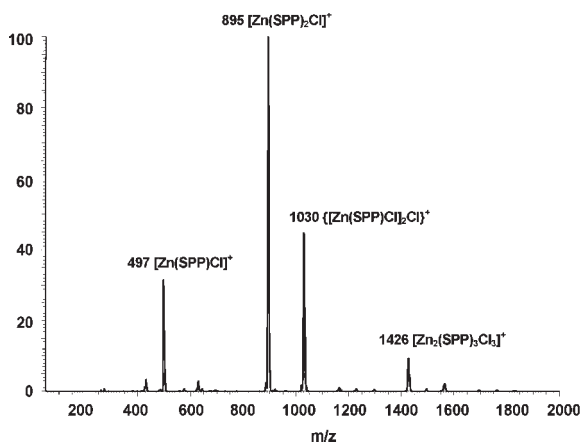$$K_2 = \frac{[\mathbf{MB}_2]}{[\mathbf{MB}][\mathbf{B}]} \tag{3}$$

Figure 4. ESI-MS spectrum of an acetonitrile solution of SPP **2** containing ZnCl$_2$, $C(\mathbf{2}) = C(\text{Zn}) = 2 \times 10^{-3}$ M

Since the concentration of a merocyanine isomer in solutions is too low to allow for its accurate evaluation, total concentration of an SPP is always known and can be used in the calculations. Concentration of species not involved in the complexation reactions may be expressed as the sum of the equilibrium concentration of the ring-closed and the merocyanine forms, and a complexation constant thus obtained represents an effective value taking into account the tautomeric equilibrium (1):[27]

$$K_i^{\text{eff}} = \frac{[\mathbf{MB}_i]}{[\mathbf{MB}_{i-1}][L]^i} \tag{4}$$

where $[L] = [\mathbf{B}] + [\mathbf{A}] = C_0^{\text{SPP}} - \sum_i i[\mathbf{MB}_i]$ is the equilibrium concentration of the SPP isomeric forms not involved in the formation of metal complexes. The K_i^{eff} values serve as a practical measure of the degree of metal complexation. The relationship between K_i and K_i^{eff} is given by Eqn (5), the validity of which requires maintaining constant ion strength by using stock electrolyte t-Bu$_4$ClO$_4$.[27]

$$K_i^{\text{eff}} = \frac{K_T K_i}{1 + K_T} \tag{5}$$

The K_i^{eff} values have been obtained using spectrophotometric technique. For this purpose, absorption spectra of solutions containing a constant amount of SPP and variable concentrations of metal salt have been recorded. In order to estimate the complex stability constants K_i^{eff}, a numerical iterative method has been applied by varying K_i^{eff} and molar absorption coefficients of the species existing in a solution until a minimum of the function (6) is reached.

$$F = \sum_{i=1}^{n_s} \sum_{j=1}^{n_\lambda} (A_{\text{obs}} - A_{\text{calc}})^2 \to \min \tag{6}$$

where n_s is the number of solutions under study, n_λ is the number of the wavelengths under observation.

$$A_{\text{calc}} = \varepsilon_{\mathbf{MB}}[\mathbf{MB}] + \varepsilon_{\mathbf{MB}_2}[\mathbf{MB}_2] + \varepsilon_L^{\text{eff}}[L] + \varepsilon_{\mathbf{M}}[\mathbf{M}]$$

$$[\mathbf{MB}] = \frac{C_{\mathbf{M}} K_1^{\text{eff}}[L]}{1 + K_1^{\text{eff}}[L] + K_1^{\text{eff}} K_2^{\text{eff}}[L]^2}$$

$$[\mathbf{MB}_2] = \frac{C_{\mathbf{M}} K_1^{\text{eff}} K_2^{\text{eff}}[L]^2}{1 + K_1^{\text{eff}}[L] + K_1^{\text{eff}} K_2^{\text{eff}}[L]^2}$$
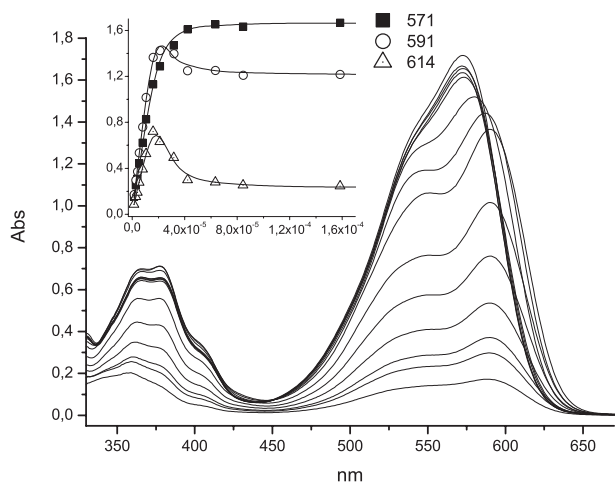
$$C_L = [\mathbf{MB}] + 2[\mathbf{MB}_2] + [L] \tag{7}$$

Figure 5. Absorption spectra of SPP **2** in acetone after addition of various amounts of Ni(ClO$_4$)$_2$. $C(\mathbf{2}) = 4.2 \times 10^{-5}$ M. (Inset: variation of the absorption at 571, 591 and 614 nm vs. concentration of Ni(ClO$_4$)$_2$. Points are experimental values, continuous lines are calculation results)

where A_{obs} and A_{calc} are the observed and calculated absorbance values at the selected wavelength. For minimisation of the function (6), the Newton–Gauss algorithm has been employed.[28] In an iterative nonlinear procedure, the dependences of absorbance *versus* concentration of metal salt at selected wavelengths have been used. A representative fit is shown in Fig. 5. The fits are, in general, reasonably good for all studied SPP. The obtained values of K_1^{eff} and K_2^{eff} are collected in Table 4. This approach allows one to derive molar absorption coefficients of the 1:1 and 1:2 metal ion/merocyanine complexes (Table 3), and to calculate the equilibrium mixture composition for the known concentrations of the initial components.

DISCUSSION

Spectral properties

Coordination of a metal cation by the phenolate oxygen of the coloured ring-open form of spiropyrans[5] and

spironaphthopyrans[27] in 1:1 complexes leads to hypsochromic (blue) shift of the absorption band caused by the polarisation of the π-system of the merocyanine form. Previously, spectral properties of 1:2 complexes of SPP with metal ions have been studied for the case of spironaphthopyran–M^{2+} system.[27] It has also been shown that the longest wavelength absorption bands of the complexes of Co^{2+} and Cu^{2+} are shifted hypsochromically relative to the absorption of the merocyanine ligand and bathochromically (red shift) with respect to the absorption of the corresponding 1:1 complex. At the same time, the spectrum of the 1:2 Ni^{2+} complex is bathochromically shifted relative to the spectrum of the merocyanine ligand.

For all 1:1 and 1:2 complexes of SPP **1–5** studied in the present work, the longest wavelength absorption bands are shifted hypsochromically with respect to these bands of the merocyanine ligand. The maxima of the longest wavelength absorption bands of the 1:2 complexes are found in the longer wavelength region of the visible spectrum than those of the 1:1 metal complexes. As it is seen from Fig. 6, there is a good linear correlation between the positions of the absorption maxima of 1:1 complexes formed by SPP **2–5** and complexes of SPP **1**.

In SPP **4** and **5**, a substituent R^1 offers an additional donor centre (hydroxy and carboxy group, respectively) that can be coordinated by a metal ion. It was shown[29] that in the complexes formed by metal ions with the merocyanine isomers of 1-(ω-carboxypolymethylene)-6-nitrospiro-[2*H*-1-benzopyran-2,2'-indoline] not only the phenolate oxygen, but also a carbonyl oxygen of the carboxy group were involved into the coordination site of the metal complex providing, thus, for the stabilisation of *cis*-configuration of the merocyanine ligand. This effect manifests itself by the appearance of two long wavelength absorption bands at 410 and 490 nm that correspond to *cis*- and *trans*-conformations of the merocyanine ligand, respectively.[29] No such splitting of the longest wavelength absorption band was observed for the case of complexes of SPP **4** and **5** with metal ions (Fig. 6), the position of which is a characteristic of *trans*-isomers of merocyanines.[30] At the same time, the formation of metal complexes of SPP **4** with Cu^{2+} ions and SPP **5** with Zn^{2+}, Co^{2+} and Cu^{2+} ions

Table 4. Logarithms of effective complexes stability constants $T = 293$ K, $I = 0.01$ M (t-Bu$_4$NClO$_4$)

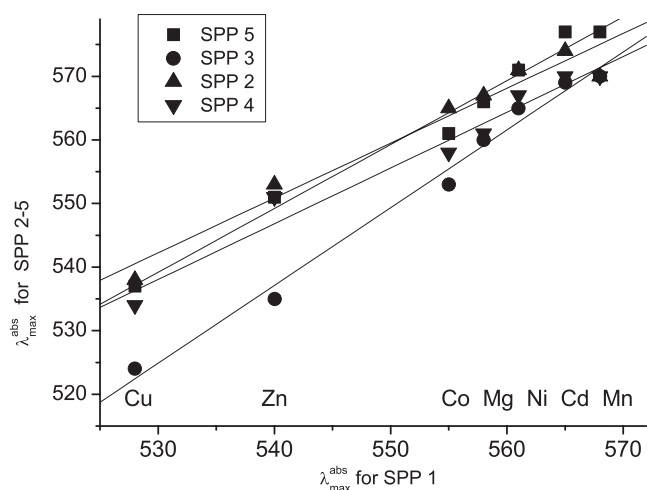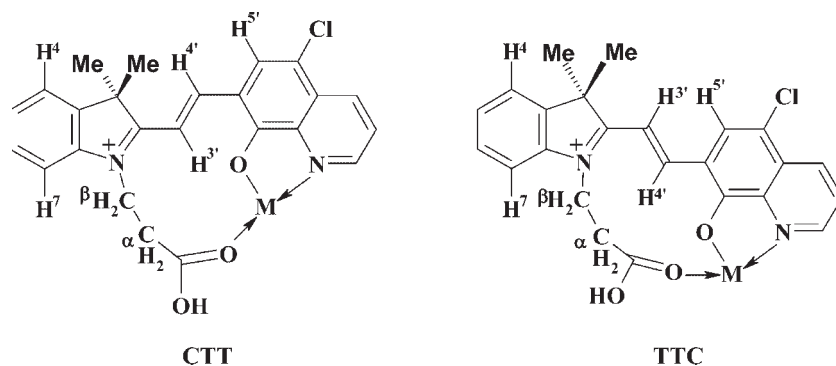| SPP	K_i^{eff}	Mg	Mn	Co	Ni	Zn	Cu
1	K_1	6.19 ± 0.12	6.63 ± 0.12	6.87 ± 0.05	7.06 ± 0.11	7.74 ± 0.02	8.09 ± 0.06
	K_2	5.31 ± 0.07	5.49 ± 0.05	5.12 ± 0.03	5.69 ± 0.07	5.59 ± 0.01	5.18 ± 0.04
2	K_1	5.44 ± 0.16	5.54 ± 0.05	6.68 ± 0.22	6.89 ± 0.13	6.62 ± 0.12	8.78 ± 0.25
	K_2	4.78 ± 0.13	4.14 ± 0.08	5.53 ± 0.13	5.49 ± 0.09	5.69 ± 0.11	5.85 ± 0.08
3	K_1	5.88 ± 0.13	5.36 ± 0.09	6.24 ± 0.09	6.44 ± 0.08	6.98 ± 0.13	7.62 ± 0.17
	K_2	5.43 ± 0.19	4.68 ± 0.02	5.11 ± 0.21	5.64 ± 0.14	5.90 ± 0.15	5.93 ± 0.20
4	K_1	5.69 ± 0.08	6.09 ± 0.03	6.61 ± 0.17	6.68 ± 0.05	6.40 ± 0.13	9.01 ± 0.23
	K_2	4.94 ± 0.01	4.12 ± 0.05	5.59 ± 0.26	5.57 ± 0.07	5.45 ± 0.11	6.00 ± 0.02
5	K_1	6.17 ± 0.16	6.33 ± 0.02	7.45 ± 0.08	7.39 ± 0.03	7.97 ± 0.04	8.02 ± 0.08
	K_2	5.01 ± 0.03	5.03 ± 0.03	6.45 ± 0.09	5.73 ± 0.04	5.68 ± 0.02	6.42 ± 0.11

Figure 6. Interrelationship between λ_{max} of SPP **1** and **2–5**

is accompanied by a significant decrease in the intensity of the absorption bands ($\varepsilon = 3.3$–3.5×10^4 L·mol^{-1}·cm^{-1} for 1:1 complexes) as compared with the same type of complexes of SPP **1–3** ($\varepsilon = 4.1$–5.1×10^4 L·mol^{-1}·cm^{-1}) (Table 3). Such an effect may be associated with the stabilization of one of the *trans*-isomeric forms of the merocyanine ligands brought about by the coordination of a metal cation by the hydroxyl (for SPP **4**) or carbonyl (for SPP **5**) oxygen centres. Of all possible *trans*-isomers, only those with *trans–trans–cis* (TTC) or *cis–trans–trans* (CTT) structures afford the steric conditions necessary for the formation of a tridentate complex with metal ions, that is for involving into the coordination site of the pyridine nitrogen, the phenolate oxygen and an oxygen centre of the substituent R^1 (Scheme 4).

The ^{1}H 2D NOESY NMR spectrum (as described in Supplementary Materials) of an acetonitrile-d$_3$ solution of SPP **5** containing an equimolar amount of ZnCl$_2$ gives a clear evidence for the TTC configuration of the merocyanine ligand in the 1:1 Zn^{2+}·**5** complex. The cross-peaks of the spectrum point to the close proximity of 3'-H and 5'-H, 4'-H and β-methylene, as well as 3'-H and *gem*-dimethyl protons. The results obtained suggest that in the complex of SPP **5** with Zn^{2+} the ligand occurs as TTC conformer.

Factors determining complex stability. Stability of a complex and therefore selectivity of complexation reaction depends both on the nature of a metal ion and on the peculiarity of the ligand structure. For the most studied spiropyrans, a sequence of the effective binding constants depending on the metal ion nature is in accordance with that observed for 8-hydroxyquinoline complexes.[31] The copper complexes are the most stable especially for SPP **2** and **4**. On the other hand, manganese complexes are among the less stable together with magnesium complexes especially for SPP **2** (Table 4). The investigated complexes are differently sensitive to the spiropyran structure. This sensitivity may be caused not only by the nature of donor atoms and feasible steric effects[32] but also by the effect of tautomerism A $\rightleftarrows$ B on the resulting complex stability. The latter is explained by the fact that reactive merocyanine isomer is engaged in two competitive processes—tautomeric equilibrium and complexation equilibrium.[33] The stability of the most stable copper complexes increases monotonically in the SPP range **3, 1, 5, 2, 4** (Table 4) with the decrease of the merocyanine concentration as a result of the tautomerism A $\rightleftarrows$ B (Table 2). For other metal ions, this regularity is characterised by the rise of the stability on going from SPP **3** to SPP **1** and then to SPP **5**. Nevertheless, the complex stability decreases on going from SPP **2** to SPP **4**. The manganese and magnesium complexes are the most sensitive to the spiropyrane structure. Zinc, cobalt and nickel complexes are of intermediate stability values (Table 4).

Conclusion

Photo- and thermally induced conversion between the spirocyclic and the merocyanine isomers of 6'-chloro substituted spiro[indolinepyridobenzopyrans] has been studied. The 1-(2-hydroxyethyl) derivative of SPP exists mainly under the most stable *trans*-(hydroxystyryl) oxazolidineindoline form. Metal ions (Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) induce isomerisation of the SPPs and the formation of intensely coloured complexes

Scheme 4.

with the merocyanine isomeric forms. By means of ESI-MS and UV–Vis spectroscopies, the complex compositions have been proved to be 1:1 and 1:2. The corresponding stepwise stability constants have been determined and spectral properties of mono- and bis- complexes have been investigated. In the mono-complex of 1-(2-carboxyethyl)-substituted SPP with Zn^{2+}, the merocyanine isomer has TTC conformation due to the supplementary coordination of the metal ion with the carboxy oxygen atom. The metal ions can be ranged in accordance to the stability of their complexes that depends on the SPP structure. Therefore, these results provide a possibility to control complexation selectivity by adjusting thermal equilibrium between the spiro- and the merocyanine forms.

EXPERIMENTAL

Compounds

6'-Chloro substituted spiro[indoline-pyridobenzopyrans] (SPP) **1–5** have been prepared by coupling corresponding 2-methyleneindolines or halides of the 3*H*-indolium in the presence of a base with 5-chloro substituted formylquinolinol.[15]

Spectral measurements

^{1}H NMR spectra were recorded on a Varian Unity-300 (300 MHz) spectrometer at 20 °C in acetone-d_6 and acetonitrile-d_3.

The absorption spectra were recorded on an Agilent 8453 diode-array thermostated spectrophotometer. The emission and excitation fluorescence spectra were taken on Varian Cary Eclipse spectrofluorimeter.

Mass spectra of acetonitrile SPP solutions containing metal salts were recorded on a Finnigan LCQTM DECA ESI-MS spectrometer. ESI-MS was performed at 20 °C under dark conditions, with a sample flow rate of $5 \, ml \cdot min^{-1}$. The sheath gas rate was set at 10 units under an N_2 pressure of 0.73 MPa.

The solutions for spectrophotometric investigations were prepared by mixing exact aliquots of standard 2×10^{-4} M solutions of SPP and a metal salt with subsequent dilution in 10 ml flasks. The solutions were allowed to stand for 24 h under dark conditions for complete metal ion complexation.

Metal salts were nitrates, chlorides or perchlorates. The compounds were dissolved in solvents of highest spectroscopic grade (Fluka).

Irradiation technique

A 250 W, IR-filtered high-pressure mercury lamp DRSh-250 equipped with fibre optics was used for UV irradiation of the samples. The wavelength $\lambda = 365$ nm was selected using an interference glass filter. The fibre optic core was appropriately placed to the thermostated cell in order to make the irradiation beam perpendicular to the scanning beam of the spectrophotometer.

REFERENCES

1. Bertelson RC. In *Organic Photochromic and Thermochromic Compounds*, Crano JC, Guglielmetti RJ (eds). Plenum Press: New York, 1999.
2. Minkin VI. *Chem. Rev.* 2004; **104**: 2751–2776. DOI:10.1021/cr020088u.
3. Inouye M. *Coord. Chem. Rev.* 1996; **148**: 265–283. DOI:10.1016/0010-8545(95)01171-4.
4. Alfimov MV, Fedorova OA, Gromov SP. *J. Photochem. Photobiol. A: Chem.* 2003; **158**: 183–198. DOI:10.1016/S1010-6030(03)00033-9.
5. Kimura K. *Bull. Chem. Soc. Jpn.* 2003; **76**: 225–245. DOI:10.1246/bcsj.76.225.
6. Inouye M, Kim K, Kitao T. *J. Am. Chem. Soc.* 1992; **114**: 778–780. DOI:10.1021/ja00028a065.
7. Takase M, Inouye M. *Chem. Commun.* 2001; 2432–2433. DOI:10.1039/b107306k.
8. Phillips JP, Mueller A, Przystal F. *J. Am. Chem. Soc.* 1965; **87**: 4020. DOI:10.1021/ja01095a067.
9. Przystal F, Rudolph T, Phillips JP. *Anal. Chim. Acta* 1968; **41**: 391–394. DOI:10.1016/S0003-2670(01)80413-X.
10. Winkler JD, Bowen CM, Michelet V. *J. Am. Chem. Soc.* 1998; **120**: 3237–3242. DOI:10.1021/ja974181p.
11. Evans L, Collins GE, Shaffer RE, Michelet V, Winkler JD. *Anal. Chem.* 1999; **71**: 5322–5327. DOI:10.1021/ac990755s.
12. Collins GE, Morris RE, Wei J-F, Smith M, Hammond MH, Michelet V, Winkler JD, Serino PM, Guo Y. *Energ. Fuel.* 2002; **16**: 1054–1058. DOI:10.1021/ef010271a.
13. Kovtun YP, Prostota YO, Tolmachev AI. *Dye. Pigment.* 2003; **58**: 83–91. DOI:10.1016/S0143-7208(03)00038-X.
14. Roxburgh CJ, Sammes PG. *Eur. J. Org. Chem.* 2006; 1050–1056. DOI: 10.1002/ejoc.200500681.
15. Voloshin NA, Chernyshev AV, Metelitsa AV, Besugliy SO, Voloshina EN, Sadimenko LP, Minkin VI. *ARKIVOC* 2004; **XI**: 16–24.
16. Hobley J, Malatesta V, Giroldini W, Stringo W. *Phys. Chem. Chem. Phys.* 2000; **2**: 53–57. DOI:10.1039/a908356a.
17. Hobley J, Malatesta V. *Phys. Chem. Chem. Phys.* 2000; **2**: 57–59. DOI:10.1039/a908360j.
18. Zaitseva EL, Prohoda AL, Kurkovskaya LN, Shifrina RR, Kardash NS, Drapkina DA, Krongauz VA. *Chem. Heterocycle Comp.* 1973; **10**: 1362–1365.
19. Atabekyan LS, Seyfetdinova ZK. *High Energy Chem.* 1999; **33**: 30–35.
20. Stauffer MT, Weber SG. *Anal. Chem.* 1999; **71**: 1146–1151. DOI: 10.1021/ac980582r.
21. Shao N, Zhang Y, Cheung SM, Yang RH, Chan WH, Mo T, Li KA, Liu F. *Anal. Chem.* 2005; **77**: 7294–7301. DOI:10.1021/ac051010r.
22. Collins GE, Choi L-S, Ewing KJ, Michelet V, Bowen CM, Winkler JD. *Chem. Commun.* 1999; 321–322. DOI:10.1039/a807994c.

23. Henderson W, McIndoe JS. In *Mass Spectrometry of Inorganic, Coordination and Organometallic Compounds*, Henderson W, McIndoe JS (eds). John Wiley & Sons Ltd: New York, 2005.
24. Kimura K, Sakamoto H, Kado S, Arakawa R, Yokoyama M. *Analyst* 2000; **125**: 1091–1095. DOI:10.1039/b002215m.
25. Nakamura M, Fujioka T, Sakamoto H, Kimura K. *New J. Chem.* 2002; **26**: 554–559. DOI: 10.1039/b111016k.
26. Nakamura M, Takahashi K, Fujioka T, Kado S, Sakamoto H, Kimura K. *J. Am. Soc. Mass. Spectrom.* 2003; **14**: 1110–1115. DOI:10.1016/S1044-0305(03)00447-1.
27. Chernyshev AV, Voloshin NA, Raskita IM, Metelitsa AV, Minkin VI. *J. Photochem. Photobiol. A: Chem.* 2006; **184**: 289–297. DOI:10.1016/j.jphotochem.2006.04.042.
28. Merny SA, Konyaev DS, Kholin YuV. *Kharkov Univ. Bull.* 1998; **420**: 112–120.
29. Wojtyk JTC, Kazmaier P, Buncel E. *Chem. Mater.* 2001; **13**: 2547–2551. DOI: 10.1021/cm010038q.
30. Guglielmetti R. In *Photochromism*, Dürr H, Bouas-Laurent H (eds). Elsevier: Amsterdam, 1990.
31. Johnston WD, Freiser H. *J. Am. Chem. Soc.* 1952; **74**: 5239–5242. DOI:10.1021/ja01141a001.
32. Hartley FR, Burgess C, Alcock RM (eds). *Solution Equilibria*. Ellis Horwood limited publishers: Chichester, 1980.
33. Chibisov AK, Görner H. *Chem. Phys.* 1998; **237**: 425–442. DOI:10.1016/S0301-0104(98)00291-2.