

Novel chelation of photochromic spironaphthoxazines to divalent metal ions

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Abstract

The chelation properties of two photochromic spironaphthoxazine derivatives to divalent metal ions were studied in acetone. Two types of chelate can be observed in the absorption spectrum: an unstable chelate which is formed in the presence of $\text{Ni}(\text{NO}_3)_2$ or $\text{Co}(\text{NO}_3)_2$ on UV irradiation and may revert to the corresponding colourless form in the dark or by bleaching with visible light; the decolouration rate is decreased significantly compared with the metal-ion-free solution; a stable chelate with intense fluorescence emission, which cannot be bleached by visible light. From the influence of the structure of the spiro-oxazines and the nature and concentration of the metal ions and their counteranions on chelate formation, the structures of the two chelates and the mechanisms of the photoreaction and thermal reaction are discussed.

Keywords: Photochromism; Spironaphthoxazine; Chelation

1. Introduction

Spironaphthoxazines are photochromic compounds analogous to spiropyrans. On UV irradiation, the C–O bond of the colourless spironaphthoxazine (SP) is cleaved and the coloured merocyanine (PMC) form is obtained (see Scheme 1). Because of their high fatigue resistance, considerable attention has been paid to the synthesis and photochromic properties of spironaphthoxazines [1–10]. In 1989, Tamaki and Ichimura [11] reported, for the first time, that derivatives of spironaphthoxazine with a coordinating group near the O atom of the naphthoxazine moiety could be transformed into the coloured form on UV irradiation and chelated to certain metal ions, such as Ni^{2+} , Ca^{2+} and Pb^{2+} . This method was used to stabilize the coloured form of spironaphthoxazine embedded in polymeric substrates [12]. However, the decolouration mechanism of the chelate is still unclear. In order to determine the mechanism of the decolouration process of the chelate and the effect of the nature and concentration of metal

ions, the chelation reactions of certain spironaphthoxazine derivatives in the presence of $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$ salts were studied in detail. It is surprising that, unlike spiropyrans, spironaphthoxazines can form two types of chelate with certain metal ions on UV irradiation or even in the dark: one is unstable and decolours to the colourless form thermally or photochemically; the other is stable and exhibits intense fluorescence emission.

2. Experimental details

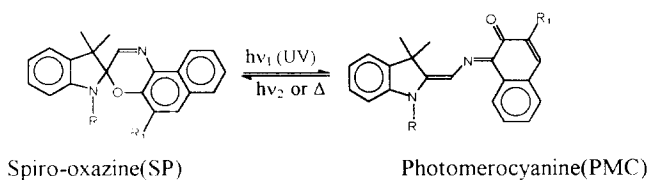
2.1. Synthesis

2.1.1. 1,3,3-Trimethyl-2-methyleneindoline

1,2,3,3-Tetramethylindoleninium iodide was suspended in water and a concentrated solution of sodium hydroxide was added. After the reaction was complete, the mixture was extracted with ether and the organic layer was washed and dried over 4A molecular sieves.

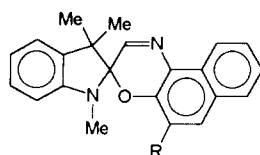
2.1.2. 1-Nitroso-3-carbomethoxy-2-naphthol

3-Hydroxyl-2-naphthoic acid was esterified with methanol in the presence of H_2SO_4 . The 3-carbomethoxy-2-naphthol (melting point (m.p.), 72–73 °C) obtained was nitrosated with NaNO_2 in acetic acid at 0–5 °C to give the orange-



Scheme 1.

yellow 1-nitroso-3-carbomethoxy-2-naphthol (m.p., 153–154 °C).



(1) R=H, (2) R=CO₂Me

2.1.3. 1,3,3-Trimethylspiro(indoline-2,3'-[3H]naphtho[2,1-b]-[1,4]oxazine) (1) and its 5'-carbomethoxy derivative (2)

To a warm solution of 1-nitroso-2-naphthol (or 1-nitroso-3-carbomethoxy-2-naphthol) in ethanol, an equimolar amount of 1,3,3-trimethyl-2-methyleneindoline in ethanol was added gradually. The mixture was refluxed for 3 h, and was cooled at room temperature overnight. Compounds **1** (m.p., 123–124 °C) and **2** (m.p., 139–141 °C) were obtained by repeated recrystallization of the brown solid precipitated from ethanol. The structures of the products were confirmed by conventional methods.

2.2. Instruments and equipment

UV–visible spectra were obtained on an HP8452A diode-array spectrophotometer. Fluorescence spectra were determined on a Hitachi 850 fluorescence spectrophotometer.

UV irradiation was performed using a 100 W xenon lamp with a suitable filter. The cell was equipped with a microstirrer.

For first-order decolouration kinetics, the observed rate constants after exposure to UV irradiation can be calculated using the equation [13]

$$\ln\left(\frac{A_t - A_e}{A_0 - A_e}\right) = k_{dc}^{ob} t \quad (1)$$

where A_0 , A_t and A_e are the absorbances of the coloured form at time 0, t and infinity after UV irradiation respectively.

Similarly, for the first-order chelate formation process in the dark, the observed rate constants can be determined using

$$\ln\left(\frac{A_e - A_t}{A_e - A_0}\right) = k_{ob} t \quad (2)$$

where A_0 , A_t and A_e are the absorbances of the chelate at time 0, t and infinity respectively.

3. Experimental results and discussion

3.1. Decolouration of photomerocyanine (PMC) and its unstable chelate with Ni(II) and Co(II) in acetone

Compound **2** shows normal photochromism in acetone. It can be transformed into the coloured form ($\lambda_{max} = 614$ nm) on UV irradiation and reverts to the original colourless form

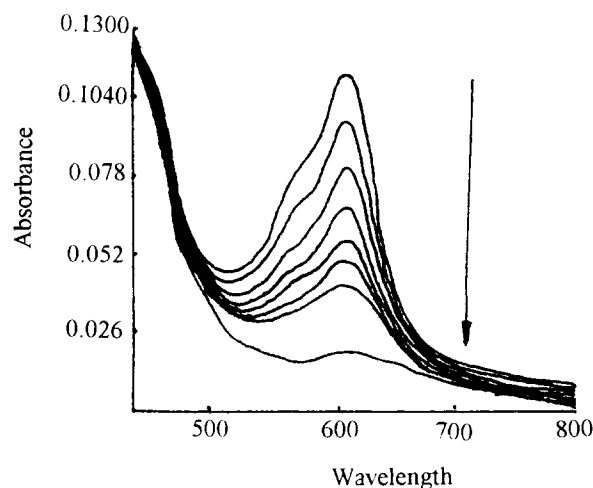


Fig. 1. Changes in the visible spectrum of 4.0×10^{-4} mol l⁻¹ of compound **2** with time in acetone after UV irradiation at 18 °C. Time (s): 0, 2, 4, 6, 8, 10, 12, ∞.

in the dark. Fig. 1 shows the visible absorption spectral changes of compound **2** in acetone after UV irradiation. By fitting the experimental data from Fig. 1 to Eq. (1), we obtain $k_{dc} = 0.11$ s⁻¹.

In the presence of Ni(NO₃)₂, the absorption band of the coloured form after UV irradiation shifts to 606 nm. This band can be attributed to the chelate formed between the PMC form of **2** and Ni(II) [11]. The chelate thus formed is unstable and can decolour to its colourless form in the dark. The thermal decolouration rate k_{dc} is decreased significantly, although the decolouration process can be accelerated by visible irradiation. Fig. 2 shows the absorption spectral changes of the chelate in Ni(NO₃)₂ after UV irradiation.

From Fig. 2(b), it can be seen that, at the Ni(NO₃)₂ concentrations used, the decolouration process of the chelate can be described by first-order kinetics. The rate constants obtained from Fig. 2(b) are listed in Table 1. Similar results can be obtained (Fig. 3 and Table 2) when Co(NO₃)₂ is used.

From Figs. 2 and 3 and Tables 1 and 2, it can be seen that, in the presence of Ni(NO₃)₂ or Co(NO₃)₂, the chelate formed by UV irradiation cannot decolour to the colourless form completely; A_e , the equilibrium absorbance at λ_{max} of the chelate, increases gradually as the concentration of metal ions is increased. This indicates that there is an equilibrium between the colourless form and the chelate. The thermal ring opening process of the colourless form should not be ignored. Therefore the physicochemical process after UV irradiation can be interpreted by Scheme 2.

From Scheme 2, we have

$$\begin{aligned} -\frac{d[C]}{dt} &= \frac{d[A]}{dt} = \left(\frac{k_{dc}}{K[M(II)]} + k_c\right)[C] - k_{op}[A] \\ &= \left(\frac{k_{dc}}{K[M(II)]} + k_{op} + k_c\right)[C] - k_{op}[T] \end{aligned} \quad (3)$$

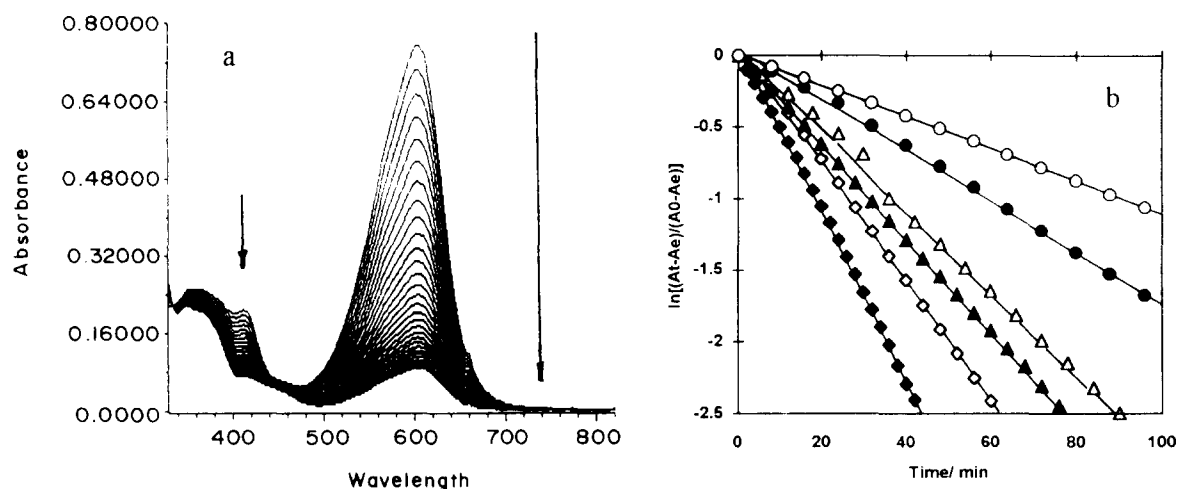


Fig. 2. (a) Absorption spectrum of $5.0 \times 10^{-5} \text{ mol l}^{-1}$ of compound **2** in the presence of $2.0 \times 10^{-4} \text{ mol l}^{-1}$ of $\text{Ni}(\text{NO}_3)_2$ at different times after UV irradiation in acetone at 18°C . Time interval, 2 min. (b) Decolouration rate plots of the chelate (604 nm) formed after UV irradiation at different concentrations of $\text{Ni}(\text{NO}_3)_2$. $[\text{Ni}(\text{NO}_3)_2] \times 10^4 \text{ mol l}^{-1}$: 2.0 (\blacklozenge), 3.0 (\diamond), 4.0 (\triangle), 6.0 (\blacktriangle), 8.0 (\bullet), 16.0 (\circ).

Table 1

Thermal decolouration rates of **2** ($5.1 \times 10^{-5} \text{ mol l}^{-1}$) in the presence of different concentrations of $\text{Ni}(\text{NO}_3)_2$ at 18°C

$[\text{Ni}(\text{NO}_3)_2] \times 10^4 \text{ (mol l}^{-1}\text{)}$	0	2.0	3.0	4.0	6.0	8.0	16.0
$A_e \text{ (604 nm)}$	1.1×10^3	0.067	0.111	0.135	0.194	0.236	0.401
$k_{dc}^{ob} \text{ (} \times 10^{-4} \text{ s}^{-1}\text{)}$		10	7.0	5.4	4.6	3.0	1.9

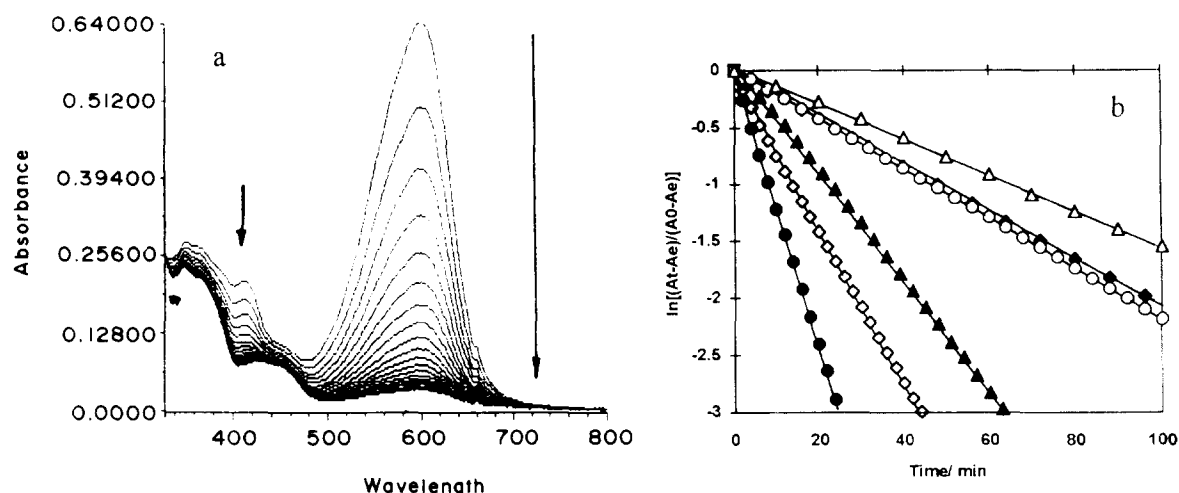


Fig. 3. (a) Absorption spectrum of $5.0 \times 10^{-5} \text{ mol l}^{-1}$ of compound **2** in the presence of $1.0 \times 10^{-4} \text{ mol l}^{-1}$ of $\text{Co}(\text{NO}_3)_2$ at different times after UV irradiation in acetone at 18°C . Time interval, 2 min. (b) Decolouration rate plots of the chelate (604 nm) formed after UV irradiation at different concentrations of $\text{Co}(\text{NO}_3)_2$. $[\text{Co}(\text{NO}_3)_2] \times 10^4 \text{ mol l}^{-1}$: 1.0 (\bullet), 2.0 (\diamond), 3.0 (\blacktriangle), 6.0 (\circ), 8.0 (\blacklozenge), 10.0 (\triangle).

Table 2

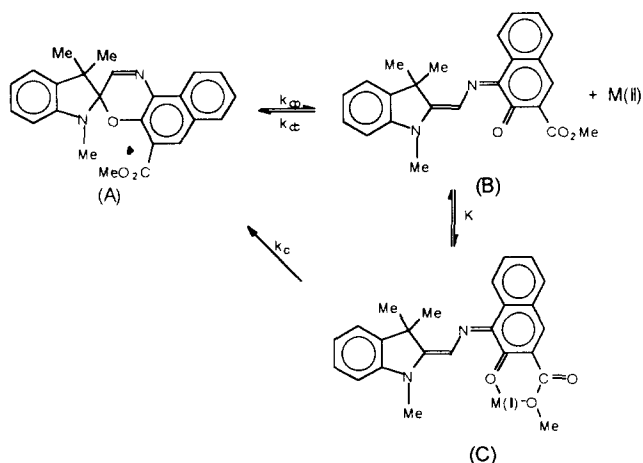
Thermal decolouration rates of **2** ($5.1 \times 10^{-5} \text{ mol l}^{-1}$) in the presence of different concentrations of $\text{Co}(\text{NO}_3)_2$ at 18°C

$[\text{Co}(\text{NO}_3)_2] \times 10^4 \text{ (mol l}^{-1}\text{)}$	1.0	2.0	3.0	6.0	8.0	10.0
$A_e \text{ (600 nm)}$	0.033	0.054	0.074	0.136	0.167	0.196
$k_{dc}^{ob} \text{ (} \times 10^{-4} \text{ s}^{-1}\text{)}$	20	11	8.1	4.1	3.4	2.6

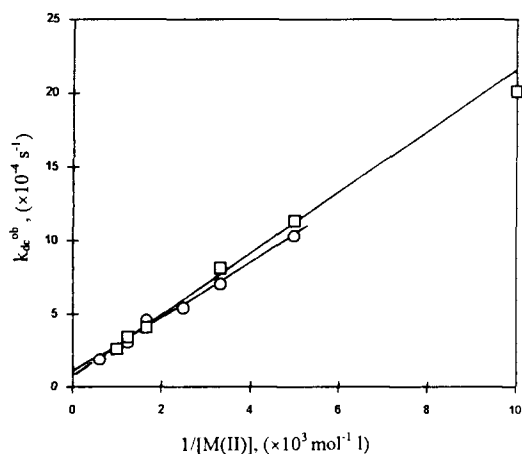
where $[T]$ is the total concentration of A and C and the meaning of the other terms can be deduced from Scheme 2. Treating Eq. (3) by Flannery's method [14], Eq. (4) can be obtained

$$\ln\left(\frac{A_t - A_e}{A_0 - A_e}\right) = \left(\frac{k_{dc}}{K[M(\text{II})]} + k_{op} + k_c\right)t \quad (4)$$

Comparing Eq. (4) with Eq. (1), we have



Scheme 2.

Fig. 4. Variation in the observed decolouration rate constants as a function of the reciprocal of $[\text{Ni}(\text{NO}_3)_2]$ (\circ) or $[\text{Co}(\text{NO}_3)_2]$ (\square).

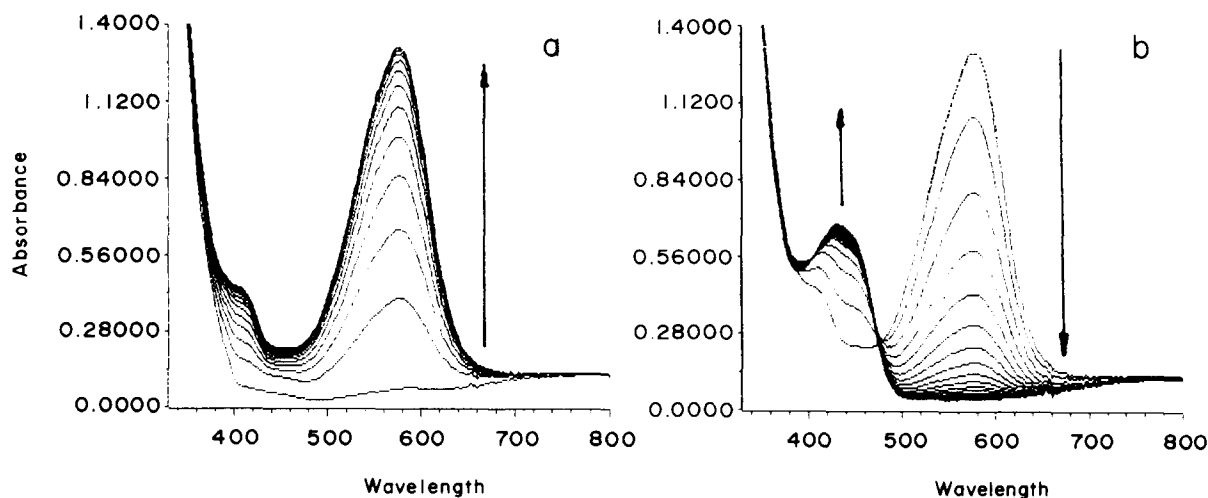
$$k_{\text{dc}}^{\text{ob}} = \frac{k_{\text{dc}}}{K[\text{M}(\text{II})]} + k_{\text{op}} + k_{\text{c}} \quad (5)$$

Treating the data in Tables 1 and 2 using Eq. (5), Fig. 4 is obtained. When Ni(II) acts as the central metal ion, we have $k_{\text{op}} + k_{\text{c}} = 8.6 \times 10^{-5} \text{ s}^{-1}$ and $k_{\text{dc}}/K = 1.9 \times 10^{-7} \text{ mol l}^{-1} \text{ s}^{-1}$. Since $k_{\text{dc}} = 0.11 \text{ s}^{-1}$, $K = 5.8 \times 10^5 \text{ mol}^{-1} \text{ l}$. Similarly, for Co(II) we have $k_{\text{op}} + k_{\text{c}} = 1.1 \times 10^{-4} \text{ s}^{-1}$ and $K = 5.7 \times 10^5 \text{ mol}^{-1} \text{ l}$.

3.2. Stable chelates between compound 2 and divalent metal ions

In order to determine the effect of the nature of the metal ion, $\text{Cu}(\text{NO}_3)_2$ was used instead of $\text{Ni}(\text{NO}_3)_2$ and $\text{Co}(\text{NO}_3)_2$. Fig. 5 shows the absorption spectra of compound 2 in the presence of $\text{Cu}(\text{NO}_3)_2$ at different time intervals. Compound 2 can form a chelate (C) with Cu(II) even in the dark (Fig. 5(a)), but the chelate formed is unstable, and is converted slowly into another stable form (D) (Fig. 5(b)). Fig. 6 shows the variation of the absorbance of C (578 nm) and D (432 nm) with time. The overall process is a typical consecutive reaction for compound 2, with $k_1 = 9.3 \times 10^{-4} \text{ s}^{-1}$ and $k_2 = 1.0 \times 10^{-4} \text{ s}^{-1}$. Because $k_1 \gg k_{\text{op}}$ (see Section 3.1), the ring-opening process cannot be the rate-determining step in the formation of C. A direct interaction between Cu(II) and the colourless form of compound 2 in this process is reasonable since there is a strong interaction between compound 2 and Cu(II). This can be seen from the large chelation-induced blue shift of λ_{max} ($\Delta\lambda$ values are 36, 10 and 14 nm for $\text{Cu}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$ and $\text{Co}(\text{NO}_3)_2$ respectively). The possible mechanism for the chelation process and the structures of the chelates (C and D) formed are shown in Scheme 3.

Unlike chelate C, chelate D is a stable complex and cannot be bleached by visible light. In accordance with its stability, an intense fluorescence is observed. In addition, chelation depends on the metal ion, the counteranions and the solvent molecules. For example, an obvious decrease in chelate formation can be induced by the addition of a small amount of

Fig. 5. Changes in the absorption spectrum of $6.0 \times 10^{-5} \text{ mol l}^{-1}$ of compound 2 in the presence of $3.0 \times 10^{-3} \text{ mol l}^{-1}$ of $\text{Cu}(\text{NO}_3)_2$ with time: (a) from $t=0$ to $t=60 \text{ min}$; time interval, 5 min; (b) from $t=65 \text{ min}$ to $t=1265 \text{ min}$; time interval, 30 min.

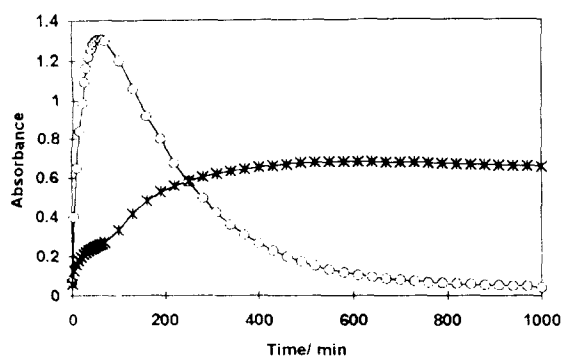
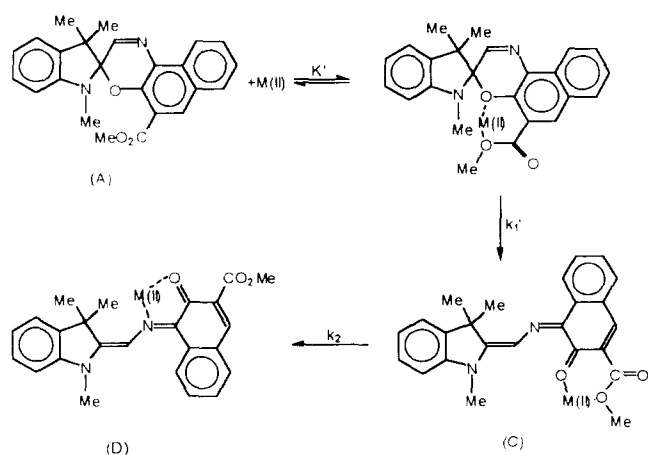


Fig. 6. Variations in the absorbance of C (O, 578 nm) and D (*, 432 nm) with time.



Scheme 3.

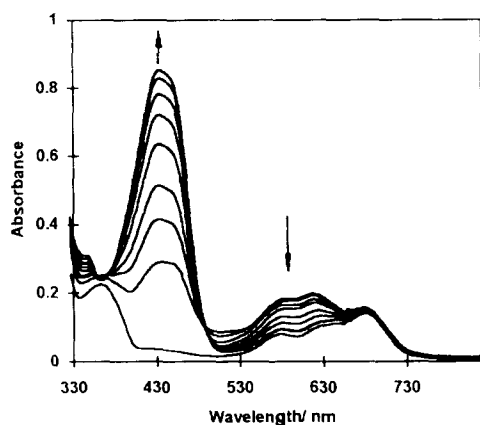


Fig. 7. Absorption spectral changes of $2.5 \times 10^{-5} \text{ mol l}^{-1}$ of compound 2 in the presence of $4.0 \times 10^{-4} \text{ mol l}^{-1}$ of CoCl_2 on UV irradiation. Time interval, 2 min.

water. For CuCl_2 , a similar result is obtained, but the peak corresponding to chelate C is very weak. For other less effective metal ions, such as $\text{Ni}(\text{NO}_3)_2$ and $\text{Co}(\text{NO}_3)_2$, only chelate C is observed after UV irradiation (see Section 3.1). However, for CoCl_2 and NiCl_2 , chelate C, formed on UV irradiation, is transformed steadily into chelate D. Fig. 7 shows the absorption spectra of compound 2 in CoCl_2 on UV irradiation at different time intervals. The spectral character-

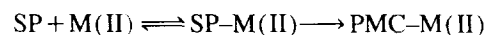
istics of the chelates formed in the presence of various salts are listed in Table 3.

3.3. Stable chelate between compound 1 and divalent metal ions

The most important difference between the structures of photochromic spiroopyran and spiro-oxazine is the imino N atom in the latter. In the work of Tamaki and Ichimura [11], it was reported that compound 1, without a coordinating group at the 5' position, could not form a complex with $\text{Ni}(\text{II})$ on UV irradiation. In their work, only $\text{Ni}(\text{NO}_3)_2$, $\text{Ni}(\text{ClO}_4)_2$ and mixed $\text{Ni}(\text{II})$ complexes were used.

In the present work, it can be seen from Scheme 3 that the imino N atom acts as the second coordinating group in chelate D. To verify the coordinating activity of the imino N atom, compound 1 was re-investigated. Compound 1 forms a stable 1:1 complex with $\text{Cu}(\text{II})$ on UV irradiation and in the dark. Fig. 8 shows the absorption spectral changes of compound 1 in $\text{Cu}(\text{NO}_3)_2$ solution on UV irradiation. The solution is nearly colourless before irradiation. On UV irradiation, a new band appears at 452 nm and increases steadily until a limit is attained. For spiroopyran, without a coordinating group near the pyranil O atom, this new band is not observed. Therefore it is reasonable to assign this band to a chelate in which the imino N atom acts as one of the two coordinating groups. Like chelate D between compound 2 and $\text{M}(\text{II})$, the chelate thus formed is stable on visible light irradiation and exhibits intense fluorescence.

Another important observation is that, even in the dark, compound 1 can form a chelate with $\text{Cu}(\text{NO}_3)_2$, but the rate is significantly slower. Unlike the chelate formation process of spiroopyran with $\text{Cu}(\text{II})$ in the dark [15], the concentration of $\text{Cu}(\text{II})$ has a significant influence on the chelation rate of compound 1 (Fig. 9(a)). However, the chelate formation reaction rates are not proportional to the concentrations of the metal ions. Thus it is more reasonable to express the mechanism of this reaction by Scheme 4 rather than by the following



By treating the process in Scheme 4 using the steady state assumption, we have

$$-\frac{d[\text{A}]}{dt} = \frac{d[\text{D}]}{dt} = \frac{k_{\text{op}}k_{\text{f}}[\text{M}(\text{II})]}{k_{\text{dc}} + k_{\text{f}}[\text{M}(\text{II})]} [\text{A}] \quad (6)$$

$$\ln\left(\frac{A_0^{\text{A}} - A_t^{\text{A}}}{A_0^{\text{A}} - A_{\infty}^{\text{A}}}\right) = \ln\left(\frac{A_t^{\text{D}} - A_0^{\text{D}}}{A_{\infty}^{\text{D}} - A_0^{\text{D}}}\right) = \frac{k_{\text{op}}k_{\text{f}}[\text{M}(\text{II})]}{k_{\text{dc}} + k_{\text{f}}[\text{M}(\text{II})]} t \quad (7)$$

where A_0^{A} (or A_0^{D}), A_t^{A} (or A_t^{D}) and A_{∞}^{A} (or A_{∞}^{D}) are the absorbances of A (or D) at $t=0$, t and ∞ respectively. Comparing Eq. (7) with Eq. (1), we obtain

$$k_{\text{ob}} = \frac{k_{\text{op}}k_{\text{f}}[\text{M}(\text{II})]}{k_{\text{dc}} + k_{\text{f}}[\text{M}(\text{II})]} \quad (8)$$

Table 3

Absorption and emission maxima of chelates C and D formed between compound 2 and different divalent metal salts

Maximum	Salt						
	Cu(NO ₃) ₂	CuCl ₂	Ni(NO ₃) ₂	NiCl ₂	Co(NO ₃) ₂	CoCl ₂	Zn(NO ₃) ₂
λ ^{ab} (nm) (C)	578	610	604	616	600	610	592
λ ^{ab} (nm) (D)	428	432		432		432	
λ ^{em} (nm) (D)	529	530		526		526	526

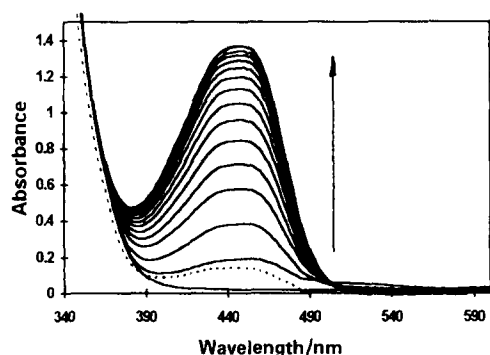
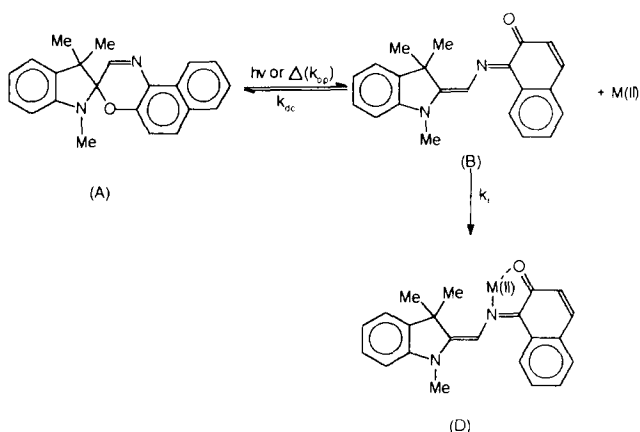
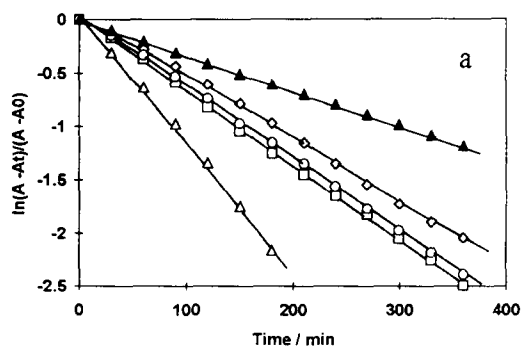


Fig. 8. Absorption spectral changes of $4.4 \times 10^{-5} \text{ mol l}^{-1}$ of compound 1 in the presence of $3.0 \times 10^{-3} \text{ mol l}^{-1}$ of $\text{Cu}(\text{NO}_3)_2$ during UV irradiation; time interval, 2 min. The broken line is the spectrum of the same solution without UV irradiation at $t = 60 \text{ min}$.



Scheme 4.



or

$$\frac{1}{k_{ob}} = \frac{1}{k_{\infty}} + \frac{k_{dc}}{k_{op}k_f[M(\text{II})]} \quad (9)$$

From Eq. (9), as the decolouration of the metal-free coloured form is slow, i.e. $k_{dc} \ll k_f[M(\text{II})]$, we have $k_{ob} = k_{op}$. In other words, the concentration of metal ions has no effect on the formation rate of the chelate. This should be the case for spiropyran [15]. When the decolouration process of the metal-free coloured form is fast, the effect of the concentration cannot be ignored, and a higher concentration of metal ion favours the formation of the chelate. This is the case for the chelation of compound 1 with $\text{Cu}(\text{NO}_3)_2$. By fitting the data to Eq. (9), Fig. 9(b) is obtained. From Fig. 9(b), we have $k_{op} = 2.2 \times 10^{-4}$ and $k_{dc}/k_{op}k_f = 14 \text{ mol l}^{-1} \text{ s}^{-1}$. k_{dc} determined from the metal-ion-free solution is about 0.34 s^{-1} . Then we have $k_f = 110 \text{ mol}^{-1} \text{ l s}^{-1}$. From the values of k_{op} and k_{dc} obtained, the equilibrium constant between the SP and PMC form of 1 can be determined

$$K_e = \frac{k_{op}}{k_{dc}} = \frac{2.2 \times 10^{-4}}{0.34} = 6.6 \times 10^{-4}$$

Apart from $\text{Cu}(\text{NO}_3)_2$, stable chelates can be formed between CuCl_2 or NiCl_2 and compound 1 in the dark or on UV irradiation. However, $\text{Ni}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$, CoCl_2 and $\text{Zn}(\text{NO}_3)_2$ are less effective. The chelate formation processes are very slow even on UV irradiation. Like chelate D of compound 2, the chelate formed by compound 1 exhibits intense fluorescence emission and cannot be bleached by visible light. Fig. 10 shows the emission spectra of the chelates formed with different divalent metal salts.

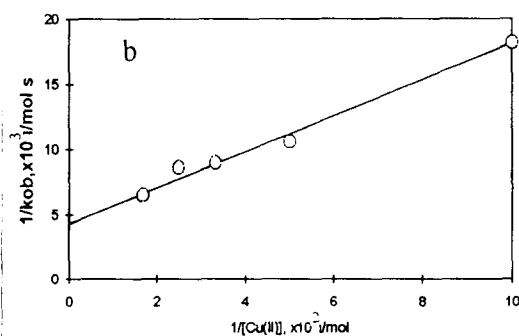


Fig. 9. (a) First-order rate plots for the chelate formation process of compound 1 with $\text{Cu}(\text{NO}_3)_2$ at different concentrations of $\text{Cu}(\text{NO}_3)_2$ in the dark. (b) Correlation between the reciprocal of the observed chelate formation rate constant and the reciprocal of $[\text{Cu}(\text{NO}_3)_2]$.

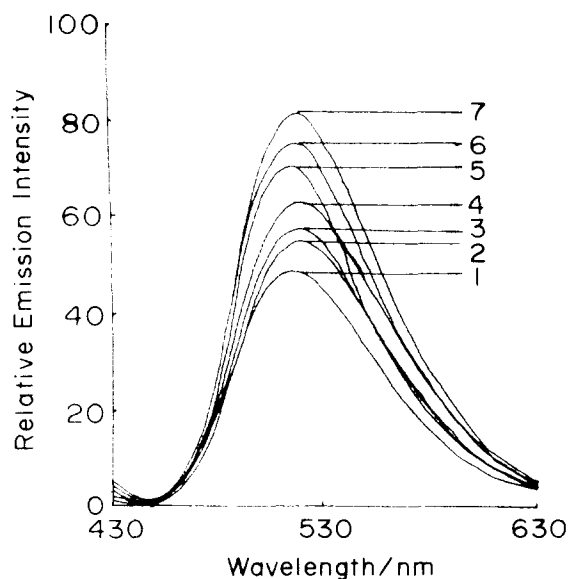


Fig. 10. Emission spectra of the stable chelate of $5.0 \times 10^{-5} \text{ mol l}^{-1}$ of compound **1** formed in the dark or on UV irradiation with different divalent metal salts: 1, $2.0 \times 10^{-3} \text{ mol l}^{-1} \text{ Ni}(\text{NO}_3)_2$; 2, $2.0 \times 10^{-3} \text{ mol l}^{-1} \text{ CuCl}_2$; 3, $2.0 \times 10^{-3} \text{ mol l}^{-1} \text{ NiCl}_2$; 4, $2.0 \times 10^{-3} \text{ mol l}^{-1} \text{ Co}(\text{NO}_3)_2$; 5, $2.0 \times 10^{-3} \text{ mol l}^{-1} \text{ CoCl}_2$; 6, $2.0 \times 10^{-3} \text{ mol l}^{-1} \text{ Cu}(\text{NO}_3)_2$; 7, $0.2 \text{ mol l}^{-1} \text{ Zn}(\text{NO}_3)_2$.

4. Conclusions

The chelation of two photochromic spironaphthoxazine derivatives with divalent metal ions on UV irradiation and in the dark was studied using UV–visible and fluorescence spectroscopy in acetone. The following conclusions can be drawn.

- (1) 1,3,3-Trimethylspiro(indoline-2,3'-[2H]naphtho[2,1-b]-[1,4]oxazine) (**1**) and its 5'-carbomethoxy derivative (**2**) show normal photochromism in acetone. In the presence of $\text{Ni}(\text{NO}_3)_2$ or $\text{Co}(\text{NO}_3)_2$, the coloured form of **2** produced by UV irradiation forms an unstable chelate with metal ions. The chelate thus formed can be transformed into the colourless form in the dark or on visible irradiation, but the decolouration rate is decreased significantly.
- (2) In the presence of $\text{Cu}(\text{NO}_3)_2$, CuCl_2 or NiCl_2 , compound **1** can form stable chelates on UV irradiation or

in the dark; the imino N atom acts as the secondary coordinating group.

- (3) In the presence of $\text{Cu}(\text{NO}_3)_2$ or CuCl_2 , compound **2** forms unstable chelates on UV irradiation or in the dark; their spectral characteristics are similar to those of the chelates formed between compound **2** and $\text{Ni}(\text{NO}_3)_2$ or $\text{Co}(\text{NO}_3)_2$ on UV irradiation. The unstable chelate thus formed can transform slowly to a stable form in the dark. As in the stable chelate of **1**, the imino N atom acts as the secondary coordinating group in the stable chelate of **2**. Other salts, such as CoCl_2 and NiCl_2 , are less effective; their chelation processes are very slow even on UV irradiation.
- (4) The unstable chelate is non-radiative, but the stable chelate emits intense fluorescence.

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