

COMPLEX FORMATION OF SPIROPYRANS WITH METAL CATIONS IN SOLUTION: A STUDY BY LASER FLASH PHOTOLYSIS

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Summary

Nanosecond flash photolysis was used to study the complexation reactions of a spiropyran of the indoline series (1',3',3'-trimethyl-6-nitro-8-methoxyspiro[2*H*-1-benzopyran-2,2'-(2*H*)-indol]) with lead(II), cobalt(II), cadmium(II) and zinc(II) in an acetone-water mixture. Two relatively unstable trans isomers of the spiropyran merocyanine form were found to be involved in the complexation. A decrease in the yield of complex was found to occur in the presence of acid. Several transient forms of the complex were revealed. The lifetime of the transient forms of the complex is the same as that of the corresponding trans isomers of the spiropyran merocyanine form. A reaction scheme of complexation is proposed.

1. Introduction

It has been previously established [1 - 6] that spiropyrans of the indoline series are able to complex with transition metal ions (Cu^{2+} , Co^{2+} , Zn^{2+} etc.). On UV irradiation of spiropyrans in acetone, ethanol, toluene and tetrahydrofuran containing copper(II), cobalt(II), zinc(II) etc. it was found that new absorption appeared and this was assigned to complex formation [1, 2, 5]. The possibility of spiropyran complexation with manganese(II), cobalt(II) and copper(II) was also confirmed by nuclear magnetic resonance [6]. It was recently revealed that addition of plumbous, cobaltous, cadmium and zinc nitrates to the spiropyran 1',3',3'-trimethyl-6-nitro-8-methoxyspiro[2*H*-1-benzopyran-2,2'-(2*H*)-indol] (Sp) in an acetone-water mixture gives rise to the production of an intensely coloured complex [7]. The complexation reaction can occur in the dark; however, the yield of the complex increases on UV irradiation of the spiropyran. It is known [8] that in polar solvents spiropyran molecules to some extent exist in the merocyanine open form and that the concentration of the open form increases on UV illumination. It has been assumed [1 - 6] that only the merocyanine form of the spiropyran is involved in the complexation reaction. The kinetics of com-

plexation of the spiropyran with Cu^{2+} , Zn^{2+} and Pb^{2+} ions has been recently investigated by a stopped-flow technique [9]. It was found that the complexation reaction proceeds via two steps and that the fast step occurs in a time shorter than the time resolution of the stopped-flow apparatus used (about 1 ms).

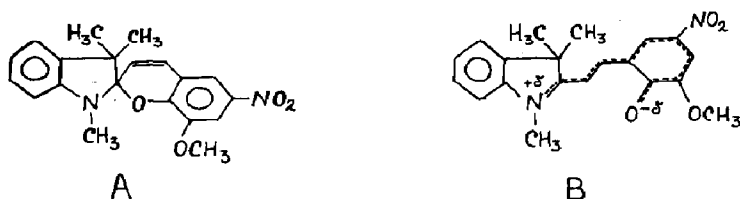
In this paper we present the results on spiropyran complexation with metal ions derived from a study employing nanosecond laser flash photolysis.

2. Experimental details

The absorption spectra and decay kinetics of the intermediates were measured using a nanosecond laser flash photolysis set-up [10]. Some measurements were carried out using laser flash photolysis apparatus coupled with a Fabri-Tek 1074 averager and a Bruker BC-104 digitizer with 100 ns address resolution. Steady state UV irradiation of the spiropyran solution was performed with a high pressure mercury lamp (250 W) through a UFS-2-BS-7 glass filter. Absorption spectra of the stable products of the photoreactions were measured by means of a Specord M-40 spectrophotometer. All measurements were carried out in standard quartz cells of path length 1 cm at room temperature on air-saturated solutions. An acetone-water mixture was used as the solvent (water content, 2.5 vol.%). The spiropyran Sp of the indoline series was used. The metals lead(II), cobalt(II), zinc(II) and cadmium(II) were added to solution as the nitrates. Sp concentrations were 10^{-4} and 2×10^{-4} M and nitrate concentrations were 10^{-6} - 10^{-2} M. Acetone was purified by the standard procedure. HNO_3 was analytical grade.

3. Results and discussion

On steady state UV irradiation of Sp solution an increase in absorption intensity in the visible was found to occur owing to the formation of the merocyanine (open) form B of Sp from the initial (closed) form A.



When a solution of Sp was irradiated in the presence of metal nitrates, changes in the absorption spectrum (Fig. 1) were observed as a result of Sp complexation with metal ions. Flashing with pulses from an Nd-YAG laser ($\lambda = 354$ nm; energy, about 0.3 mJ; $\tau_{0.5} = 10$ ns) of an Sp solution containing metal nitrates also gives rise to changes in the absorption of the Sp. Figures 2 and 3 show oscilloscope traces of Sp measured at different sweeps

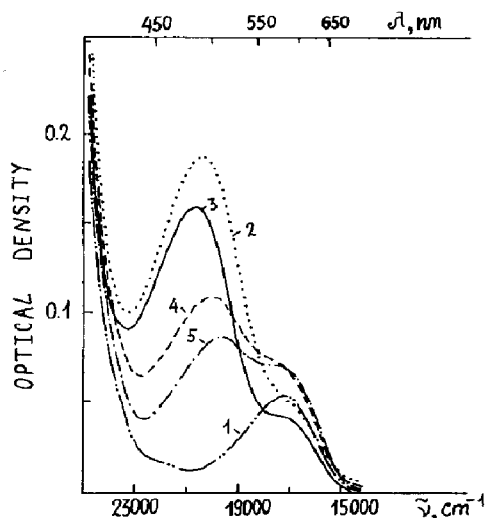


Fig. 1. Absorption spectrum of the Sp merocyanine form (curve 1) and the complex of Sp with lead(II) (curve 2), cobalt(II) (curve 3), cadmium(II) (curve 4) and zinc(II) (curve 5) nitrates in acetone (concentrations: Sp, 10^{-4} M; metal nitrates, 6×10^{-5} M).

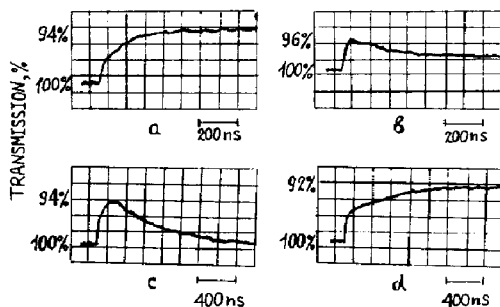
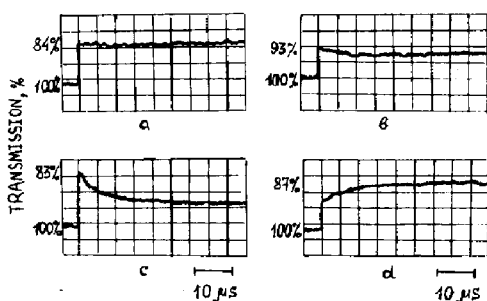


Fig. 2. Oscilloscope traces of Sp transient absorption in the absence of $\text{Pb}(\text{NO}_3)_2$ (curves a and b) and in its presence (curves c and d) (concentrations: $[\text{Pb}(\text{NO}_3)_2] = 8 \times 10^{-5}$ M; $[\text{Sp}] = 2 \times 10^{-4}$ M): curves a and c, $\lambda = 580$ nm; curves b and d, $\lambda = 490$ nm.

Fig. 3. Oscilloscope traces of Sp transient absorption in the absence of $\text{Pb}(\text{NO}_3)_2$ (curves a and b) and in its presence (curves c and d) (concentrations: $[\text{Pb}(\text{NO}_3)_2] = 10^{-3}$ M; $[\text{Sp}] = 2 \times 10^{-4}$ M): curves a and c, $\lambda = 580$ nm; curves b and d, $\lambda = 490$ nm.

of the oscilloscope in the presence and absence of $\text{Pb}(\text{NO}_3)_2$ at wavelengths corresponding to the absorption maxima of the merocyanine form of Sp ($\lambda = 580$ nm) and of its complex with the metal ($\lambda = 490$ nm) respectively. It follows from Figs. 2 and 3 that the absorption changes observed on laser excitation of Sp in the presence of $\text{Pb}(\text{NO}_3)_2$ differ markedly from those obtained in the absence of metal ions, both on the microsecond and the nanosecond time scale. Figures 2 and 3 also show that the rate of decrease in absorption measured in the presence of $\text{Pb}(\text{NO}_3)_2$ at $\lambda = 580$ nm matches the rate of growth of absorption at $\lambda = 490$ nm. Similar behaviour was observed on laser excitation of Sp in the presence of zinc, cadmium and cobaltous nitrates.

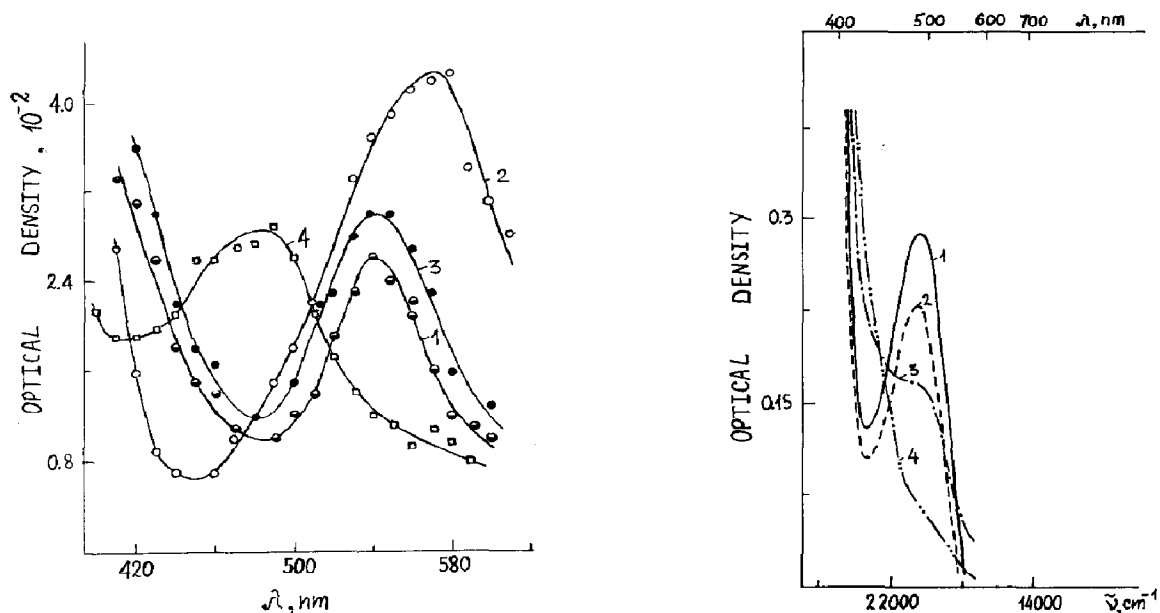


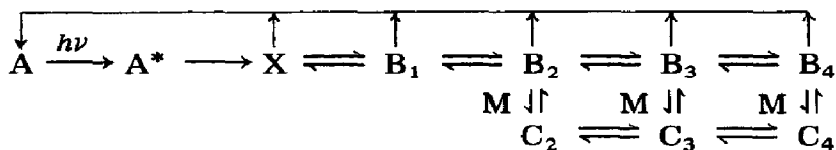
Fig. 4. Differential absorption spectra of Sp (curves 1 and 2) and its complex with lead(II) (curves 3 and 4) measured at 30 ns (curves 1 and 3) and 500 ns (curves 2 and 4) after the laser pulse (concentrations: $[Sp] = 10^{-4} M$; $[Pb(NO_3)_2] = 4 \times 10^{-3} M$).

Fig. 5. Absorption spectrum of the complex of Sp with lead(II) in the absence (curve 1) and the presence of HNO_3 at a concentration of $5 \times 10^{-6} M$ (curve 2), $2 \times 10^{-5} M$ (curve 3) or $5 \times 10^{-5} M$ (curve 4) ($[Sp] = 2 \times 10^{-4} M$; $[Pb(NO_3)_2] = 2 \times 10^{-4} M$).

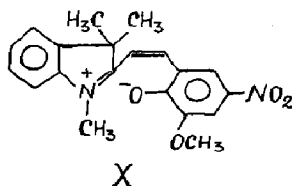
The differential spectra of Sp in the presence and absence of $Pb(NO_3)_2$ were measured at different time intervals after laser pulse irradiation. Figure 4 presents differential spectra obtained after 30 ns and 500 ns. It follows that the differential spectra measured at 30 ns (Fig. 4, curves 1 and 3) are similar, but the differential spectra obtained at 500 ns (Fig. 4, curves 2 and 4) are similar to the absorption spectra measured on UV steady state irradiation of Sp solution (Fig. 1, curves 1 and 2). The complexation between Sp and lead(II) is complete by 500 ns (lead(II) concentration, $4 \times 10^{-3} M$).

The effect of acid on complexation of Sp with metal ions was also studied in this work. The absorption spectra obtained on UV steady state irradiation of Sp plus lead(II) in the presence and absence of HNO_3 are given in Fig. 5. It follows from Fig. 5 that a decrease in the absorption intensity of the complex ($\lambda = 490 nm$) takes place when the concentration of HNO_3 is increased. From a comparison of the spectral curves in Fig. 5 it follows that HNO_3 suppresses the complexation of Sp with metal ions.

Photochromic reactions of spiropyrans occurring in solution in the presence of metal ions may be presented as follows:



According to refs. 11 - 14 the intermediate X is a cis-cisoid isomer with a lifetime of 10^{-9} - 10^{-7} s.



The states B_1 - B_4 are different trans isomers whose stability increases on passing from B_1 to B_4 [15, 16]. The absorption spectrum given in Fig. 4, curve 1, could be assigned to the less stable trans isomer B_1 . This is indicated firstly by the similarity between the spectrum presented in Fig. 5 and that measured 5 ns after picosecond laser excitation of the spiropyran solution [11], and secondly by the characteristic time of the trans-trans conversion $B_1 \rightarrow B_{2,3,4}$ being 10^{-7} s [11], which is in good agreement with our experimental data (Fig. 3, curves a and b). So the spectral changes observed on laser excitation of Sp solution in the absence of metal nitrates are caused by the reaction $B_1 \rightarrow B_2$ (Fig. 3, curves a and b). It is important to note that the absorption spectra of the B_2 , B_3 and B_4 isomers are similar [17 - 19] and that the oscilloscope traces given in Figs. 2 and 3 present the transient absorption of all the trans isomers.

However, the use of the averaging technique and repetitive laser excitation made it possible to observe the trans-trans conversion of the merocyanine form even though the spectra of the ground state absorption of the trans isomers were very similar. Figure 6 (curves a and b) presents the oscilloscope traces of Sp transient absorption which were obtained when the laser was operated in the repetitive mode and the averaging technique was used. The time course of the optical density presented in Fig. 6 (curves a and b) may be assigned to B_2 - B_3 - B_4 trans isomer interconversion.

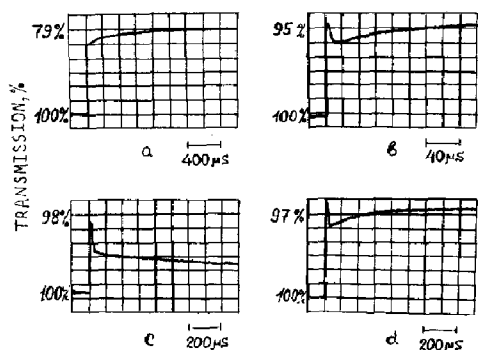


Fig. 6. Oscilloscope traces of Sp transient absorption in the absence (curves a and b) and in the presence (curves c and d) of $Pb(NO_3)_2$ ($[Sp] = 10^{-4}$ M; $[Pb(NO_3)_2] = 2 \times 10^{-3}$ M): curves a and c, $\lambda = 580$ nm; curves b and d, $\lambda = 490$ nm. (Number of averages, 10.)

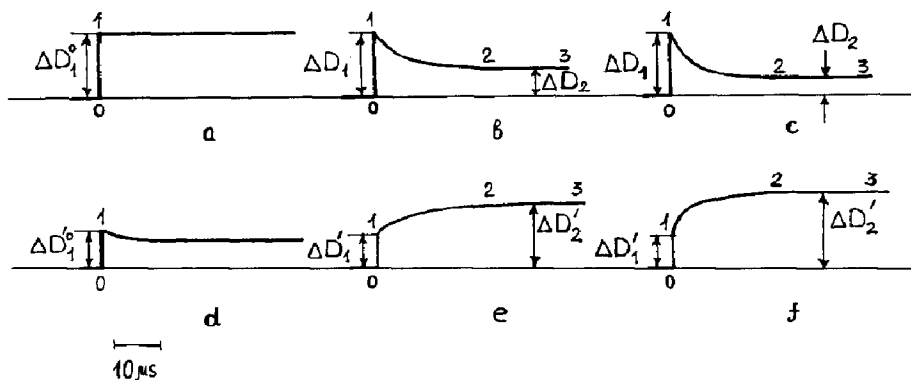


Fig. 7. Schematic oscilloscope traces measured in the absence of $\text{Pb}(\text{NO}_3)_2$ (curves a and d) and in its presence at a concentration of $8 \times 10^{-5} \text{ M}$ (curves b and e) or $1.5 \times 10^{-4} \text{ M}$ (curves c and f): curves a, b and c, $\lambda = 580 \text{ nm}$; curves d, e and f, $\lambda = 490 \text{ nm}$. ($[\text{Sp}] = 2 \times 10^{-4} \text{ M}$.)

For the analysis of the results for the complexation of Sp with metals we shall consider the oscilloscope traces obtained on laser excitation of Sp plus $\text{Pb}(\text{NO}_3)_2$ which are presented schematically in Fig. 7. The traces consist of three portions: 0 - 1, the fast increase in optical density ΔD_1 ($\Delta D_1'$); 1 - 2, characterized by a monotonic decrease in optical density to ΔD_2 (Fig. 7, curves b and c) or by an increase in optical density to $\Delta D_2'$ (Fig. 7, curves e and f); 2 - 3, the constant optical density. An increase in the concentration of metal ions results in both a decrease in ΔD_2 and an increase in the rate of reduction in optical density (portion 1 - 2 of Fig. 7, curves b and c). Also, the increase in both $\Delta D_2'$ and the rate of rise of optical density are due to increases in the metal ion concentrations (Fig. 7, curves e and f; portion 1 - 2). A decrease in optical density ΔD_2 (portion 2 - 3) when compared with ΔD_1^0 occurred in the presence of lead(II) and may be caused by a decrease in the yield of the most stable isomer B_4 of Sp as a result of complexation of the B_3 trans isomer competing with the trans-isomer conversion $B_3 \rightleftharpoons B_4$. The formation of product C_3 , which is accompanied by an increase in optical density at 490 nm (portion 1 - 2 of Fig. 7, curves e and f) is the result of B_3 complexation with lead(II). The B_2 isomer becomes involved in complexation at a lead(II) concentration which is higher than that for the B_3 isomer because the lifetime of B_2 is less than that of B_3 [15, 16]. When the concentration of lead(II) is increased the complexation between lead(II) and B_2 takes place and gives rise to the formation of the product C_2 . The complexation is accompanied by a shortening of the lifetime of the transient absorption and by a further decrease in ΔD_2 (Fig. 7, curve c). The similarity between the absorption spectrum of B_1 (Fig. 4, curve 1) and that measured in the presence of lead(II) (Fig. 4, curve 3) indicates that the less stable trans isomer B_1 is not involved in complexation even when the concentration of lead(II) is increased to 10^{-2} M . This result may be explained by the short lifetime of B_1 .

We have previously established [7, 9] that spiropyran molecules are able to undergo a thermal complexation reaction with metal cations (lead(II), cobalt(II), cadmium(II) etc.). This indicates that the most stable isomer B_4 is also involved in complexation.

Moreover, additional experimental evidence of the involvement of B_4 in complexation is obtained from a comparison between the oscilloscope traces obtained on laser excitation of Sp solutions in the absence and in the presence of $Pb(NO_3)_2$ (Fig. 6, curves a and c). The fast decrease in optical density presented in Fig. 6, curve c, may be caused by the participation of B_2 and B_3 trans isomers in the complexation. But the slow decrease in optical density is probably because of B_4 trans isomer involvement in complexation. The results presented in Fig. 7, curves b and c (portion 1 - 3), indicate that the rate of B_4 trans isomer complexation is lower than that of the B_3 trans isomer. This may be explained by the steric hindrance in the complexation of B_4 compared with that for the $B_1 - B_3$ isomers.

The existence of several products of complexation of Sp with lead(II) (C_2 , C_3 and C_4) is confirmed by measurements of the kinetics of the reaction of trans isomers carried out in the presence and the absence of lead(II) (Fig. 6). From a comparison between the oscilloscope traces presented in Fig. 6, curves c and d, it follows that the slow increase in optical density at the maximum absorption of the complex (Fig. 6, curve d) does not relate to the trans-trans conversion of the merocyanine form of Sp ($B_2 \rightarrow B_3 \rightarrow B_4$). This may be concluded because the complexation is complete at 500 ns after the laser pulse. The oscilloscope trace given in Fig. 6, curve d, is the time course of the only complex formed. The slow increase in optical density presented in Fig. 6, curve d, cannot be assigned to complex production as a result of reaction between B_4 and $Pb(NO_3)_2$ because the rate of slow decrease in optical density (Fig. 6, curve c) does not match the rate of slow growth of optical density (Fig. 6, curve d). Thus the existence of several complexes between Sp and lead(II) ($C_2 \rightarrow C_3 \rightarrow C_4$) may be looked on as the explanation. The rate of conversion of these complexes matches that of the trans isomers, $B_2 \rightarrow B_3 \rightarrow B_4$. The absorption spectra of $C_2 - C_4$ are similar, this following from the resemblance of the differential absorption spectrum of Sp plus lead(II) measured at 500 ns after the laser pulse to that obtained on UV steady state irradiation of the same solution (Fig. 4, curve 4, and Fig. 1, curve 2).

In accordance with the above scheme it may be expected that the yield of the most stable trans isomer B_4 will decrease linearly on increasing the lead(II) concentration, because of the participation of B_3 in complexation with lead(II). On further increasing the lead(II) concentration the decrease in the yield of B_4 is described by a quadratic function which also accounts for the involvement of B_2 in the complexation. Figure 8 shows the experimental dependence of the relative yield of B_4 on lead(II) concentration. From the plot it follows that the dependence is linear at lead(II) concentrations up to 4×10^{-5} M and becomes quadratic when the lead(II) concentration is increased. Thus the experimental dependence is in good agreement

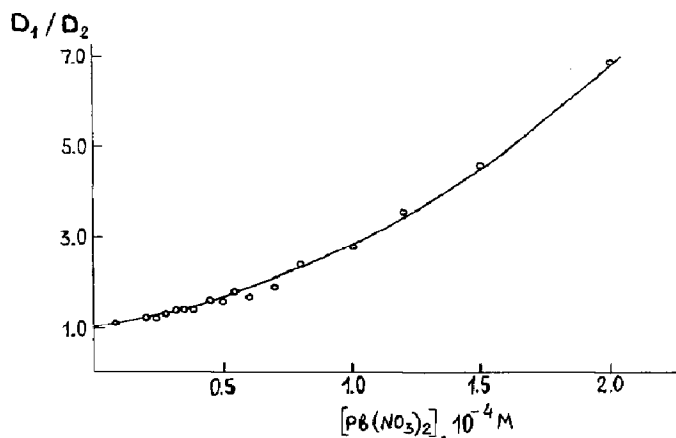


Fig. 8. Dependence of the relative change ΔD_2 in optical density on lead(II) concentration ($[Sp] = 2 \times 10^{-4} M$; $\lambda = 580 \text{ nm}$).

with the above-cited scheme. From this dependence it follows that B_2 takes part in complexation at a lead(II) concentration of $4 \times 10^{-5} M$. The measurement of the kinetics of complexation of B_2 and B_3 with lead(II) (the concentration of lead(II) being higher than that of B_2 and B_3) revealed that the rate of reaction follows pseudo-first-order kinetics. The rate constant was found to be $2 \times 10^9 M^{-1} s^{-1}$. Thus the trans isomers B_2 and B_3 are involved in complexation with equal rate constants which are different from the rate constant for B_4 . It has been established previously [10] that the trans isomers of spiropyrans also take part in protolytic reactions. Based on data of the effect of acid on the yield of the complex between Sp and lead(II) (Fig. 5), one can conclude that the protolytic reaction competes with the complexation.

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