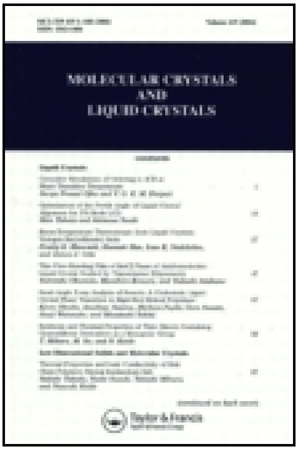

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Spiropyrans Complexes with Metal Ions. Kinetics of Complexation, Photophysical Properties and Photochemical Behaviour

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SPIROPYRANS COMPLEXES WITH METAL IONS. KINETICS OF COMPLEXATION, PHOTOPHYSICAL PROPERTIES AND PHOTOCHEMICAL BEHAVIOUR

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Abstract The results on spectrophotometric, luminescent, stopped-flow and ns-laser flash-photolysis study of complexation between indoline spiropyrans and metal ions are discussed.

INTRODUCTION

It has been previously reported[1-3] that indoline spiropyrans in merocyanine form are able to complex with transition metal ions. In our previous publications[4-9] it was shown that indoline spiropyrans in merocyanine form react with many transition metal ions and rare earth elements resulting in the formation of complexes. The present paper aims to summarize the results obtained in our works on spectrophotometric, luminescent, stopped-flow and ns-laser flash-photolysis study of complexation between indoline spiropyran (Sp):1,3,3-trimethyl-6-nitro-8-methoxy-spiro[2H-1-benzopyran-2,2-(2H)-indol] and metal ions (Pb(II),Zn(II), Co(II) etc and Er(III),Ce(III),Tb(III) etc) in acetone-water mixture (water content, 0.5-2.5 vol.%).

SPECTRA AND STEADY-STATE ILLUMINATION

Solutions of Sp in acetone-water mixture are characterized by a pronounced absorption around 580 nm which is associated with thermaly formed merocyanine. UV irradiation of Sp solutions results in strong increase in absorption band intensity which returns to its original level after UV illumination is ceased. Adding of metal nitrates (10^{-4} M) to Sp solutions immediately gives rise to appearance of a new absorption band which is shifted to shorter wavelengths (Fig. 1) and should be associated with a complex formation. UV irradiation of Sp solutions in the presence of metal nitrates gives rise to increase in the intensity of complex absorption band which reaches its original level when UV irradiation is ceased. These results imply the reaction of complexation is reversible. Spiropyrans complexes were found to exhibit relatively weak fluorescence (quantum yield is 0.02 for complex between Sp and Zn(II)) at room temperature with maximum shifted to shorter wavelengths in comparison with that for noncomplexed merocyanine (Fig. 1). Merocyanine and its complexes demonstrate at 77K long-lived phosphorescence with maximum emission around 660-670 nm and life time $\tau_{1/2}$= 10-20 ms (complexes with Zn(II), Cd(II), Pb(II), Y(III)). Complexation results in significant increase in phosphorescence intensity by the factor of 15 (complex with Cd(II)) probably due to heavy atom effect.

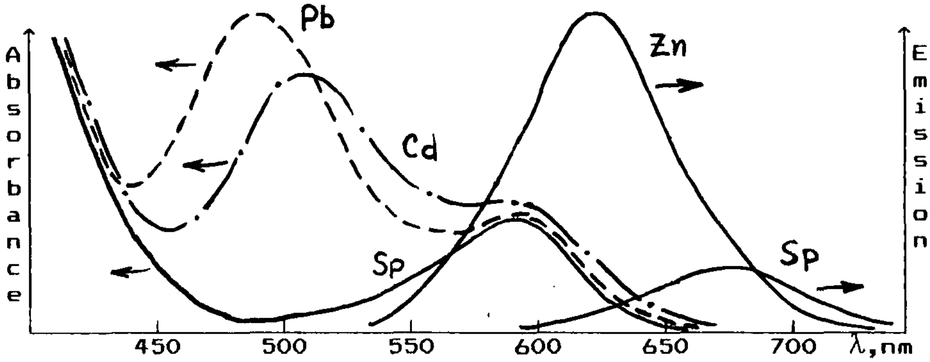

FIGURE 1 Absorption and emission spectra of Sp and its complexes with metal ions

KINETICS OF COMPLEXATION

Kinetics of complexation was studied by both stopped-flow and ns-laser flash-photolysis methods. In stopped-flow experiments it was found that changes in absorption spectra of merocyanine caused by the complexation with Zn(II),Cu(II) and Pb(II) (10^{-4} M) take place at $\leqslant 2.10^{-3}$s after mixing of the reagents. This fast step of the complexation is followed by the slow one which is accompanied by strong and permanent increase in intensity of absorption band at 490 nm during the following 15 min. In our previous works we have found that the reaction photocolouration of indoline spiropyrans occurs *via* trans-isomers of different stability[7-10]. In ns-laser flash experiments we aimed to confirm fast complexation and find more fast steps in the reaction. In these experiments it was found that life-time of unstable trans-isomer of Sp decreased when concentration of metal ions added was increased. The shortening of life-time of trans-isomer is accompanied with increase in the rate of growth of optical density caused by the complexation. Detailed kinetic analysis revealed the following features. 1) Most stable trans-isomer with life-time more than 10 s is not practically involved in the complexation. 2) At highest concentration of $Pb(NO_3)$ used (10^{-3}M) the complexation between short-lived trans-isomer and Pb(II) is completed for 800 ns resulting in the formation of short-lived complex. 3) Short-lived complex may convert into most stable complexes *via* unstable complexes. 4) Complexes between trans-isomers of different stability and metal ions are characterized by very similar absorp-

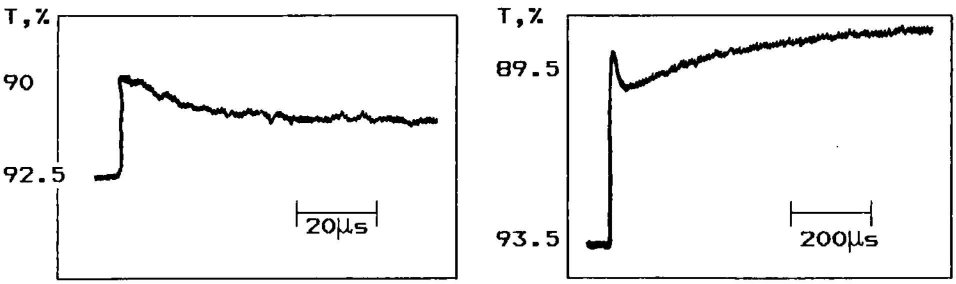

FIGURE 2 Oscilloscope traces of Sp transient absorption in the presence of $Pb(NO_3)_2$. λ=490 nm, 10 repetitive flashes

tion spectra which can be discriminated using repetitive flashes and averaging technique (Fig. 2). 5) Results on kinetics of complexation carried out by means of stopped-flow are in a good agreement with that obtained using ns-laser flash-photolysis.

PHOTOREACTIONS OF COMPLEXES

On ns-laser irradiation of spiropyrans complexes both short and long-lived changes in absorption of complexes were found. Short-lived changes lasting for about 20 μs in degaussed solutions should be associated with triplet state of a complex. Complex between Sp and Zn(II) in a triplet state absorbs around 430 nm. Long-lived changes in absorption are characterized by reversible bleaching of the complex absorption in the visible and originated from the cleavage of metal-oxygen bond. So the complexes in the excited state demonstrate its ability to electronic energy losses due to fluorescence, intersystem crossing to the triplet state, phosphorescence (77K) and reaction of complex dissociation with the following formation of Sp closed form.

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