Photochromic Chelating Spironaphthoxazines

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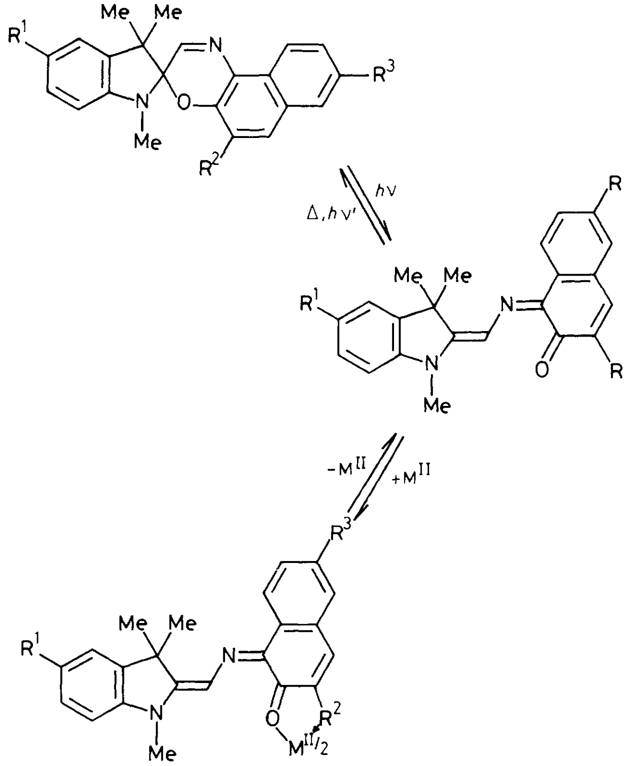
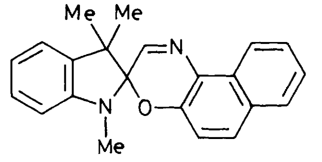
The chelation of spironaphthoxazine derivatives in the coloured form to divalent metals induced considerable shift of the absorption spectra and significant retardation of the decolouration rate in the dark.

Organic photochromic compounds have attracted much attention, because they change not only their colours but also their molecular properties and functions. Spiropyrans are among the most popular photochromic compounds.[1] The photochromic reaction of this family is the reversible heterolytic cleavage and rebinding of the pyranyl C(spiro)–O bond, yielding a coloured open and colourless closed form, respectively. It has been reported that the derivatives which possess



(**2a**) $R^1 = H$, $R^2 = SO_3^-$, $R^3 = SO_3^-$
(**2b**) $R^1 = OMe$, $R^2 = SO_3^-$, $R^3 = SO_3^-$
(**3**) $R^1 = H$, $R^2 = OMe$, $R^3 = H$

Scheme 1



(**1**)

Table 1. Absorption maxima and thermal decolouration rates of (**2**) (1×10^{-3} M) in the presence of metal ions (1×10^{-3} M) at 20 °C.

	(**2a**)		(**2b**)	
Metal ions	λ_{max}/nm	k_{dc}/min^{-1}	λ_{max}/nm	k_{dc}/min^{-1}
None	598	1.0	604	2.0×10^{-3}
Ca^{2+}	596	1.1[a]	570	4.7×10^{-4}
Cu^{2+}	—[b]	—[b]	552	2.8×10^{-4}
Pb^{2+}	564	0.34	558	4.4×10^{-5}

[a] k_{dc} = 0.51 min^{-1} at 1×10^{-2} M Ca^{2+}. [b] Photochromic reaction hardly occurred because of intense absorption due to Cu^{2+} in the near u.v. region.

Table 2. Absorption maxima and thermal decolouration parameters of (**3**).

			21 °C	
Ni^{II}	λ_{max}/ nm	ΔE_a/ kJ mol^{-1}	k_{dc}/ s^{-1}	$\Delta S^{\ddagger}$/J mol^{-1} deg^{-1}
		In 1,2-dichloroethane		
None	580	64	0.64	−38
$[Ni(aca)(tmen)]ClO_4$	624	93	0.0042	17
$[Ni(aca)(tmen)]BPh_4$	624	105	0.0096	66
$[Ni(bza)(tmen)]BPh_4$	624	116	0.0051	97
		In acetone		
None	570	62	0.55	−47
$Ni(NO_3)_2$	598	69	0.20	−33
$Ni(ClO_4)_2$	598	64	0.011	−73
$[Ni(aca)(tmen)]ClO_4$	610	78	0.053	−11
$[Ni(aca)(tmen)]BPh_4$	610	75	0.096	−17
$[Ni(bza)(tmen)]BPh_4$	610	73	0.11	−23

a co-ordinating group near the pyranyl O atom,[2—6] and others,[7] can act as a chelating agent in the coloured open form.

1,3,3-Trimethylspiro(indoline-2,3'-[3*H*]naphtho[2,1-*b*]-[1,4]oxazine) (**1**) and its derivatives are photochromic compounds analogous to spiropyrans.[8] This paper describes the first example of chelate formation by spironaphthoxazine derivatives (Scheme 1). M^{II} represents divalent metal ions or co-ordinated divalent metal complexes.

The compounds (**1**)—(**3**) were prepared by usual procedures and identified by n.m.r. spectroscopy. The irradiation was done with a 500 W high pressure Hg lamp through a suitable coloured glass filter. The absorption spectra and decolouration rates were measured with a diode-array spectrophotometer (Hewlett Packard HP8452A).

The compound (**2**) in aqueous solutions showed normal photochroism, being coloured upon irradiation and colourless in the dark. They form chelates with Cu^{II}, Ca^{II}, and Pb^{II} ions in aqueous solutions when irradiated with u.v. light. No chelate was formed from the colourless form in the dark. As shown in Table 1, the chelation induces slight blue shift of the peak maxima, λ_{max} and significant retardation of the thermal decolouration rate, k_{dc}, in the dark. The amount of blue shift and the thermal stability of the chelate are dependent on the metal ($Ca^{II} < Cu^{II} < Pb^{II}$). Other divalent metals such as Cd^{II}, Zn^{II}, Mg^{II}, and Co^{II} were less effective. Monovalent metals had no ability to act as a central metal.

It has been further observed that the solid gel of the chelate is formed as thin leaves in solutions containing metal ions in high concentrations (above 10^{-3} M). The gel network may be a consequence of intermolecular cross co-ordination by the sulphonate group at the C-8' position.

The coloured chelate disappeared upon exposure to visible light; the solid gel also dissolved in aqueous solution on visible light irradiation, though it was very stable in the dark. Thus, the system studied here may be used as an optical memory. Indeed, the optical image made of the gel in a thin glass cell (depth 0.1 mm) by irradiation with u.v. light through an optical mask was stable even after several months in the dark.

Compound (**3**) is also a photochromic chelating spironaphthoxazine in the presence of Ni^{II} ions or mixed Ni^{II} chelates with *N,N,N',N'*-tetramethylethylenediamine (tmen) and acetylacetone (aca) or benzoylacetone (bza).[9] For these experimental runs, 1,2-dichloroethane (DCE) and acetone were used as solvents, because they interact less with the metal. No chelation was observed in highly polar solvents such as alcohols or dimethylformamide, which can co-ordinate to metals more effectively. It also has been confirmed that no complex is formed between (**1**) and Ni^{II}, indicating that the methoxy group at C-5′, but not the imino N atom, is essential for the complex formation.

In Table 2 are listed the absorption maxima and thermodynamic parameters of the thermal decolouration process. The chelation to Ni^{II} leads to hyper- and batho-chromic shifts of the absorption spectra. The chelation effect on the thermal decolouration parameters (rate, k_{dc}, activation energy, E_a, and activation entropy, S) is more prominent in DCE than in acetone. The thermal co-ordination to the metal in the dark took place to a much smaller extent, giving a pale blue solution which was stable for months without losing its photochromic ability.

The chelate formation depends on metals and counteranions. The mixed Cu^{II} complexes were less effective than the mixed Ni^{II} complex. $Ni(Cl)_2$ and $Ni(aca)_2$ had less or no interaction. These facts suggest that the co-ordinating ability of this photochromic ligand is not sufficient to enable co-ordination with a central metal(II) ion tightly co-ordinated by other powerful ligands, counteranions, or solvent molecules.

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