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Synthesis, spectroscopic and thermal properties of a series of azo metal chelate dyes

Shuangqing Wang, Shuyin Shen, Huijun Xu*

Laboratory of Photochemistry, Institute of Photographic Chemistry, Chinese Academy of Sciences, Beijing, 100101 People's Republic of China

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Abstract

A series of azo metal chelate dyes have been synthesized. The UV-Vis absorption spectra of the azo dye and its metal complexes were measured. The stoichiometry of the complex was determined by the spectroscopic titration method to be 1:2 (ML_2), and the formation constants of the complexes were evaluated. Thermal decomposition with a sharp exothermic peak was observed by TG-DT Analysis. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Azo metal chelate dye; Optical recording medium; Complex formation; Thermal properties

1. Introduction

One of the currently popular forms of optical storage of information is the compact disk or CD. Writeable CD optical recording elements based on an active organic dye layer such as cyanine dyes with added stabilizers and metal phthalocyanine dyes have been widely known in patents [1,2]. Azo metal chelate dyes [3] have been also developed in view of their excellence in sensitivity and stability as optical recording medium. In recent years, the development of semiconductor lasers having short wavelength has progressed and optical recording media capable of recording information in high density by means of a laser beam having shorter wavelength of 635–650 nm instead of 780–830 nm are desired [4]. We have previously reported the synthesis of an azo nickel chelate dye useful in an optical recording layer for recording by a conventional semiconductor laser having a wavelength of 780–830 nm [5]. In this paper, we report the synthesis of a series of azo metal chelate dyes whose spectra are capable of matching a semiconductor laser having wavelength of 635–650 nm. Studies of their spectroscopic and thermal properties are also included.

2. Experimental

2.1. Synthesis of the azo dye and its metal chelate compounds

2.1.1. Diazotization and coupling

The diazotization of 2-amino-6-carbomethoxybenzothiazole and coupling with 3-(tolylsulfonylamino)-*N,N*-diethylaniline was carried out according to the published methods [5,6].

2-Amino-6-carbomethoxybenzothiazole 208 mg (1 mmol) was dissolved in 2.5 ml 85% phosphoric

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* Corresponding author. Fax: + 86-106-4879-375.
E-mail address: g201@ipc.ac.cn (H. Xu).

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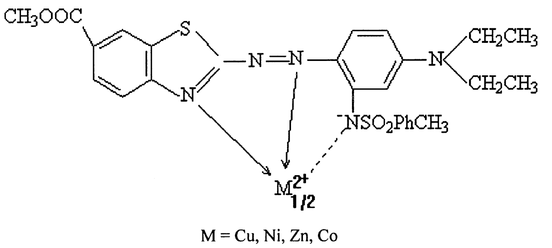
acid. The solution was then cooled to 0–5°C in an ice-brine bath and maintained at this temperature. Sodium nitrite 76 mg (1.1 mmol) was added as a solid over a period of 20 min and stirring was continued for 2 h, keeping the temperature between 0–5°C. A small amount of urea was then added to destroy excess nitrous acid.

3-(Tolylsulfonylamino)-*N,N*-diethylaniline 318 mg (1 mmol) was dissolved in a mixture of 5 ml water and 5 ml acetic acid and sodium acetate 3 g was then added to maintain pH about 4. The solution was cooled to 0–5°C in an ice-brine bath. The diazonium solution was added portionwise to the coupling component, and maintained at 0–5°C for 2 h. After filtering, 460 mg crude dye was obtained (yield 85.7%). The crude dye was purified by column chromatography on neutral aluminum oxide using dichloromethane as eluant. MALDI-TOF-MS ($C_{26}H_{27}N_5O_4S_2$) *m*/*z*: 538 $(M+1)^+$, 560 $(M+Na)^+$.

2.1.2. Metallization

The azo dye, 134 mg (0.25 mmol), was dissolved in 10 ml tetrahydrofuran, and 2 ml of an aqueous solution of copper sulfate (0.7 mmol) was added. The mixture was stirred at room temperature for 1 h. An alkali salt such as sodium fluoroborate (6.2 g sodium fluoroborate in 10 ml water) was added, followed by 10 ml water. The precipitate was filtered and dried, giving 103 mg of the azo copper chelate dye (yield 72.6%). MALDI-TOF-MS ($C_{52}H_{52}N_{10}O_8S_4$) *m*/*z*: 1158 (^{64}Cu), 1160 (^{66}Cu) $(M+Na)^+$.

Other nickel, zinc and cobalt chelates were synthesized using nickel acetate, zinc acetate and cobalt chloride, respectively, by the same procedure. The structure of the azo metal chelate dye was shown in Fig. 1.



M = Cu, Ni, Zn, Co

Fig. 1. Structure of the azo metal chelate dyes.

2.2. Instrument and methods

Mass spectra were determined by matrix assisted laser desorption/ionization time of flight mass spectrometer (MALDI-TOF-MS) on a Bruker Biflex III. Absorption spectra were performed on a Hitachi 557 double wavelength double beam spectrophotometer. Thermogravimetric analysis (TG) and differential thermal analysis DTA) were carried out on a Setaram TG-DTA 92 thermal analyser at a heating rate of 10°C/min in the range of 50–450°C.

For determining the stoichiometry and formation constant of the azo metal complex, the absorbance of a series of metal salt (in 85% THF +15% H_2O) + ligand (in THF) mixtures which were prepared from their 10^{-5} mol/l solutions as 2+8 ml, 4+6 ml, 5+5 ml, 6+4 ml, 6.7+3.3 ml, 7+3 ml, 8+2 ml, 9+1 ml, etc. were measured. The data were analyzed using Job's method [7,8].

3. Results and discussion

3.1. Spectroscopic properties of the azo dye and its metal chelates

Fig. 2 shows the absorption spectra of the azo dye in solvents of different polarity. In chloroform, the γ_{max} of the dye was 535 nm ($\varepsilon=4.83\times10^4$), while in methanol it showed a bathochromic shift to 575 nm ($\varepsilon=4.41\times10^4$),

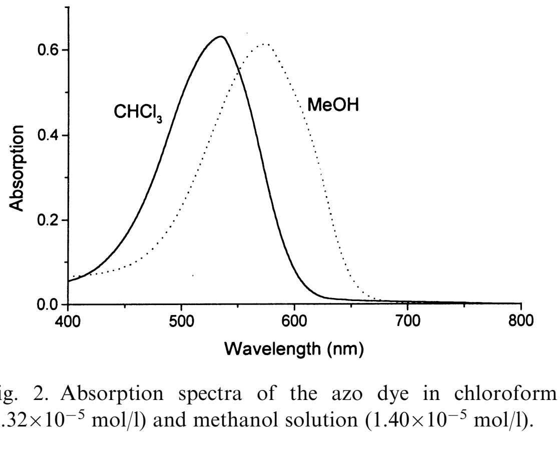


Fig. 2. Absorption spectra of the azo dye in chloroform (1.32×10^{-5} mol/l) and methanol solution (1.40×10^{-5} mol/l).

indicating that the absorption band is due to a π-π^* transition. Fig. 3 gives the spectra of the azo metal chelates in chloroform. In the azo metal chelate compound (Fig. 1), one of the nitrogen atoms of the azo group with its sp^2 lone pair electrons, together with the nitrogen atom of the benzothiazole ring bonded to the metal ion, gives a 5-membered ring. The hydrogen atom in the sulfonamide group is ionized to give a negative ion -$^{-}$NSO$_2$-, which forms an inner salt. The formation of inner salt by the sulfonamide group with the metal ion results in an increase in the electron-donating ability of the coupling component. Consequently, the energy of the π-π^* transition is lowered, so the absorption band of the azo metal chelate compound is red-shifted compared with the azo dye. The $\gamma_{\max}$ and extinction coefficient ε of the azo dye and its metal chelates in chloroform are listed in Table 1.

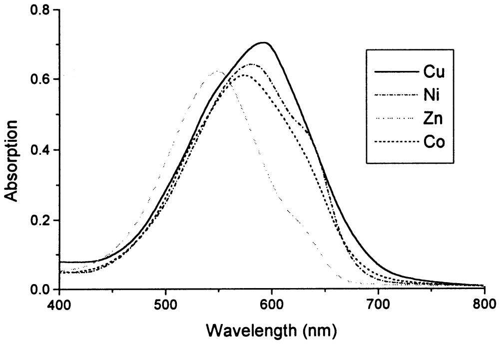


Fig. 3. Absorption spectra of the azo metal chelate dyes in chloroform solution (Concentration: Cu, 9.62×10^{-6}mol/l; Ni: 1.48×10^{-5}mol/l; Zn: 8.35×10^{-6}mol/l; Co: 1.62×10^{-5}mol/l).

Table 1
Electronic spectra data for the different metal chelate dyes in chloroform solution

Metal	$\lambda_{\max}$(nm)	ε
Azo dye	535	4.83×10^4
Cu	592	7.35×10^4
Ni	585	4.45×10^4
Zn	549	7.51×10^4
Co	578	3.86×10^4

3.2. *Formation constant of the azo metal complexes [8,9]*

The complex formation equilibrium and formation constant of the complex can be represented by Eqs. (1) and (2):

$$M + nL \rightleftharpoons ML_n \tag{1}$$

$$K = \frac{[ML_n]}{[M][L]^n} \tag{2}$$

in which $[M]$, $[L]$ and $[ML_n]$ represent the molar equilibrium concentrations of the metal ion, ligand dye and the complex, respectively.

The Job's diagram, in the case of the azo copper complex, obtained by plotting the absorbance A at 600 nm. $A = A_{ML} - (\varepsilon_L C_L + \varepsilon_M C_M)$ vs f_L [mol fraction of the ligand, $f_L = C_L/(C_M + C_L)$] is shown in Fig. 4. It consists roughly of two straight lines intersecting at $f_L = 0.67$, indicating that a 1:2 complex (ML_2) is formed. If the complex is very stable, the absorbance value at 600 nm should be A_0. Deviation from A_0 value is due to dissociation of the complex. At equilibrium, Eq. (3) pertains,

$$C_{ML2} = (1-\alpha)C,\ C_M = \alpha C,\ C_L = 2\alpha C \tag{3}$$

where C is the concentration of the azo metal complex without dissociation, and α [Eq. (4)] denotes the fraction of dissociation of the complex which can be deduced from Fig. 4.

$$\alpha = \frac{A_0 - A}{A_0} \tag{4}$$

and then, $K = \dfrac{(1-\alpha)C}{(\alpha C)(2\alpha C)^2} = \dfrac{1-\alpha}{4\alpha^3 C^2}$

The results are listed in Table 2, which indicate that the complexes are quite stable.

3.3. *Thermal properties of the azo metal chelate dyes [10]*

Fig. 5 gives the TG-DTA chart of the azo copper chelate dye as an example. A clear threshold of thermal decomposition with a sharp exo-thermic peak at 277°C is shown in the DTA curve, while the TG curve exhibits a not rather sharp weight

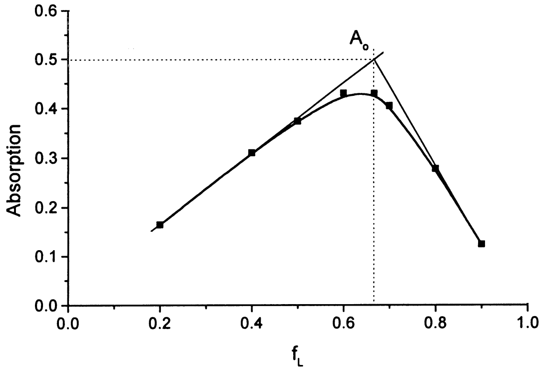


Fig. 4. Job's diagram for the azo dye copper complex in chloroform ($\gamma = 600$ nm).

Table 2
Formation constants K and decomposition temperature T of different azo metal chelate dyes

Metal	K	T (°C)
Cu	1.57×10^{12}	277
Ni	9.16×10^{12}	285
Zn	1.25×10^{12}	311
Co	1.82×10^{12}	295

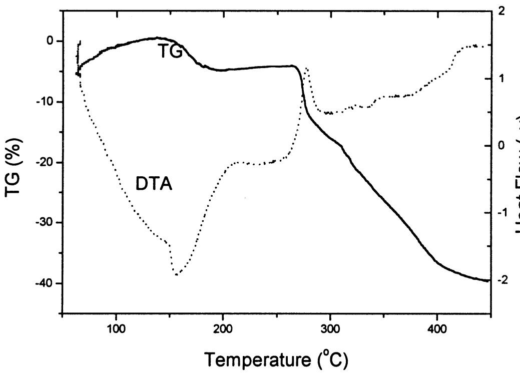


Fig. 5. TG-DTA chart of the azo copper chelate dye.

reduction, which consists of 2 steps across the wide temperature region from 150–400°C. TGA and DTA of the other azo metal chelate dyes all show a clear threshold of thermal decomposition with sharp exothermic peaks. The results are shown in Table 2.

4. Conclusion

Spectroscopic studies of the complexation of metal ions with an azo dye showed that the absorption maxima of the complexes are bathochromically shifted compared with the azo dye as the consequence of inner salt formation. The stoichiometry of the complex was determined by Job's titration method to be 1:2 (ML_2); the complexes are quite stable. The formation constants of the complexes are in the order of 10^{12}. TGA and DTA results show a clear threshold of thermal decomposition with sharp exothermic peaks. These azo metal chelate dyes are suitable for optical disks designed to be used with semiconductor lasers of short wavelength.

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