

Synthesis and Characterization of New Metal Complex Dye

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Abstract: The present paper describes the synthesis of a new complex dye formed by an acid dye, Acid Orange 7 (C.I. 15510) with a metallic ion (Cu^{2+}). The resulted compound was characterized *via* physico-chemical methods FT-IR, UV-VIS, AAs spectroscopy and thermal analysis. The obtained complex dye may have a good affinity for wool, natural silk, leather, and polyamide fibres. Self association of the complex has been investigated by spectroscopic studies, as a function of its concentration.

Keywords: Acid Orange 7, metallic complex dye, aggregation, copper

1. Introduction

Among the synthetic organic dyes, azo dyes is one of the most representative and large classes. All these dyes contain the azo group $-\text{N}=\text{N}-$ as part of their molecular structures and it was estimated that more than half of the commercial dyes belong to these dyes [1-3]. The practical applications of the azo dyes are related to coloring fibers, due to their affinity for wool and silk [4], photoelectronics, optical storage technology [5], biological reactions [6] analytical chemistry, printing systems [7, 8] and food chemistry [9].

The interest towards these dyes increased due to their thermal properties, mixed donor characters (soft-hard) [1], properties that include them as candidates for metal complexes. One of the most investigated complexes reported in the recent years are related to copper coordinated compounds [10] due to their ease of preparation, structural flexibility, better resistance of the dye for washing, and applicability in biological systems [11, 12].

It was demonstrated that azo dyes are able to form stable azo-metal chelate complexes with outstanding thermal and optical properties [13]. The synthesis of the complex combination of the azo dyes with different metallic ions can or cannot involve the participation of the azo group to the coordination process [14].

Apart of chemical properties, in aqueous solutions the dye molecules or ions present an association tendency to form dimers and higher aggregates. This phenomenon could be influenced by the presence of the metals and is closely related to the color.

Photophysical and colouristic properties of the dyes are modified in case of aggregates formation (molecular association) in solution. The self-association of dyes in solution is due to the interactions by Van der Waals forces, hydrogen bonds and hydrophobic interactions [15, 16]. The dye aggregation is affected by parameters such as dye concentration, dye structure, pH, temperature, solvents and ionic strengths [17].

In the present work, a new azo-dye with metallic ion (Cu^{2+}) complex was synthesized and characterized, using

the acid dye Acid Orange 7 as ligand. At the same time, spectrophotometric analysis was performed for the qualitative investigation of the aggregation behavior of the metal complex dye, at different concentrations in aqueous solutions.

2. Experimental

2.1. Synthesis of the metal complex-dye

The synthesis of the Cu^{2+} complex combination with Acid Orange 7 (C.I. 15.510) has included the following steps. 0.87g ($0.25 \cdot 10^{-2}$ moles) of dye (ligand) were dissolved in 25 mL ethanol:water 1:1 solution at 60°C. An aqueous solution of 0.31 g of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ in 2 mL of water was dropwise added to the previously obtained solution. The pH of the reaction mixture was maintained around 7.0 by gradually addition of 25% NH_3 solution. The reaction mixture was magnetically stirred for 2.5 h. After cooling, the precipitate was separated by filtration, washed with distilled water and dried in an oven at 50°C.

The resulted complex was purified by recrystallization from ethanol:acetone mixture in 1:2 ratio. The purity of the compound was checked by melting point analysis. All chemicals employed in this study as p.a. *p.a.* commercial products were provided by Acros Organics and Chimopar S.A.

Electronic absorption spectrum (UV-VIS) of the complex dye in water ($c = 1.0 \cdot 10^{-5}$ mol/dm³) was performed on a CECIL CE 7200 spectrophotometer in the range 300–800nm.

The FT/IR (KBr) spectrum was recorded on a JASCO FT/IR-4200 spectrometer in the range 400-4000 cm^{-1} .

To determine the copper content from the acid dye Acid Orange 7 copper complex, two parallel samples were digested as follows: 0.02567 g, respectively 0.02529 g, were weighted and transferred into a 100 mL Digesdahl digestion flask. Then 4 mL of concentrated sulfuric acid were added and the temperature was set at 440°C. When the proper temperature was reached the water to the aspirator was turned on and 16.7 mL of 32% hydrogen

peroxide were added to the sample. The excess of hydrogen peroxide was boiled off by heating for one minute. The digested samples were diluted to 500 mL with distilled water. For determination of the copper content, digestion of the sample was applied, using Digesdahl® Digestion Apparatus, model 23130-18.

The copper content was determined by SensAA flame atomic absorption spectrometer (GBC Scientific Equipment) equipped with a hollow cathode lamp, wavelength 324.7 nm, slit width 0.5, and integration time 3s. The flame used was an acetylene-air mixture. Three absorbance values were recorded and the average absorbance value was further used.

Thermal analysis was carried out using a Mettler TGA/SDTA 851/LF/1100 thermoanalyzer system. The measurement of the sample of about 6 mg was conducted in dynamic nitrogen atmosphere with the flow rate of 50 ml/min, using alumina crucibles of 150 μ L. The heating rate was 10°C/min, in the temperature range of 25-800°C.

2.2. Aggregation study

UV-visible absorption spectra were obtained using a CECIL CE 7200 spectrometer in the wavelength range 200-700 nm for seven initial dye concentrations, varying between $1 \cdot 10^{-6}$ and $1 \cdot 10^{-3}$ M. All measurements were carried out at $27 \pm 2^\circ\text{C}$. The obtained results are graphed together, plotted as $\epsilon = A/C \cdot l$

3. Results and Discussion

Acid Orange 7 dye with the structure I shown in Figure 1 underwent complexation reaction with Cu^{2+} ion, using metal-ligand =1:2 molar ratio, in which only the atoms of the -OH functional group are involved in the coordination reaction.

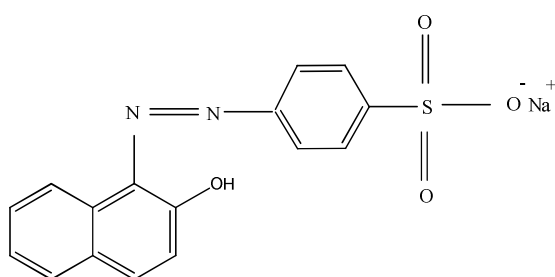


Figure 1. Structure of the acid azo dye (I)

The proposed formula of the new azo-complex dye is presented in Figure 2.

The above structure was confirmed by structural data acquired using FT-IR, electronic, and AAs spectra measurements, as well as thermal analyses. The FT-IR has proven to be, in this particular case, a suitable technique to give relevant information to elucidate the way of bonding of the ligands. The study of the infrared spectra reveals the migration of vibration frequencies for the functional groups which were directly involved in the metal ligand

coordinative link process. For this reason, the valence vibration of the -OH group, which take part in the coordination, and of the -C=N=N-C framework changed from the ligand to the complex due to the involvement of a nitrogen group in the metal-ligand coordinative link. The most characteristic frequency likely to demonstrate the formation of the M-L link is -OH group band from 1200 cm^{-1} (s), which migrates towards higher energies: 1220 cm^{-1} (O-Cu). The -C=N=N-C- framework in the ligand at $1580\text{-}1585 \text{ cm}^{-1}$ (s) migrates in the complex in the same way, to higher wavenumbers, $1592\text{-}1594 \text{ cm}^{-1}$ (Cu-N). These results prove the participation of the nitrogen atom of the azo group in the coordination [18].

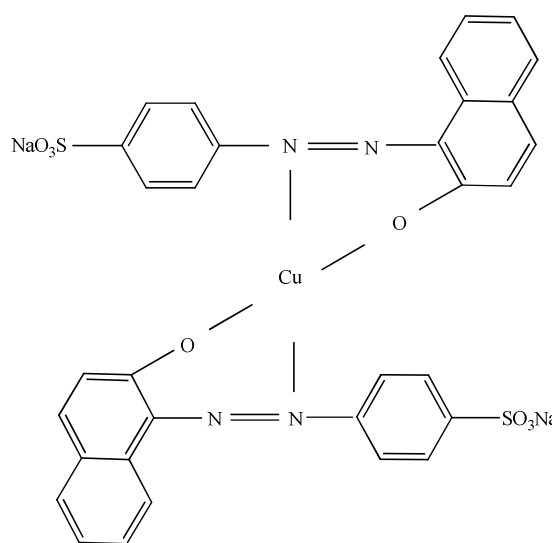


Figure 2. Structure of the complex azo dye (II)

In the UV-VIS spectra, the maximum absorption at $\lambda=487 \text{ nm}$ indicates a colored product due to the Acid Orange 7 dye used as ligand. At the same time it can be noticed the absence of any electronic transition in the 550-800 nm, which favor a square-planar geometry around the metal ion [19].

Atomic absorption spectroscopy was used to determine the total copper content of the digested samples. Four reference standard solutions of copper were prepared in the range of 1-5 $\mu\text{g/mL}$. The absorbance for the standard solutions was measured at 324.7 nm, using the background correction technique. A calibration graph was plotted from the obtained values.

The two diluted digested samples were aspirated in the acetylene-air flame and the absorbance values were measured at 324.7 nm. The copper percentages were calculated [20], as presented in Table 1.

TABLE 1. Cooper measurements by atomic absorption spectroscopy

Sample	Sample weight (g)	% Cu calculated from the proposed formula	% Cu (found)
1	0.02567	7.9	8.23
2	0.02529		8.25
Average copper content (%)			8.24

The TG/DTG curves for thermal decomposition of the complex dye II show the loss of water in two steps (Figure 3). The first step corresponds to the loss of the physically adsorbed water and of the water molecules bound by weak hydrogen bonds, in the temperature range of 25-70°C. The second step corresponds to the removal of crystallization water at 100°C, and confirms the copper tetracoordination. As it can be seen from the TG curve, a significant mass loss occurs at 300°C, probably due to the decomposition of the complex dye [21].

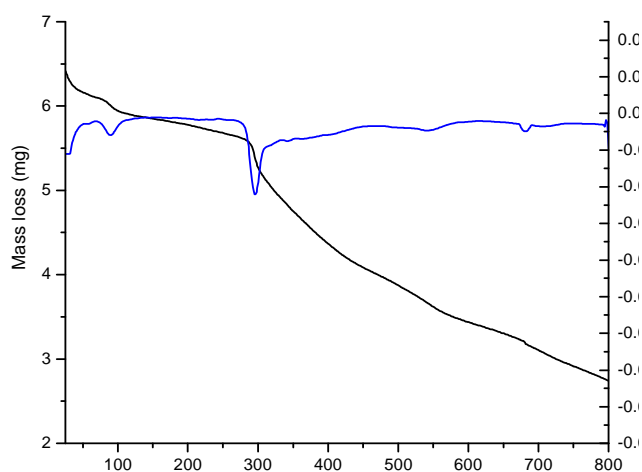


Figure 3. TG and DTG curves for thermal decomposition of the complex dye II (heating rate 10°C/min)

The molecular aggregation has been investigated spectrophotometrically in aqueous solutions, as a function of the concentration of the complex dye in the $1 \cdot 10^{-6}$ – $1 \cdot 10^{-3}$ mol/L concentration range. Different changes in the UV-VIS spectra of the complex dye II were observed at increasing concentration values, indicating the aggregation process of the molecules (Figure 4).

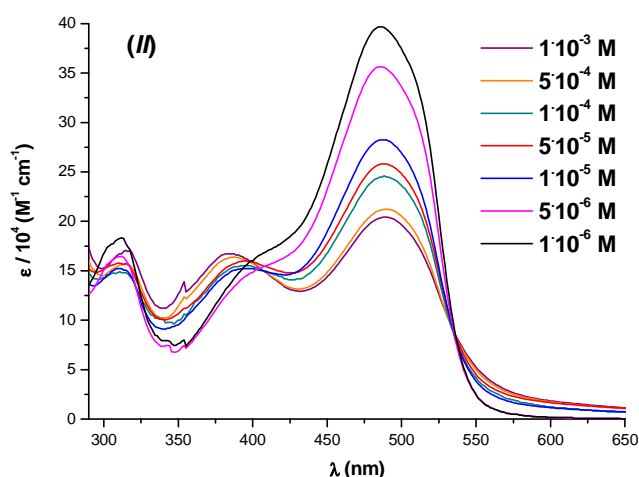


Figure 4. Absorption coefficients in the UV-visible range for different concentrations

The visible absorption spectra of the complex dye II changed with the concentration, showing an isosbestic point at 536 nm, which indicates the presence of

equilibrium between two species of the complex dye II, monomer and dimer, in the tested concentration range [22]. These data are in concordance with the experimental data previously reported by Muntean *et al.* for direct dyes [23]. The extinction coefficient corresponding to 488 nm decreased with increasing dye concentration. Increasing the concentration the shape of the spectra was changed, as well. Starting from $1 \cdot 10^{-5}$ M, a second peak began to form out of the main one, whose wavelength shifted toward lower values with increasing the concentration. All this shifts indicates the aggregation of the complex dye II, in the investigated concentration domain.

4. Conclusions

Metallic ion Cu^{2+} as ligand and the acid dye Acid Orange 7 (C.I. 15510) were used in the synthesis of a complex combination dye. The proposed formula for this compound was demonstrated by physico-chemical methods, FT-IR, UV-VIS, AAs spectroscopy and thermal analysis. The absorption spectra graphs indicate the formation of the complex dye II as new species with the increasing of the concentration and could be associated to the aggregation of the dye complex.

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