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Synthesis of Ru(III) and Al(III) Complexes Containing Anthraquinone Moiety and Interactions of the UV Radiations

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The purpose of this study is to synthesize Ru(III) and Al(III) complex compounds of alizarin moiety as UV-absorber and investigated their UV interactions. Ru(III) and Al(III) complexes of alizarin and alizarin sulfonic acid sodium salt were synthesized in basic medium. Their structures were determined by ^{1}H NMR, FT-IR and magnetic susceptibility methods. The synthesized complex compounds and chosen compounds which are anthraquinone, alizarin, alizarin sulfonic acid sodium salt, 1,2,5,8-tetrahydroxyantraquinone were investigated whether they have photochromic properties or not. To determine these properties, all the compounds were exposed UV radiation during various irradiation times such as 0, 2, 4, 6 min at 365 nm. It was observed that the solutions of the anthraquinone derivatives are sensitive to UV irradiation in ethyl acetate. It is suggested that the synthesized complexes are able to absorb UV light more than their ligands within 2 min and any significant change could not record about photochromism.

Key Words: Anthraquinone, Photochromism, Ruthenium(III) and Aluminum(III) complexes, UV-absorber.

INTRODUCTION

Hydroxyphenyl substitute ketone compounds are well-known as a UV absorber. They obstruct harmful UV energy by means of intramolecular proton transfer (ESIPT) process[1]. For that reason they are widely used made in sun glasses. The first commercial glasses were made of glass lenses impregnated with inorganic salts but in recent years, organic photochromic lenses, which are lighter and therefore more comfortable to wear despite their limited lifetime, have made an important breakthrough in the world market[2]. A very simple way to protect adhesives against UV light is to prevent UV absorption, *i.e.* reducing the amount of light absorbed by chromophores. This can be achieved by incorporating UV absorbers in the adhesives, which function by preferentially absorbing harmful ultraviolet radiation and dissipating it as thermal energy[3].

UV absorbers are most frequently used in cosmetics to prevent sunburns and skin cancer[4,5]. The UV protection of skin can be also reached by textiles modified with UV absorbers[6].

In this study, some metal complex compounds including alizarin moiety were synthesized and some compounds containing anthraquinone group were selected to investigate their properties of UV absorber or photochromic behaviours under the UV irradiation simultaneously. Herein, the alizarin-Al complex was synthesized only to compare the properties of the other metal complexes. It is a well known a method using for determination of the aluminum ion.

EXPERIMENTAL

UV lamp (λ = 365 nm) was used as Model UVG-54, electronic spectra on Model Shimadzu UVG-54 spectrophotometer in the range 200-600 nm. ^{1}H NMR spectra were recorded on a Bruker XWIN-NMR spectrometer. Chemical shifts are reported in ppm downfield from TMS. FT-IR spectra were recorded on Perkin-Elmer Spectrum RXI spectrometer in KBr pellets.

Preparation of alizarin-Ru(III) metal complex (1): $RuCl_3.3H_2O$ (0.76 mmol, 0.20 g) was dissolved in 30 mL methyl alcohol. KOH (33 mmol, 0.36 g) was poured into the mixture in room temperature and mixed under reflux for 20 min. Alizarin (3.33 mmol, 0.80 g) was added and reaction continued for 24 h. The crude reaction product which was blackish green precipitated. It was washed and dried (Fig. 1). UV-vis, IR spectra and magnetic susceptibility of the product were investigated. m.w. 673 g mol^{-1}, m.p. > 300 ºC, yield: 74 %, magnetic susceptibility: n = 0 antiferromagnetic. Molar conductivity: 27 µS (pure water), microanalysis (%): C (calculated; found): 49.9; 51.73. H (calculated; found): 2.08; 2.62. O (calculated; found): 19.02; 19.25. FT-IR (KBr pellet, ν_{max}, cm^{-1}): 3388 (Ar-OH broad band), 1625, 1584 (C=O), 1450-1650 (aromatic ring), 826 (M-O peak). UV-vis (ethyl alcohol, nm): 261, 336 (aromatic B band π-π*, Aromatic R band n-π*). ^{1}H NMR ($CDCl_3$, ppm): O-H, δ 12.8 ppm; Ar-H, δ 7.2-8.3 ppm.

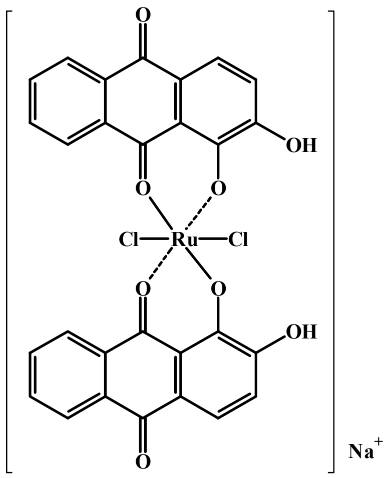


Fig. 1

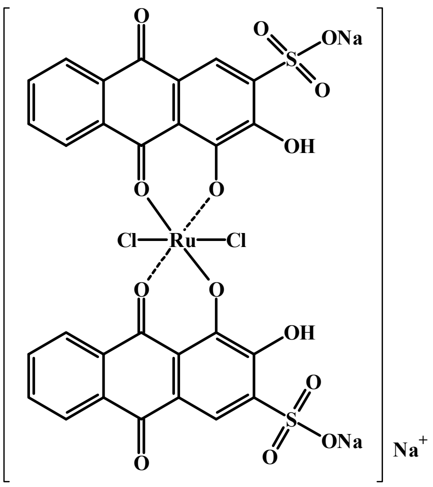


Fig. 2

Preparation of alizarin sulfonic acid sodium salt-Ru(III) metal complex (2): $RuCl_3.3H_2O$ (0.76 mmol, 0.20 g) was dissolved in 30 mL methyl alcohol. KOH (6.36 mmol, 0.367 g) was poured into the mixture in room temperature and mixed under reflux for 20 min. Alizarin sulfonic acid sodium salt (3.15 mmol, 1.141 g) was added and reaction continued under reflux for 24 h. Precipitate was as dark violet crystals. It was washed and dried (Fig. 2). UV-vis, IR spectra and magnetic susceptibility of the compound were investigated. m.w. 877 g mol^{-1}, m.p. >300 ºC. Yield: 68 % magnetic susceptibility: n = 0 antiferromagnetic. Molar conductivity: 41 µS (pure water). FT-IR (KBr pellet, ν_{max}, cm^{-1}): 3448 (Ar-OH broad band), 1635, 1591 (C=O), 1250-1043 (sulfonic group), 869 (M-O). UV-vis (ethyl alcohol, nm): 260, 335, 557 (aromatic B band π-π^*, Aromatic R band n-π^*).

Preparation of alizarin-Al(III) metal complex (3): $AlCl_3$ (0.76 mmol, 0.114 mg) dissolved in 30 mL methyl alcohol. Alizarin (3.15 mmol, 0.760 g) added and pH of the solution was adjusted 6.2 with KOH. Reaction mixture was mixed under reflux for 24 h. The crude product which was red colour was filtrated off and dried. It was recrystallized with ethyl alcohol. m.w. 599 g mol^{-1}, yield: 73 %, m.p. 302 ºC (decomp.) diamagnetic in nature. FT-IR (KBr pellet, ν_{max}, cm^{-1}): 3424 (Ar-OH board band), 1636-1591 (C=O), 1250-1043 (sulfonic group), 767 (M-O). UV-vis (ethyl alcohol, nm): 249 (Ar. B band π-π^{**}), 332, 446, 550 (R band, n-π^* band).

Investigation of photochromic properties of the synthesized and selected compounds: All the synthesized compounds (**1**, **2**, **3**) and chosen compounds which are anthraquinone, alizarin, alizarin sulfonic acid sodium salt, 1,2,5,8-tetrahydroxyanthraquinone were dissolved in ethyl acetate as 1×10^{-5} mol L^{-1} (Fig. 3). After all solutions were exposed to UV light at 365 nm wavelength during various irradiation time ranges 0, 2, 4, 6 min, their UV spectra were measured.

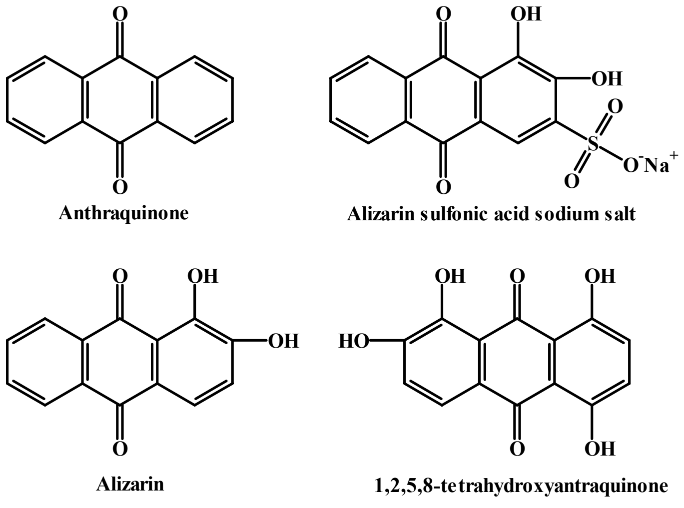


Fig. 3

RESULTS AND DISCUSSION

Characterizations of the synthesized compounds: The alizarin complexes **1**, **2** and **3** were obtained in alkaline medium. The products were obtained in 68-74 % yield after purification. The determination of structure analyses of them are in good agreement with their formulation. They have ionic character according to their values of molar conductivity such as 27 and 41 µS for **1**, **2** compounds. Both of them displayed antiferromagnetic property which is involving σ interactions between the half-filled e_g orbitals of Ru^{3+} ions and the filled ps orbitals of oxide ions[7].

The characteristic bands of the aromatic -OH moiety at 3448 and 3424 cm^{-1} were observed for **1** and **2**, respectively. The region between 826 and 869 cm^{-1} represented the peaks of metal-oxygen bond which is expected in this region. The band observed in the region 1635 cm^{-1} for $\nu_{carbonyl}$ stretching vibrations. The ^1H NMR spectrum of **1** in DMSO-d_6 displayed one slightly broad singlet at 12.8 ppm, which were probably due to the OH moiety.

Two electronic spectral bands were observed for **1** in the region of 261 and 330 nm due to π-π* of the aromatic system and n-π* transitions, respectively. The transitions of aromatic B and R bands (π-π*, n-π*) were observed at 260, 335, 557 nm for **2**.

According to result of magnetic property of the red product, the complex was occurred molar ratio of 1:3 as expected. So, it proved the structure of alizarin-Al(III) metal complex, **3**.

Effects of UV irradiation: The band below 250 nm gave hyperchromic shift for anthraquinone (**4**). Change was not observed for the bands over 250 nm. There is no auxochrome group in anthraquinone structure to provide electron moving and increase to colour intensity. After stimulation with 365 nm UV light, there was no bathochromic shift due to its structure stability as shown in Fig. 1. For that reason, **4** did not exhibit photochromic properties as would be expected.

The absorbance intensity of the π-π* transition band of 1,2,5,8-tetrahydroxy-anthraquinone (**5**) decreased as hypochromic shift because of -OH moieties when its wavelength was stable with the UV irradiation times. Those of bands over 250 nm, both of them, were stable as shown in Fig. 4. Forming intramolecular H-bonds in 5 structure obstructed photochromism.

While wavelength of alizarin (**6**) was constant, its absorbance intensity increased (hyperchromic shift) 2 min later. After 4 and 6 min, its absorbance was changed minimal level. **6** have an auxochrome group which occurred intramolecular H-bond. For that reason photochromic property of **6** is restricted for the band in visible region[8], at 425 nm, as shown in Fig. 5. The bands which are below 250 nm exhibited hyperchromic shift at the end of 2 min in UV spectra of alizarin sulfonic acid sodium salt (**7**). Absorption intensities of the bands over 250 nm decreased and its wavelengths were stable. The SO_3^- group in **7** enriches based on unpaired electrons. By UV interaction, it is promoted to high energy level easily. The wavelength of **7** was stable in ethyl acetate solution in Fig. 5. As shown in Fig. 6, expectation of its structural

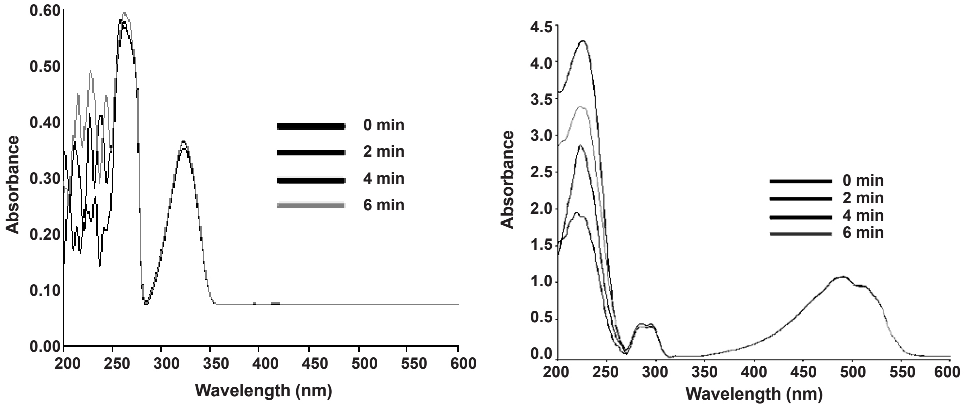


Fig. 4. Spectral changes of anthraquinone and tetrahydroxy anthraquinone by UV light, 1×10^{-5} mol L^{-1} in ethyl acetate

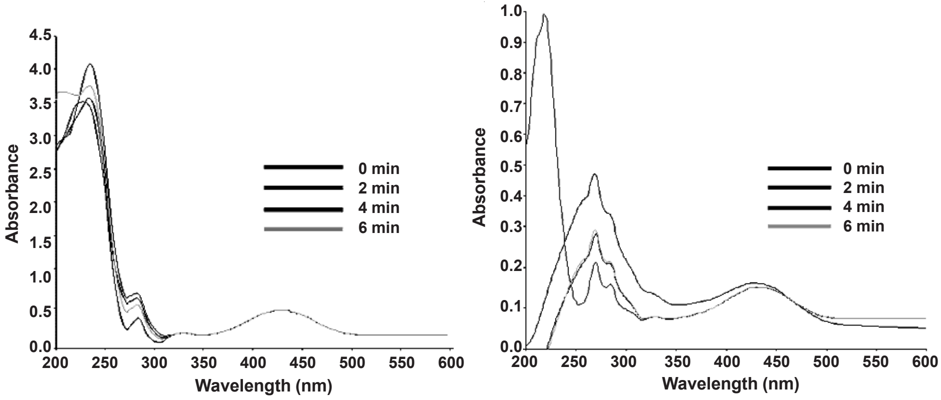


Fig. 5. Spectral changes of alizarin and alizarin sulfonic acid sodium salt by UV light in various irradiation times, 1×10^{-5} mol L^{-1} in ethyl acetate

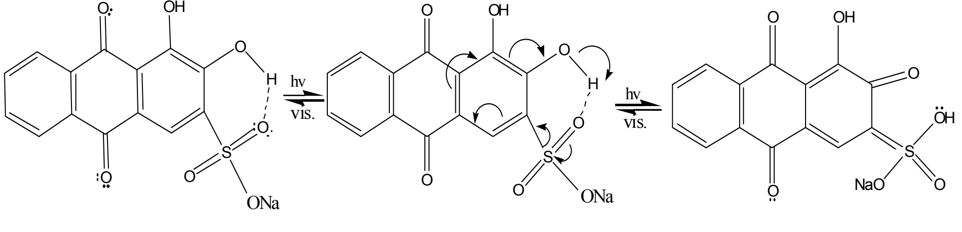
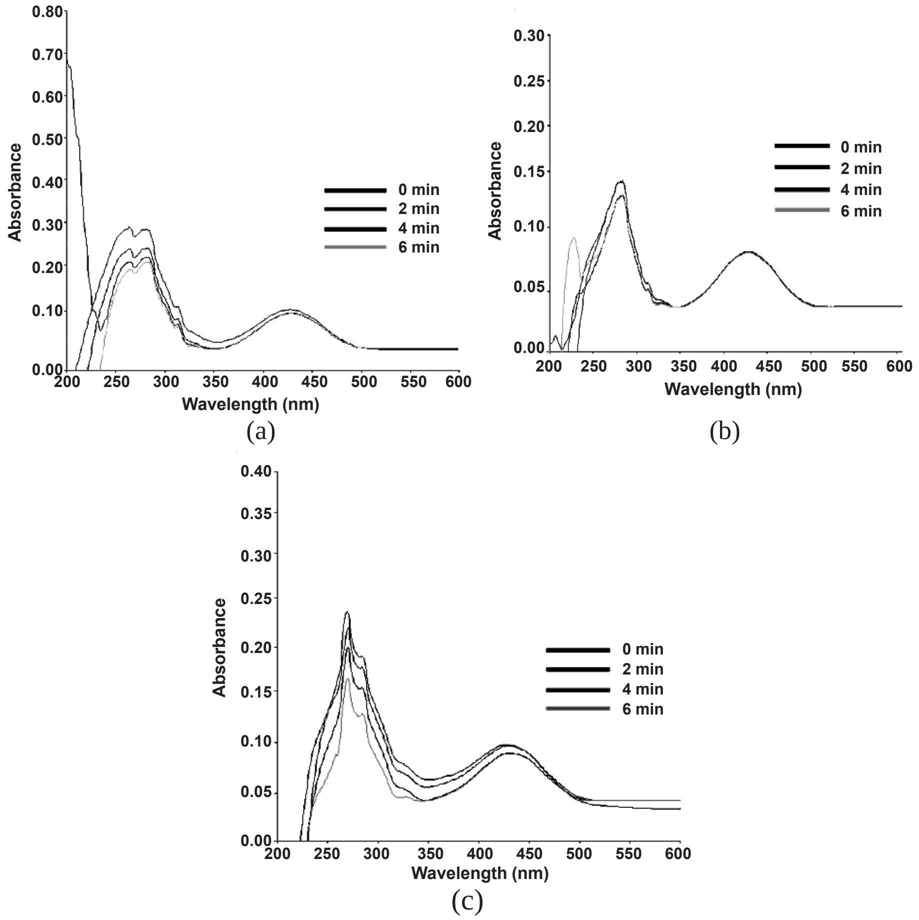


Fig. 6. Expected structural changes in the alizarin sulfonic acid sodium salt molecule during UV irradiation

change would occur if the compound dissolves in non-polar solvent as benzene completely. The forming H-bond between the solvent and **7** obstructed photochromism.

When the wavelength of **1** metal complex in ethyl acetate in UV spectra was stable its absorbance increased at the end of 2 min. In UV spectra of **1**, wavelength and absorbance almost were not change in Fig. 7,b. The unpaired electrons in auxochrome group of alizarin obstructed photochromism with effect of H-bond and Al(III) binding. The π-π* band which is *ca.* at 280 nm showed hyperchromic shift after 4 min UV irradiation. In Fig. 7,a and c showed the ruthenium complexes cause hyperchromic shift at the end of 2 min during irradiation.



(a) (b)

(c)

Fig. 7. Spectral changes of (a) alizarin-Ru(III), **1**, (b) alizarin-Al(III), **2** and (c) alizarin sulfonic acid sodium salt-Ru(III), **3**, by UV light, 1 × 10^{-5} mol L^{-1} in ethyl acetate

In Figs. 5 and 7, either the ligands **6**, **7** or their metal complexes gave hyperchromic shifts. The blue shifts were observed for the complexes of **6** at the over 300 nm peaks with compared their ligand **6**. If the interaction increases between the donor and steric group, λ_{max} shift hypsochromically[9]. Herein, the blue shifts were observed due to the steric obstruction of the metal and chloride groups.

Conclusion

In the ruthenium complexes reported here, both the UV-visible spectroscopic properties and the determination of their structure can be studied.

In conclusion, the solutions of the anthraquinone derivatives sensitive to UV irradiation in ethyl acetate when they exposure the UV light. The synthesized complexes were more effective than their ligands according to power of absorbing the UV radiation within 2 min. It is not reported here about the significant change of their photochromism, but in our opinion, all of them can be used as UV absorber except anthraquinone as expected.

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