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Synthesis, spectroscopic and thermal properties of nickel (II)–azo complexes with blue-violet light wavelength

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Abstract

A novel azo dye containing isoxazole ring and β-diketone derivative (TIAD) and its two nickel (II) complexes (Ni (II)–ETIAD and Ni (II)–HTIAD) were synthesized in order to obtain a blue-violet light absorption and better thermal stability as a promising organic storage material for next generation of high density digital versatile disc-recordable (HD-DVD-R) systems that uses a high numerical aperture of 0.85 at 405 nm wavelength. Their structures were confirmed on the basis of elemental analysis, MS, FT-IR, UV–Vis and magnetic data. Their solubility in 2,2,3,3-tetrafluoro-1-propanol (TFP) and absorption properties of thin film were measured. The difference of absorption maximum from the complexes to their ligands was discussed. In addition, the TG analysis of the complexes was also determined, and their thermal stability was evaluated.

Keywords: Metal (II)–azo complex; Synthesis; Absorption spectra; Thermal stability

1. Introduction

High-density optical storage technology which uses a 405 nm short wavelength laser and an objective lens of high numerical aperture (NA) of 0.85 is developing rapidly due to its high optical disc capacity over 23 GB on a single layer of a 120-mm-diameter disc and great interest on commercial demand [1–3]. The storage media are the bottleneck in optical storage. Obviously, the new technology requires a new optical storage medium with high performance matching with 405 nm short wavelength laser. Organic storage material can be an attractive optical storage medium with various advantages, such as good sensitivity, easy fabrication, reasonable cost and structural flexibility, etc., compared to inorganic storage material. Consequently, intensive efforts have been made to seek for new organic storage material with short wavelength absorption and new preparation approaches to obtain high quality recording films in recent years [4–7]. Metal (II)–azo complexes can be attracted much attention because they are more stable than cyanine dyes against light, can provide easier control of the wavelength according to the substituted group, have good thermal stability, and have good solubility in many organic solvents [8], and recently, it has been reported that some novel metal (II)–azo complexes containing isoxazole ring and β-diketone derivative with absorption bands in the blue-violet light wavelength region have good optical properties such as low extinctive coefficient *k* value of 0.2 and high refractive index *n* value of 2.08 at 405 nm wavelength [9], however, no investigations have been reported in detail on the syntheses and thermal properties of blue-violet light wavelength metal (II)–azo complexes. Based upon the consideration of the above requirements, in

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this work we reported on the syntheses of an novel azo dye (TIAD) containing isoxazole ring and β-diketone derivative and its two nickel (II) complexes (Ni (II)–ETIAD and Ni (II)–HTIAD) with the absorption in the region of blue-violet light wavelength. In addition, we also studied the thermal properties of the two Ni (II)–ETIAD and Ni (II)–HTIAD and the solubility in TFP as well as the absorption maximum of their films. These properties are very important for the practical application of organic material as a high-density optical storage medium.

2. Experimental

2.1. Materials

Fig. 1 shows that the synthetic schemes of azo dye and its two nickel (II)–azo complexes.

3-Amino-5-*tert*-butyl-isoxazole used as the initial synthetic material has been prepared following the procedure of Kenneth et al. [10]. The product was filtrated with lot of water and dried as colorless needles (m.p. 109 ± 1 °C). Acetoacetanilide used as the coupling component in the synthesis of the TIAD was purchased from Acros Chemical Co. and was used without further purification. All other chemicals and solvents were of analytical grade and were used as received.

2.1.1. Synthesis of the azo dye (TIAD)

3-Amino-5-*tert*-butyl-isoxazole was dissolved in a solution containing acetic acid and phosphoric acid ($V_1/V_2 = 2:1$) at a temperature range of −5 to 0 °C, and then 43% nitrosyl sulfuric acid was added at a temperature range of −5 to 0 °C, followed by stirring for 2 h. The coupling component (acetoacetanilide) was dissolved in sodium hydroxide solution (pH = 12–14) and cooled to −5 to 0 °C in an ice salt bath. Then the above diazo salt solution was stirred into the coupling component solution. The mixture was stirred for 4 h, and then the pH value was regulated to 6–7, further stirred for 1 h and then filtered. The solid was washed with lot of water and recrystallized with ethyl acetate.

2.1.2. Synthesis of the Ni (II)–ETIAD complex

The resulting azo dye (TIAD) was dissolved in tetrahydrofuran (THF) and sodium methoxide (NaOMe), and a solution having nickel (II) acetate hydrate dissolved in methanol was added into it at room temperature. Then, the mixture was stirred at room temperature for 3 h, and water was added. Precipitated solid was collected by filtration and dried to obtain Ni (II)–ETIAD. The solid was purified by column chromatography.

2.1.3. Synthesis of the Ni (II)–HTIAD complex

The resulting azo dye (TIAD) was dissolved in ethanol, and a solution having nickel (II) acetate hydrate dissolved in methanol was added into it at room temperature. Then, the mixture was stirred at room temperature for 3 h, and the mixture was concentrated by rotary evaporation under reduced pressure until the onset of precipitation of the products, which were washed successively with H_2O and warm MeOH followed by purifying with column chromatography.

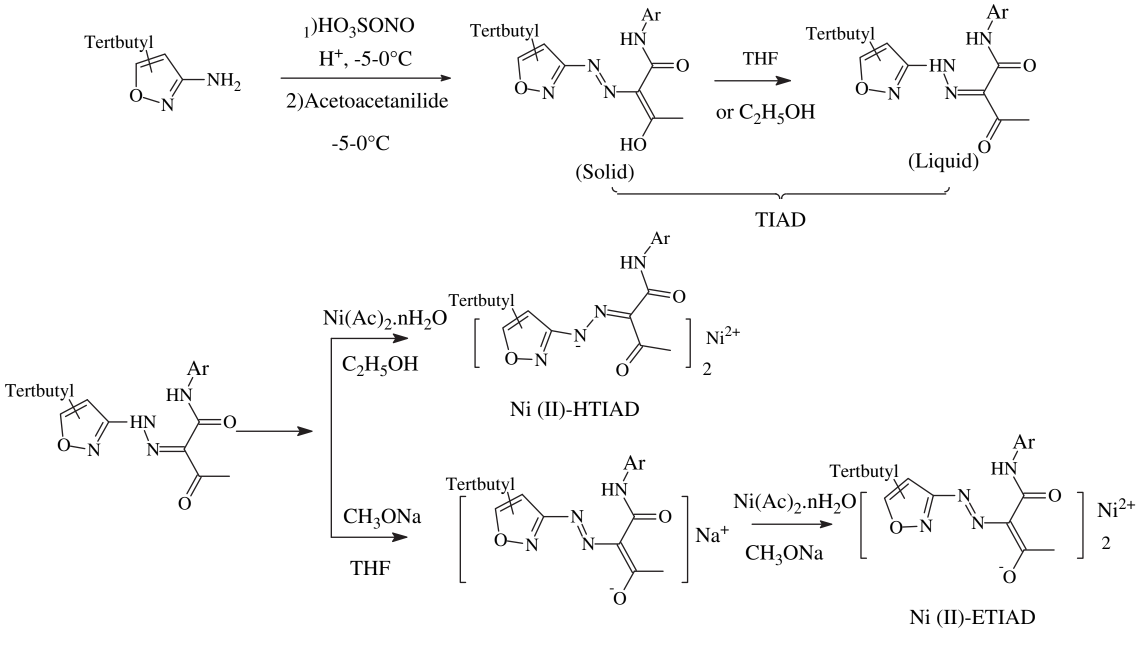

Fig. 1. Synthetical schemes of azo dye and its nickel (II)–azo complexes.

Product was then collected and dried to obtain Ni (II)–HTIAD.

2.2. Preparation of thin films

Thin films of the compounds were prepared by the spin-coating method. TIAD was poorly soluble in 2,2,3,3-tetrafluoro-1-propanol (TFP) but easily soluble in the mixed solvents of $CHCl_3$ and TFP ($CHCl_3$: TFP = 1:9) to give the concentration of 30 mg/ml of solutions. The nickel (II)–azo complexes were highly soluble in TFP to give the concentration of 30 mg/ml of solutions. The solutions were filtered using a 0.22 μm micropore filter to obtain the coating solutions. Smooth films were easily spin-coated on clear K9 glass substrates (diameter 30 mm). The substrates were kept at room temperature throughout the deposition process.

2.3. Instrument and methods

FT-IR spectra were recorded in the solid state and in the solution state over the range 4000–400 cm^{-1} using a Perkin–Elmer Instruction system. Elemental analyses were performed with an elemental analyzer (Elementar Vario EL). Metal contents were determined by EDTA complexometric titration and atomic absorption technique. UV–Vis spectra were measured using a Perkin–Elmer Lambda 9 UV/VIS/NIR spectrophotometer. EI and ESI mass spectra were, respectively, determined using an Agilent spectrometer and a Mariner LCT spectrometer. Molar magnetic susceptibilities measurements at room temperature were made on powdered samples using a Cahn D-20 Magnet Susceptibility Instrument (USA). The effective magnetic moments were calculated from the equation $\mu = 2.83 \times (\chi T)^{1/2}$ (B.M.), where χ is the molar susceptibility of sample. Thermal properties were analyzed with a Perkin–Elmer Instruction system at a heating rate of 10 °C/min from 30 °C to 600 °C under a nitrogen atmosphere.

3. Results and discussion

3.1. Synthesis and characterization

The diazonium salt was easily obtained by using sodium nitrite. Azo dye (TIAD) was easily synthesized by azo coupling. TIAD can be regarded as one kind of β-diketone or isoxazolylazo derivative where a coupling component is replaced by an acetoacetanilide. Because of this substitution, two carbonyls and one azo group of TIAD are not chemically conjugative, so that TIAD may have hydrazoketo and azoenol tautomeric isomers as seen in Fig. 1. The structure of TIAD was characterized by the elemental analysis, MS and FT-IR spectra, respectively. The C, H, N analysis and EI mass spectrum of TIAD agree well with its formula (TIAD: requires for $C_{17}H_{20}O_3N_4$: C, 62.18; H, 6.14; N, 17.06%; found: C, 62.12; H, 6.10; N, 17.03%; EI-MS: *m/e* (328)). The FT-IR spectra for TIAD solid and its methanol (MeOH) and carbon tetrachloride (CCl_4) solution confirm the existence of two tautomeric forms as shown in Fig. 2 (a and b). CCl_4 is a more appropriate non-polar solvent for an infrared measurement around the 3100 cm^{-1} region since it has no absorption there. The reference of the spectra in organic solution is the pure solvent MeOH or CCl_4. As seen in Fig. 2a, two strong absorption bands around 1670 cm^{-1} and 1650 cm^{-1} in the region 1600–1680 cm^{-1} which can be, respectively, attributed to two carbonyl stretching vibrations appear in the strong polar MeOH solution and in the non-polar CCl_4 solution of TIAD, however, only one strong absorption band around 1670 cm^{-1} in the region 1600–1680 cm^{-1} which can be attributed to one carbonyl stretching vibration appears in the solid state of TIAD. Furthermore, as seen in Fig. 2 b, a broad band due to the hydrogen-bonded enolic hydroxyl OH stretching vibration [11] appears around 3150 cm^{-1} for TIAD solid, whereas for TIAD in the CCl_4 solution it can be seen that this band is absent even in a low concentration and a broad and not rather obvious shoulder band appeared around 3250 cm^{-1} which may be due to the hydrogen-bonded NH stretching vibration of the HN–N=C fragment [12]. These spectral facts show distinctly that in the solid state TIAD exists as the azoenol form, whereas in the solution state, whether in strong polar solvent or in non-polar solvent, TIAD exists as the hydrazoketo form.

Based on the tautomerism of TIAD, we synthesized two different nickel (II) complexes using the isomers of TIAD as ligands. The Ni (II)–ETIAD complex used the azoenol form as ligand was synthesized in THF and NaOMe solution by the chelation between nickel ion

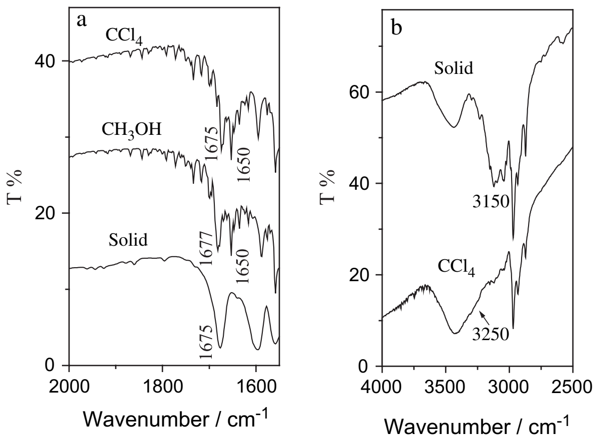

Fig. 2. FT-IR spectra of solid and solutions (CH_3OH and CCl_4) for TIAD: (a) CH_3OH (saturated) (≈20 × expanded) and CCl_4 (0.01 mol/l) (10 × expanded); (b) CCl_4 (0.01 mol/l) (5 × expanded).

and azo dye, whereas the Ni (II)–HTIAD complex with the ligand of the hydrazoketo form was synthesized in MeOH solution and in the absence of NaOMe by the chelation between nickel ion and azo dye. The action of NaOMe on TIAD in THF solution converts the hydrazoketo form into the azoenol form (see Fig. 1) [13]. Their structures were confirmed by elemental analysis, spectroscopic data (MS, FT-IR, UV–Vis) and magnetic data, respectively. The elemental analytical data and ESI mass spectra agree well with their formulae (Ni (II)–HTIAD: requires for $Ni(C_{17}H_{19}O_3N_4)_2$: C, 57.24; H, 5.37; N, 15.71%; Ni, 8.23%; found: C, 56.97; H, 5.89; N, 15.44%; Ni, 8.36%; ESI-MS: M^+(713), Ni (II)–ETIAD: requires for $Ni(C_{17}H_{19}O_3N_4)_2$: C, 57.24; H, 5.37; N, 15.71%; Ni, 8.23%; found: C, 57.09; H, 5.92; N, 15.33%; Ni, 8.48%; ESI-MS: M^+(713)), indicating that the azo dye forms stable complexes. FT-IR spectrum of TIAD solid shows a strong and broad band at 3438 cm^{-1}, which can be attributed to νNH of the –NHAr group [14]. This band is observed at the same frequency (Ni (II)–ETIAD: 3439 cm^{-1}; Ni (II)–HTIAD: 3439 cm^{-1}) in the two nickel (II) complexes, indicating that this group do not take part in complexation. FT-IR spectra of the two nickel (II)–azo complexes show a strong band (Ni (II)–ETIAD: 1638 cm^{-1}; Ni (II)–HTIAD: 1643 cm^{-1}) each assigned to νC=O, indicating that at least one conjugated C=O group is present in the complexes. However, these C=O bands are shifted appreciably to lower frequency in the complexes compared with the spectrum of TIAD solid, this shows that in the complexes the coordination of azo ligand to Ni^{2+} ion can produce increased effective conjugation and π-electrons delocalization. It is noticed in the spectra of Ni (II)–HTIAD that νN=N [15], observed at 1470–1420 cm^{-1} in the ligand, disappears and a new peak assigned as conjugated νC=N of the –HN–N=C– moiety [12] appears at 1610–1600 cm^{-1}. This shows that the azo ligand is coordinated as the hydrazoketo form (–HN–N=C–C=O) in its nickel (II) complexes. Furthermore, νC=O appears at lower frequency (1643 cm^{-1}) and νHN disappears in the region 3200–3300 cm^{-1}. It further shows that TIAD is coordinated through one of carbonyl oxygen and imino nitrogen to the center Ni^{2+} ion. On the other hand, in the case of the FT-IR spectrum of Ni (II)–ETIAD complex, a broad enolic hydroxyl νHO around 3100–3200 cm^{-1}, observed in the spectrum of TIAD solid, disappears and νN=N, observed at 1470–1420 cm^{-1} in the ligand, is shifted to lower wave numbers at ~1400 cm^{-1}. These disappearance or downward shifts show that the azo ligand acts as azoenol form (–N=N–C=C–OH) which coordinated through enol hydroxyl oxygen and azo group nitrogen to the center Ni^{2+} ion. In the far FT-IR spectra of the complexes, there are new bands observed in the region 430–650 nm which are absent in the spectrum of the free ligand. The bands observed at 625–640 cm^{-1} (Ni–O) (Ni (II)–HTIAD: 632 cm^{-1}; Ni (II)–ETIAD: 625 cm^{-1}) and 445–475 cm^{-1} (Ni–N) (Ni (II)–HTIAD: 469 cm^{-1}, 452 cm^{-1}; Ni (II)–ETIAD: 478 cm^{-1}, 455 cm^{-1}) provide conclusive evidences concerning the bonding of nitrogen and oxygen to the Ni^{2+} ion [16]. In addition, it can be also seen that FT-IR spectrum of TIAD solid reveals a strong band at ~1559 cm^{-1} which can be due to conjugated νC=N of the isoxazole ring [17]. This band is shifted to a lower frequency (Ni (II)–ETIAD: 1549 cm^{-1}; Ni (II)–HTIAD: 1546 cm^{-1}) in the nickel (II) complexes, indicating that it has been affected upon coordination to the Ni^{2+} ions. In conclusion, the FT-IR spectra indicate that the Ni (II)–HTIAD complex may have to form a tridentate chelate, in which the azo ligand acts as the hydrazoketo form and is coordinated to an Ni^{2+} ion via one of carbonyl O, imino N and isoxazole N atoms, and the Ni (II)–ETIAD complex may also have to form a tridentate form, in which the azo dye acts as the azoenol form and is coordinated to the Ni^{2+} ion through the enol hydroxyl O, azo N and isoxazole N atoms.

As further structural tools, the room temperature magnetic studies have been used to confirm the geometry of the two nickel (II) complexes. The magnetic moment of the Ni (II)–ETIAD complex has been found to be 3.17 B.M., which is within the range of values (2.8–3.5 B.M.) corresponding to octahedral complex of nickel (II) ions [18,19]. For the Ni (II)–HTIAD complex, the magnetic moment is 2.75 B.M. suggesting an octahedral structure. The slight lowering might be attributed to distortion of the molecule from idealized symmetry; however, the value indicates that metal–metal interaction is absent. These results agree well with those of the FT-IR spectra.

The formation of the nickel (II)–azo complexes is also confirmed by UV–Vis spectra in solution. The values for the UV absorptions given for the free ligand in Fig. 3 255 and 333 nm, are associated with the C=O and hydrazo group [20]. In the Ni (II)–HTIAD complex, the fact that these maxima have undergone

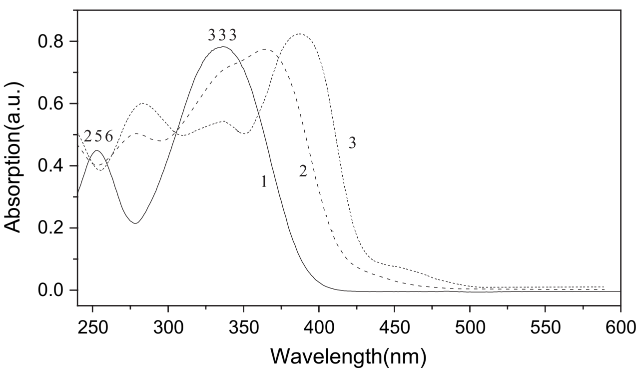

Fig. 3. Absorption spectra of azo dye and its nickel (II) complexes in $CHCl_3$: (1) TIAD; (2) Ni (II)–HTIAD; (3) Ni (II)–ETIAD.

a shift to higher wavelength indicates that the oxygen and nitrogen atoms are involved in the chelating process. However, for the Ni (II)–ETIAD complex, the larger red shifts of the absorption values as well as the different absorption bands is, we believe, due to the fact that since TIAD acts as the azoenol form which coordinated through hydroxyl oxygen and azo group nitrogen to the center Ni^{2+} ion, this coordination can produce much effective conjugation and π-electrons delocalization. According to the strong absorption of the complexes in a near ultraviolet region, the obvious bathochromic shifts for the two nickel (II)–azo complexes cannot come from the forbidden d–d transition, which is generally too weak and in visible light or near infrared regions, but probably arises from the energy change of the intense $\pi \rightarrow \pi^*$ transition of the conjugated chromophore due to the chelation between Ni^{2+} ion and azo ligand [8,21]. Consequently, because of the effect of π-electrons delocalization the energy of the $\pi - \pi^*$ transition in the Ni (II)–ETIAD complex is lower than the Ni (II)–HTIAD complex, so the absorption band of the Ni (II)–ETIAD complex is red-shifted obviously compared with the Ni (II)–HTIAD complex.

3.2. Solubility and absorption spectra of thin films

It is anticipated that the introduction of a *tert*-butyl group into the 5-position of the isoxazole ring will impact high solubility in organic solvents. The increased solubility may be due to the higher affinity of *tert*-butyl-substituted azo dye in organic solvent and the steric hindrance of *tert*-butyl substituent makes it impossible to form dimmers of the nickel (II) complex molecule. It is found that the *tert*-butyl-substituted azo dye and its nickel (II) complexes show good solubility in weakly polar or medium polar solvents such as benzene, toluene, chloroform, ethylacetate and tetrahydrofuran (THF), but their solubility decrease in strongly polar solvents such as methanol and ethanol. In addition, the *tert*-butyl-substituted azo dye shows a lower solubility than its nickel (II) complexes in medium polar solvents, but their solubility has not much difference in strongly polar solvents. The recording dye must be soluble in specific organic solvents, such as TFP or diacetone alcohol (DAA), 4-hydroxy-4-methyl-2-pentane, because the recording layer is applied on a polycarbonate substrate by the spin-coating method. In general, more than 2.0 wt% solubility is necessary. The synthesized nickel (II)–azo complexes are easily soluble in TFP solvent to give the concentration of over 30 mg/ml of solutions except for the azo dye. Although the absorption property of the azo dye is good, disc fabrication will be hard due to poor solubility in TFP. However, the azo dye is easily soluble in the mixed solvents of $CHCl_3$ and TFP ($CHCl_3$: TFP = 1:9) to give the concentration of over 30 mg/ml of solutions. Thus, smooth thin films of the azo dye and its nickel (II) complexes are easily spin-coated on clear K9 glass substrates (diameter 30 mm). Table 1 gives the some physical and absorption properties of the azo dye and its nickel (II) complexes thin films on the K9 glass substrate. The maximum absorption peak of the azo thin film is at 335 nm, whereas the absorption peaks of the nickel (II)–azo complexes thin films are distinctly red-shifted to around 360–390 nm (Ni (II)–HTIAD: 366 nm and Ni (II)–ETIAD: 385 nm), which have steep absorption edges and a small absorbance at the 405 nm side. It is believed that a steep absorption edge and a small absorbance at the 405 nm side will be easy to obtain high refractive index and reflectivity based on their thin films, and the high refractive index results in a high-modulated amplitude of the recording signal [22–24].

Table 1
Summary of physical and absorption properties for azo dye and its nickel (II)–azo complex films

Product	Solubility[a]	Abs.[b] λ_{max} (nm)	Abs.[b] at 405 nm	T_d[c] (°C)
TIAD	W	1.0/335	0.10	140 (m.p.)
Ni (II)–HTIAD	O	1.0/366	0.42	250
Ni (II)–ETIAD	O	1.0/385	0.71	295

[a] In TFP solvent (W: <1 wt%; O: >2 wt%).
[b] On K9 substrate with TFP solvent.
[c] 10 °C/min under N_2 gas.

3.3. Thermal properties of the nickel (II) complexes

Figs. 4 and 5 give the TGA curves of the Ni (II)–HTIAD and the Ni (II)–ETIAD complexes. It can be seen that the TGA curves of the two complexes show no any mass loss up to 230 °C, indicating the absence of water molecule in the two nickel (II) complexes. As the temperature is increased, the TGA curves of the Ni (II)–HTIAD and the Ni (II)–ETIAD

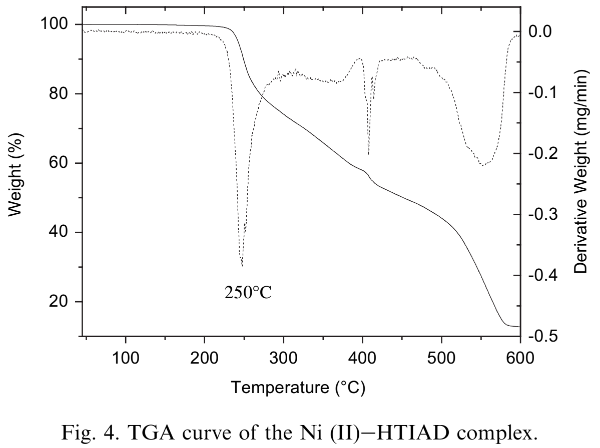

Fig. 4. TGA curve of the Ni (II)–HTIAD complex.

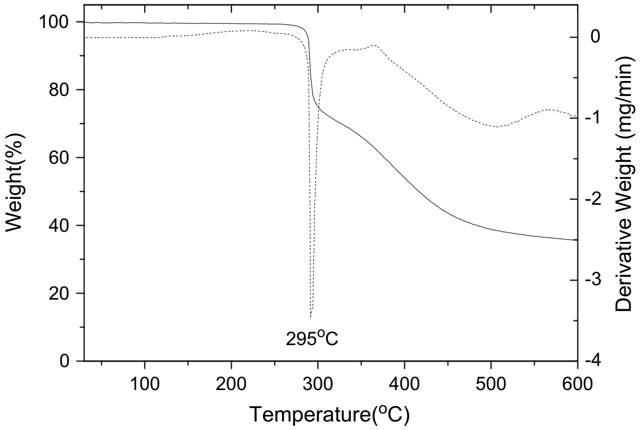

Fig. 5. TGA curve of the Ni (II)–ETIAD complex.

complexes exhibit a sharp decomposition at temperature of about 250 °C and 295 °C, respectively, which may be due to the loss of one ligand molecule. Moreover, for the Ni (II)–HTIAD complex another not rather sharp threshold of mass loss at around 560 °C indicates the loss of the second ligand of the complex, leaving nickel or a small quantity of organic part of the chelate at the final temperature. However, for the Ni (II)–ETIAD complex mass loss is progressive until a plateau is reached at 600 °C, indicating the little mass loss of another organic ligand of the chelate. These data show that the Ni (II)–ETIAD complex is thermally more stable than Ni (II)–HTIAD complex and possible to fabricate a small and sharp recording mark edge due to its higher and sharper thermal decomposition threshold.

4. Conclusion

In conclusion, we have described the synthesis and some spectroscopic and thermal properties of two novel nickel (II)–azo complexes with blue-violet light absorption. It is found that the Ni (II)–HTIAD complex used the hydrazoketo form of TIAD as ligand had potential application for high-density optical recording media due to their good solubility in TFP and suitable absorption spectra in thin films, and the Ni (II)–ETIAD complex used the azoenol form of TIAD as ligand would be suitable for high-density optical recording medium because of its higher thermal stability and sharper thermal decomposition threshold.

Acknowledgements

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