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# The synthesis and properties of highly organosoluble metal(II) complexes with hydrazone ligands derived from pivaloylacetonitrile

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# 1. Introduction

Since the development of blu-ray discs (BD's), in which a higher data density than in CDs and DVDs is achieved by using shorter wavelength laser diodes (405 nm) and high numerical aperture (NA = 0.85) lenses, much effort in material science has focused on the upgrading and updating of recording materials for the new generation of blue laser optical media [1–4]. Recordable optical data media, such as compact disc recordable (CD-R) and digital versatile disk recordable (DVD  $\pm$  R), have been widely used for archival and data storage because of their advantages of low-cost, portability and sufficient data lifetime [5]. The huge commercial demand for inexpensive blu-ray disc recordable (BD-R) is anticipated to increase based on the boom noted for both CD-R and  $DVD \pm R$ . The choice of the recording material for use in BD-R is between an organic dye and an inorganic material (alloy, oxide, nitride, etc.) [6–9]. Inorganic recordable blu-ray discs, which have been partially commercialized recently [10], may encounter

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#### ABSTRACT

Using pivaloylacetonitrile as starting material and coupling component, a novel hydrazone ligand and four ,highly organosoluble metal(II) complexes were synthesized via the procedure of oximation, cyclization, diazotization, coupling and metal chelation. In addition to elemental analysis, the structures of the novel compounds were postulated based on a series of spectroscopic methods. Smooth thin films of these metal(II) complexes on K9 glass substrates were prepared by spin-coating from 2,2,3,3-tetrafluoro-1-propanol solutions. The behaviour and relationships of the absorption bands both in solution and in spin-coated films are discussed; the thermal properties, photostability and the solubility of the metal(II) complexes were investigated. The synthesized Ni(II) complex exhibited a remarkable combination of excellent solubility and photostability, suitable absorption band and desirable thermal properties and, therefore, offers the potential of becoming a recording material for the recordable blu-ray disc system. © 2009 Elsevier Ltd. All rights reserved.

numerous obstacles restricting their popularization. Among them, high-cost production of these discs, due to their complicated layer structures and the use of large, multichamber sputtering systems for film preparation are the major problems to be solved [11–13]. By contrast, the organic dye-based, recordable media have few layers, and can be manufactured using a cost-effective spin-coating technology. The spin-coating process not only ensures a uniform thickness and a flat, smooth surface, it enables manufacturers to use current CD-R and DVD  $\pm$  R facilities for BD-R production lines with only minor adjustments [14–16]. This will enable the company to respond quickly and cost-effectively to the rapid increases in demand.

However, due to their poor solubility in specific solvents and low absorption in the blue-violet light region, organic dyes are currently difficult to apply to the new generation, blue laser recordable media [17]. Furthermore, both the weak light resistance and poor thermal properties of organic dyes make recordable media susceptible to light-induced damage, which would cause data lifetime problems [5,18]. Consequently, considerable effort has been increasingly devoted to seek for new organic recording materials with improved properties in recent years [19–24]. Azo dyes, sometimes referred to as hydrazone dyes because they may exist in either the azo or hydrazone tautomeric forms, are key chromophores in dyestuff chemistry [25]. The solubility,





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absorption, and thermal behaviour of this class of materials can be efficiently controlled by functionalization using a variety of different synthetic procedures [26]. Moreover, these chemical modifications have allowed their widespread application as functional dyes. Recently, we have reported that some hydrazone metal (II) complexes with blue-violet absorption bands and high thermal stability, are proposed for applications in blu-ray recordable optical storage [27–29]. However, to avoid over-corrosion of the plastic substrate caused by the chloroform-mixed solvents, the solubility of the dyes in specific solvents still requires improvement.

In this paper, we present a new syntheses of four highly organosoluble metal(II) complexes with hydrazone ligands derived from pivaloylacetonitrile. Smooth thin films of the metal(II) complexes can be prepared easily by spin-coating from 2,2,3,3tetrafluoro-1-propanol (TFP) solutions. The absorption behaviour from metal(II) complexes with different metal(II) ions to ligand in solution and in spin-coated films was discussed. Furthermore, we also investigated the thermal properties, the photostability and the solubility of these metal(II) complexes in detail.

# 2. Experimental

# 2.1. Materials

All chemicals and solvents in this work were of analytical grade and were used as-received. 4,4-Dimethyl-3-oxopentanenitrile (Synonym: pivaloylacetonitrile; caution; toxic, flammable liquid and vapour; incompatible with moist air or water, strong bases, alcohols, amines), used as the starting synthetic material and coupling component in the synthesis of the hydrazone ligand, was purchased from Acros Chemical Co. and was used without further purification. The synthetic schemes together with suggested structures are shown in Fig. 1.

#### 2.2. Instrument and methods

The melting points of the compounds were determined on an X-4 microscopic melting point apparatus (made in China) and were uncorrected. Elemental analyses of C, H and N were carried out on a Vario EL elemental analyzer. Metal(II) contents were estimated by complexometric EDTA titration (after complete decomposition of the complexes in concentrated nitric acid several times) using murexide (for Ni(II), Co(II) and Cu(II) content) and Eriochrome Black T (for Zn(II) content) as indicator in buffer (NH<sub>3</sub>-NH<sub>4</sub>Cl solution) and calculated from the expression  $X \ \approx C_{EDTA} \times V_{EDTA} \times M/m_s$ , where X is the metal content of sample,  $C_{EDTA}$  is the concentration of EDTA titration,  $V_{EDTA}$  is the volume of EDTA used in

titration,  $m_s$  is the mass of sample and M is the molecular weight. FT-IR spectra were obtained in KBr pellets on a Nicolet Avatar 360 FT-IR spectrometer in the 4000–400 cm<sup>-1</sup> region. <sup>1</sup>H NMR spectra (CDCl<sub>3</sub> solutions) were recorded at 500 MHz on a Bruker Advance AV-500 instrument with tetramethylsilane (TMS) as an internal standard. EI and MALDI mass spectra were performed using an Agilent spectrometer (HP 5973N, at 70 eV) and an IonSpec 4.7T HiResMALDI fourier-transform mass spectrometer (IonSpec, USA, 2,5-dihydrobenzoic acid (DHB) as matrix), respectively. UV–Vis spectra were measured using a Perkin–Elmer Lambda 9 UV/VIS/ NIR spectrophotometer. Thermal properties were analyzed with a TA instruments, the SDT Q600 Simultaneous DSC/TGA Analyzer, at a heating rate of 10 °C min<sup>-1</sup> from 50 to 800 °C under a nitrogen atmosphere.

#### 2.3. Synthesis of 3-amino-5-tert-butylisoxazole

3-Amino-5-*tert*-butylisoxazole was synthesized by a modification of the literature method [30,31]. Typical procedures are detailed as follows.

# 2.3.1. Oximation

Sodium hydroxide (4.40 g, 0.11 mol) in flake form, was added to a stirred suspension of pivaloylacetonitrile (12.52 g, 0.10 mol) in water (140 mL). The resulting, clear solution was then mixed with hydroxylamine hydrochloride (7.64 g, 0.11 mol). The reaction mixture was stirred at room temperature for 30 min, adjusted to pH 8–9 with aqueous NaOH (10%), heated at 50–55 °C for 10 h, allowed to cool to ambient temperature and permitted to react for an additional 2 h. The reaction mixture was extracted 2–3 times with carbon tetrachloride (30 mL) to remove the by-product, 5-amino-3-*tert*-butylisoxazol. The resulting N'-hydroxy-4,4-dimethyl-3-oxopentanimidamide solution was then used directly for the next step.

#### 2.3.2. Cyclization

Following phase separation, the aqueous phase, N'-hydroxy-4,4dimethyl-3- oxopentanimidamide solution, was acidified by addition of concentrated aqueous HCl (36%) to pH 4–5 and permitted to react, with stirring, at 50–55 °C for about 2 h. After cooling, the pH of the reaction mixture was adjusted to pH 11–12 by addition of aqueous NaOH (25%). The resulting precipitate was collected by vacuum filtration, washed with water, and then dried, affording 3amino-5-*tert*-butylisoxazole 11.14 g (79.5% yield) yellowish needles (m.p. 120–121 °C). The analysis results are in agreement with the well-known results in the literature [30].



Fig. 1. Synthetical schemes of the free ligand (HL) and its four transition metal(II) complexes,  $M(L)_2$  [M = Ni(II), Co(II), Cu(II), Zn(II)].

# 2.4. Synthesis of N'-(5-tert-butylisoxazol-3-yl)-3,3-dimethyl-2oxobutanehydrazonoyl cyanide ligand (HL)

# 2.4.1. Diazotisation

3-Amino-5-*tert*-butylisoxazole (2.80 g, 0.020 mol) was dissolved in 40 mL concentrated phosphoric acid (85%) at room temperature. The solution was then cooled to -5 to 0 °C in an icesalt bath and maintained at this temperature while a solution of sodium nitrite (1.52 g, 0.022 mol) in water (10 mL) was then added dropwise within 1 h under continuous stirring, and the ensuing mixture was stirred at 0–5 °C for a further 1 h. The resulting diazonium solution was then used directly for the next step.

#### 2.4.2. Coupling

The coupling component (Pivaloylacetonitrile, 2.75 g, 0.022 mol) was dissolved in sodium hydroxide solution (150 mL, 2.5%) and cooled to -5 to 0 °C in an ice-salt bath. The above diazonium solution was added to the stirred coupling component solution at -5 to 0 °C over 30 min. The mixture was allowed to rise to room temperature over 4 h and the pH value was lowered to about 5. The precipitated solid was collected by filtration, washed with water, and then vacuum dried. The rough product was finally recrystallized from ethanol/water mixtures (3:1) to form light yellow crystals. Yield: 3.66 g (66.3%). M.p. 119-121 °C. Anal. Calcd (found) for C<sub>19</sub>H<sub>24</sub>N<sub>4</sub>O<sub>3</sub>: C, 60.85 (60.72); H, 7.30 (7.17); N, 20.28 (20.32). <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, δ ppm): 1.37(s, 4.5H, -C(CH<sub>3</sub>)<sub>3</sub>), 1.38 (s, 4.5H, isoxazole-C(CH<sub>3</sub>)<sub>3</sub>), 1.39(s, 4.5H, isoxazole-C(CH<sub>3</sub>)<sub>3</sub>), 1.42 (s, 4.5H, -C(CH<sub>3</sub>)<sub>3</sub>), 6.02(s, 0.5H isoxazole-H), 6.28(s, 0.5H isoxazole-H), 9.54(s, br, 0.5H, hydrazone NH), 14.30(s, br, 0.5H, enol OH). Electronic absorption spectrum (UV–Vis) in chloroform:  $\lambda_{max}$  $(nm)(log\epsilon) = 320(4.29)$ . FT-IR spectra (KBr pellets) v: 3223, 3088, 2974, 2933, 2875, 2224, 1662, 1608, 1568, 1522, 1468, 1383, 1277, 1209, 1180, 1092, 933, 852, 793, 723, 652, 579, 457 cm-1. EI-MS Found(Calcd):  $m/z = 276(276)[M^+]$ .

# 2.5. General procedure for the synthesis of the transition metal(II) complexes

The metal(II) complexes were prepared by the same general method: the resulting hydrazone ligand (0.50 g, 1.81 mmol) was dissolved in absolute methanol solution (20 mL) at room temperature and the corresponding metal(II) acetate (1.00 mmol) in powders was added under vigorous stirring. The ensuing mixture was stirred under reflux for further 4–5 h, and after cooling, water (20 mL) was added under stirring. The volatile components of the reaction mixture were carefully removed on a rotary evaporator under reduced pressure without any heating. The precipitated solid was collected by filtration, washed with water and then vacuum dried. The acquired products were characterized and used directly without further purification. Specific details for each compound are given below.

# 2.5.1. Ni(L)<sub>2</sub> complex

Dark-brown powder. Yield: 95.3%. M.p. 265–270 °C (dec.). Anal. Calcd (found) for  $C_{28}H_{38}N_8O_4Ni$ : C, 55.19 (55.24); H, 6.29(6.32); N, 18.39(18.43); Ni, 9.63(9.71). Electronic absorption spectrum (UV–Vis) in chloroform:  $\lambda_{max}$  (nm)(log $\epsilon$ ) = 417(4.50), 316(4.05), 252(4.40). FT-IR spectra (KBr pellets) v: 2972, 2937, 2874, 2202, 1570, 1554, 1479, 1365, 1313, 1265, 1215, 1182, 1090, 999, 706, 559, 474 cm<sup>-1</sup>. MALDI-MS Calcd (Found): m/z = 608.24(609.2) [M + H<sup>+</sup>].

#### 2.5.2. $Co(L)_2$ complex

Dark-brown powder. Yield: 90.4%. M.p. 180–200 °C (dec.). Anal. Calcd (found) for  $C_{28}H_{38}N_8O_4Co: C$ , 55.17 (55.06); H, 6.28(6.37); N, 18.38(18.29); Co, 9.67(9.11). Electronic absorption spectrum

 $\begin{array}{l} (UV-Vis) \mbox{ in chloroform: } \lambda_{max} \mbox{ (nm)}(log\epsilon) = 401(4.42), \mbox{ 307}(3.99). \\ FT-IR \mbox{ spectra (KBr pellets) } \nu: \mbox{ 2972, 2935, 2877, 2204, 1570, 1547, } \\ 1481, \mbox{ 1363, 1306, 1263, 1213, 1182, 1088, 993, 702, 552, 476 \mbox{ cm}^{-1}. \\ MALDI-MS \mbox{ Calcd (Found): } m/z = 609.23(610.2) \mbox{ [M + H^+]}. \end{array}$ 

# 2.5.3. *Cu*(*L*)<sub>2</sub> complex

Dark-brown powder. Yield: 92.7%. M.p. 178–179 °C (dec.). Anal. Calcd (found) for  $C_{28}H_{38}N_8O_4Cu$ : C, 54.75 (54.69); H, 6.24(6.29); N, 18.24(18.17); Cu, 10.35(10.16). Electronic absorption spectrum (UV–Vis) in chloroform:  $\lambda_{max}$  (nm)(log $\epsilon$ ) = 410(4.45), 318(4.19), 253(4.24). FT-IR spectra (KBr pellets) v: 2972, 2935, 2874, 2204, 1576, 1551, 1481, 1367, 1311, 1267, 1215, 1182, 1088, 999, 702, 559, 474 cm<sup>-1</sup>. MALDI-MS Calcd (Found): m/z = 613.23(614.2) [M + H<sup>+</sup>].

#### 2.5.4. $Zn(L)_2$ complex

Red-brown powder. Yield: 76.2%. M.p. 220–240 °C (dec.). Anal. Calcd (found) for  $C_{28}H_{38}N_8O_4Zn$ : C, 54.59 (55.67); H, 6.22(6.45); N, 18.19(18.03); Zn, 10.61(9.98). <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS,  $\delta$  ppm): 1.29(s, 18H, isoxazole-C(CH<sub>3</sub>)<sub>3</sub>), 1.36(s, 18H, CH<sub>3</sub>), 6.28 (s, 2H, isoxazole-H). Electronic absorption spectrum (UV–Vis) in chloroform:  $\lambda_{max}$  (nm) (log $\epsilon$ ) = 405(4.38), 316(4.31), 251(4.09). FT-IR spectra (KBr pellets) v: 2972, 2935, 2874, 2206, 1578, 1560, 1481, 1365, 1311, 1267, 1215, 1182, 1086, 993, 702, 557, 474 cm<sup>-1</sup>. MALDI-MS Calcd (Found): m/ z = 614.23(615.2) [M + H<sup>+</sup>].

# 2.6. Preparation of the spin-coated thin films

Solutions were prepared by dissolving the respective metal(II) complexes in 2,2,3,3-tetrafluoro-1-propanol (TFP) to give a concentration of 30 mg mL<sup>-1</sup>. The solutions were filtered through a millipore membrane filter (0.22  $\mu$ m) to obtain the coating solution. The K9 glass substrates (diameter 30 mm) were cleaned in an ultrasonic bath with acetone, ethanol and deionized water for several times and dried, successively. The films were prepared with a KW-4A precision spin-coater (Chemat Technology Inc.) using a syringe. A two-step procedure, 800 rpm for the first 4 s and 3000 rpm thereafter for 40 s, was used to prepare smooth films. The substrates were kept at room temperature and 50% relative humidity throughout the deposition process. The resulting films were then heated at 50 °C for 2–3 h to ensure removal of the solvent.

#### 3. Results and discussion

#### 3.1. Synthesis and characterization

A facile synthetic route was adopted in the synthesis of the hydrazone ligand and its transition metal(II) complexes, as depicted in Fig. 1. 3-Amino-5-tert-butylisoxazole, the key intermediate, was synthesized from pivaloylacetonitrile in 79.5% yield by a sequence involving oximation with hydroxylamine hydrochloride under mildly basic conditions at ca. 55 °C and cyclization under acidic conditions at ca. 55 °C. The reaction mixture was cooled made basic and the precipitated 3-amino-5-tert-butylisoxazole was isolated by vacuum filtration. The careful control of the pH ( $\sim$ 8.0) of the reaction mixture between the hydroxylamine and the pivalylacetonitrile is important and should extend over the first few hours of the reaction time since this reaction is sensitive to the pH. Aliphatic compounds containing an activated methylene group, such as  $\beta$ -diketones, are known to react with aromatic diazonium salts to form azo compounds or their hydrazone tautomers [32,33]. As remarked in our previous work [27], the isoxazole heterocyclic amine could be diazotized smoothly in a solution of concentrated phosphoric acid at -5 to 0 °C on addition of sodium nitrite. In the present study, it was found that the diazotised 3-amino-5-tertbutylisoxazole coupled successfully with a reactive methylene coupling component, pivalylacetonitrile, in sodium hydroxide solution, and a reasonable yield (66.3%) of the hydrazone ligand containing isoxazole and pivalylacetonitrile moieties was obtained.

The coupling of diazonium salts with  $\beta$ -diketones has been studied extensively because the products have found use as yellow dyes and pigments [32,34]. The coupling products may be formulated as existing in both keto-hydrazone and azo-enol tautomeric forms. Much of the early work with the above mentioned coupling reaction was prompted by the desire to determine whether the products were of the azo or hydrazone structure [35]. It was generally assumed from a series of investigations using a variety of techniques, such as IR, NMR, and X-ray crystallography, that the keto-hydrazones are the stable forms both in solution and in the solid-state [34,36,37]. A six-membered intramolecular hydrogen bridge linking one of the carbonyl groups to the NH-moiety of the hydrazone unit was found to be a characteristic feature of this compound class. The ligand, prepared in this study, with an  $\alpha$ -cyano- $\beta$ -ketone as coupling component, may exist in tautomeric forms as shown in Fig. 1. The infrared spectra which provides comprehensive structural information, and in particular the position of the carbonyl stretching vibrations, has been of considerable importance in establishing that the compounds exist exclusively in the keto-hydrazone form. The solid-state IR spectra of the synthesized ligand shows a single carbonyl absorption band appearing at 1674 cm<sup>-1</sup> consistent with a keto-hydrazone form with extensive intramolecular H-bonding, a feature that has been confirmed by previously published data on keto-hydrazone analogues [34,36]. Another typical feature of the free ligand is the existence of an NH vibration around 3223 cm<sup>-1</sup> furnishing proof of the existence of an H-bonded hydrazone structure in the solidstate. The remaining vibration frequencies obtained from the IR spectra and their tentative assignments are shown in Table 1. An interesting observation was that the <sup>1</sup>H NMR spectra of this ligand shows two sets of sharp signals of similar intensity in close proximity in CDCl<sub>3</sub> solution at 25 °C. This result demonstrates conclusively the presence of a tautomeric equilibrium in chloroform solution produced by two geometrical isomers, the keto-hydrazone and the azo-enol, in roughly equal proportions [38]. At the low-field region of the spectral, two broad singlets at 9.54 and 14.30 ppm could be assigned to the hydrazone NH and enol OH protons, respectively [39,40]. Nevertheless, as discussed earlier, the ligand crystallizes exclusively as keto-hydrazone isomer in the solid-state. The obtained IR spectra, <sup>1</sup>H NMR, EI mass spectra and elemental analytical data agree well with the structural formula of the ligand.

Syntheses of the four transition metal complexes,  $M(L)_2$  [M = Ni (II), Co(II), Cu(II), Zn(II)], were essentially the same and involved heating and stirring of stoichiometric amounts of the free ligand and a slight excess of different metal(II) acetate in an appropriate solvent, preferably either methanol or ethanol under reflux. Only in the case of the synthesis of Zn(II) complex the standard conditions (procedure similar to Ni(II), Co(II), Cu(II) complexes) gave a low yield of an impure product probably due to the weak metalation of Zn(II) ion, so the addition of a small amount of sodium methoxide in methanol solution (1.0 mL, 1.0 mol L<sup>-1</sup>) was needed to induce the

ligand deprotonation, and thereby to allow metal chelation to take place [27,41]. The desired metal(II) complexes easily crystallized from the reaction solution when water was added and the organic solvent was slowly removed under reduced pressure. Washing with water and vacuum drying gave the corresponding high purity products in good yields (78–95%). The pure crystalline powders of the metal(II) complexes are various shades of dark-brown, except for Zn(II) complex which is red-brown. All of these metal(II) complexes were characterized by the accurate matrix-assisted laser desorption ionization (MALDI) mass spectrometry technique. Values of the molecular ions  $[M + H]^+$  show good agreement with the calculated values for Ni(L)<sub>2</sub> (m/z 609.2), Co(L)<sub>2</sub> (m/z 610.2), Cu  $(L)_2$  (m/z 614.2) and Zn(L)<sub>2</sub> (m/z 615.2). In addition to the MALDI mass spectrometry results, the NMR spectra are also important for structure confirmation. Only the Zn(II) complex was employed for <sup>1</sup>H NMR analysis in CDCl<sub>3</sub> solution since Zn(II) is diamagnetic. It was observed that only one set of signals appears in the <sup>1</sup>H NMR spectra of the Zn(II) complex and the two singlets in low-field, due to the tautomeric hydrazone NH and enol OH protons in the spectra of the free ligand, totally disappear. This result indicates that the ligands exist as a single form in metal(II) complexes and these functional groups are involved in the chelation process [27], which consequently support the structure proposed from the FT-IR spectra for the metal(II) complexes given below. The metal-to-ligand ratio of the metal(II) complexes was found to be 1:2 from the results of the elemental analysis and mass spectra.

#### 3.2. Solubility and photostability

The synthesized metal(II) complexes exhibit excellent solubility in most common organic solvents at room temperature, such as dimethylformamide, acetone, dioxane, ethyl acetate, tetrahydrofuran, chloroform and toluene, but they are sparingly soluble in ethanol and methanol and practically insoluble in water. Since the organic recording layer is applied on a polycarbonate (PC) substrate by the spin-coating method for optical recording media, the organic dye must be well soluble in specific organic solvents such as fluoroalcohols, particularly 2,2,3,3-tetrafluoro-1-propanol (TFP), which do not attack the PC resins and have the appropriate volatility to prepare smooth thin films [44]. Previous studies have shown that some organic dyes are poorly soluble in pure TFP solvent [27–29]. The solvents of mixing for film preparation, for example mixing with chloroform, are generally corrosive and toxic therefore not preferred for use in device fabrication. The metal(II) complexes in this study give a solubility high enough ( $>50 \text{ mg mL}^{-1}$ ) in pure TFP solvent at room temperature, which renders film and device preparation easy. The improvement in solubility can be attributed to the higher solubility of four peripheral tert-butyl substituents in weakly and medium polar organic solvents. On the other hand the solubility in polar organic solvents has been further enhanced by the insertion of cyano groups within the backbone according to the theory of "similarity and intermiscibility". In addition, the solubility of the four metal(II) complexes is also affected by the central metal ions;  $Zn(L)_2$  shows a lower solubility than those of Ni(L)<sub>2</sub>, Co(L)<sub>2</sub>,

Table 1

Significant FT-IR bands an	d tentative assignments o	f the ligand and its	s metal(II) complexes (	cm <sup>-1</sup> ).
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Compound	<i>vH—N</i> (hydrazone)	νCH (CH <sub>3</sub> )	vC≡N	vC=0	vC=C, vC=N (isoxazole)	<i>vN—N=C</i> (azomethine)	vN=N	vC−O (enol hydroxyl)	<i>vN</i> − <i>H</i> ···0	vM-N
Ligand	3223	2974	2224	1662	1608, 1568	1522	_	_	933	_
Ni(L) <sub>2</sub>	-	2972	2202	-	1570, 1554	-	1313	999	-	474
$Co(L)_2$	-	2972	2204	-	1570, 1543	-	1306	993	-	476
$Cu(L)_2$	-	2972	2204	-	1576, 1551	-	1311	999	-	474
$Zn(L)_2$	-	2972	2206	-	1578, 1560	-	1311	993	-	474

and  $Cu(L)_2$ , but their solubility is not appreciably different in identical solvents.

All metal(II) complexes are stable in the dry state under ambient conditions. However, their stability in solution is not as good as in solid-state. It has been found that they could be degraded by sunlight in chloroform solution, especially for Zn(L)<sub>2</sub>. Upon irrradiation under midday sunlight, the color of the dilute solution for Zn(II) complex converts from vellow to colourless after several hours with the characteristic absorption band around 400 nm disappears. From the enhanced UV absorbance at 250-350 nm, it is suggested that the free ligand should be the main product resulting from the degradation of the Zn(II) complex. The solution of  $Cu(L)_2$ shows color change after a few days and the solutions of Ni(L)<sub>2</sub>, and  $Co(L)_2$ , do not undergo a color change even if after one week. The photodegradation of the metal(II) complexes in chloroform solution might be ascribed to the photocatalysis of the excited-state singlet oxygen generated by it, which is similar to previously reported data [45,46]. Meanwhile, the hydrogenchloride (HCl), readily produced by exposure of chloroform solution to sunlight, should also be an important factor to accelerate the degradation of the metal(II) complexes [47,48].

# 3.3. FT-IR spectra and mode of bonding

The infrared spectra of the free ligand and its four metal(II) complexes are shown in Fig. 2 and important characteristic absorption bands, along with their proposed assignments, are summarized in Table 1. As seen from Fig. 2, the IR spectra of four meta(II) complexes are very similar to each other, except for some slight shifts and intensity changes of a few vibration bands caused by different metal(II) ions, which indicate that the complexes are of similar structures. However, there are some significant changes between the meta(II) complexes and their free ligand upon chelation. The coordination mode and sites of the ligand to the metal(II) ions were investigated by comparing the infrared spectra of the free ligand with its metal(II) complexes. It is noteworthy that the peak at 1662 cm<sup>-1</sup> attributed to vC=0 vibration, originating from ketohydrazone form of the free ligand with extensive six-membered intramolecular hydrogen bonding, completely disappears on complexation with the metal(II) ions. This result indicates that the ligand acts as an azo-enol form in the metal(II) complexes which



Fig. 2. FT-IR spectra of the ligand and its metal(II) complexes in KBr pellets.

naturally forms an enolic hydroxyl oxygen, with consequent replacement of the enolic hydrogen by the metal(II) ion [27,49]. A new moderate band due to the v(C-0) vibration appearing at ca. 1000 cm<sup>-1</sup> in the spectra of all complexes is further evidence for bonding the enol hydroxyl oxygen to the metal(II) ions. Furthermore, the medium-intensity band at 3223  $\text{cm}^{-1}$  of the free ligand. due to v(NH) stretches, is not observed in all metal(II) complexes. suggesting that the NH proton is lost via enolization and the resulting enolic oxygen and azoic nitrogen take place in coordination [40,50]. Moreover, the v(N-N=C) absorption band at 1522  $\text{cm}^{-1}$ , appearing in the spectra of free ligand, is absent but a new band due to v(N=N) vibration appears around 1306–1313  $cm^{-1}$  in the spectra of all complexes, which supports the azo-enol form of the ligand in the metal(II) complexes. The appearance of this peak at relatively lower field may indicate coordination via the N=N group [51,52]. In addition, IR spectrum of the ligand reveals a strong band at  $1568 \text{ cm}^{-1}$  corresponding to the  $\nu(C=N)$  of isoxazole ring, which is obviously shifted to lower wavenumber by about  $8-25 \text{ cm}^{-1}$  and is greatly diminished in intensity after complexation, suggesting that nitrogen atom of the isoxazole ring also contributes to the complexation [53–55]. Therefore, from these IR spectra, it is concluded that the ligand should exist in azo-enol form during complexation and behave as an *O*,*N*,*N*'-monobasic tridentate ligand coordinated to the metal(II) ions via the deprotonated enolic *O*, azoic group *N* and isoxazole *N*, and the probable geometry is octahedral for metal(II) ions [42,43]. There are additional factors which might affect the mode of bonding of these complexes such as the possibility of various stereoisomeric forms (e.g. cis, trans, mer and fac), bulkiness of the ligand, the nature of the metal(II) ions and intermolecular hydrogen bonds, however, due to instrument limitation, we are not able to explore the precise structure of these isomeric forms.

# 3.4. UV-vis electronic absorption spectra

The UV–Vis electronic absorption spectra of the free ligand and its metal(II) complexes in chloroform solutions  $(5.0 \times 10^{-5} \text{ mol L}^{-1})$ are shown in Fig. 3. The values of absorption band positions together with the molar absorptivities are listed in Section 2. The free ligand shows only one strong absorption band at 320 nm in the range of 250–700 nm, which can be attributed to the  $n \rightarrow \pi^*$ electronic transition involving the keto-hydrazone and the azoenol equilibrium system of the free ligand [56,57]. For the metal(II) complexes, the absorption spectra curves are very similar to each



Fig. 3. Absorption spectra of the ligand and its metal(II) complexes in chloroform.



Fig. 4. Absorption spectra of the metal(II) complex films on K9 glass substrates.

other and display a strong absorption band with absorption maxima  $(\lambda_{max})$  around 401–417 nm. This band is probably a consequence of extended conjugation in the deprotonated, coordinated ligand, compared to the free ligand, as it is noteworthy from Fig. 3 that a weak band near 320 nm in the metal(II) complexes is inversely related to the 401–417 nm one in intensity. The high-energy  $\pi \rightarrow \pi^*$  transition band of the isoxazole ring moiety in the free ligand may be below 250 nm and could not be determined in chloroform solution. However, this band is bath-ochromically shifted to ca. 250 nm in the spectra of the complexes

because of the increased conjugation effect of the isoxazolemoiety- $\pi$ -orbital with the central-metal-d-orbital [58]. Furthermore, in the case of the Co(II) complex a very weak and broad band is observed at ca. 550-650 nm, which is considered to arise from the forbidden d-d transitions, while two others(Ni(II) and Cu(II) complexes) show no apparent bands or peaks in the 450–700 nm region [40]. In addition, the relative effectiveness of the various metal(II) ions, in producing a bathochromic shift on absorption maximum ( $\lambda_{max}$ ), is clearly shown in Fig. 3. The sequence for  $\lambda_{max}$  is as follow: Ni(II) >Cu(II) > Zn(II) >Co(II), the values extending from 401 to 417 nm. This indicates that the nature of the metal(II) ions affects the position of the absorption bands significantly. As previously reported [27,59], in the case of the metal(II) complexes with the same ligand, the main reason of bathochromic or hypsochromic shifts is generally related to the electronegativity of the metal ions which can influence the electronic density and energy levels of conjugated system. Besides the electronegativity of the metal ions, there are other factors, such as distortion, electronic shell structure, solvent effects and radius of the metal ions, that probably work in combination and contribute to the absorption band shifts.

The spin-coated thin films of different metal(II) complexes, prepared on K9 substrates, using the TFP as coating solvent, were also investigated by UV–visible absorption spectroscopy. As presented in Fig. 4, the thin films show similar main absorption bands compared with those obtained in the chloroform solutions, but noticeable bathochromic shifts in the positions of the maxima are also observed, except for Cu(II) complex. According to the exciton theory and the previously published results [60], these shifts could be interpreted as the formation of aggregates in the solid films of the metal(II) complexes. As is known, disc recordable organic recording material should decompose by laser absorption. In addition, the same laser source is used for reading the disc



Fig. 5. TG/DTG and DSC curves of the metal(II) complexes.

 Table 2

 The important thermal decomposition data of the metal(II) complexes

				-	
Compound	Temp. range (intervals) (°C)	%Weight loss found (Calc.)	DTG peak temp. (°C)	DSC peak temp. (°C)	$\Delta H$ (J g <sup>-1</sup> )
$\begin{array}{c} Ni(L)_2\\ Co(L)_2\\ Cu(L)_2\\ Zn(L)_2 \end{array}$	259–272(13) 175–213(38) 160–202(42) 214–317(103)	48.2(45.3) 14.8(17.6) 16.2(17.4) 42.4(44.8)	270.6 189.0 177.1 287.6	270.7 194.1 182.8 296.1	249.2 340.3 492.4 360.7

recorded. This means that a material should have moderate absorption at the laser wavelength. Moreover, in order to obtain high reflectivity contrast, a steep absorption edge at the longer wavelength side is helpful [29,44]. Based on the current developmental trend of the blu-ray recording media, organic materials, for the recordable recording media, used at laser beams with 405 nm, preferably has a light absorption at a wavelength of from 350 nm to 450 nm where the material has a sharp tail in the longer wavelength region [21–24]. The thin films of newly synthesized metal (II) complexes exhibit a typical blue-violet light absorption at 403–419 nm (Ni(II): 419 nm; Co(II): 403 nm; Cu(II): 408 nm; Zn(II): 408 nm) very closed to the required peak position and shape for blu-ray optical storage application.

# 3.5. Thermal properties

The thermal properties of the four metal(II) complexes were investigated by thermogravimetric analysis (TGA), differential thermogravimetric (DTG) and differential scanning calorimetry (DSC). Fig. 5 presents the recorded TGA/DTG and DSC curves of the metal(II) complexes under a nitrogen atmosphere, and important data are summarized in Table 2. It can be seen that the TGA curves of the complexes show no weight loss up to 150 °C, indicating the absence of water molecule and any other adsorptive solvent molecules. As the temperature is increased, the TGA/DTG curves of all the complexes exhibit a steep weight loss at 180–300 °C, which are accompanied with a major exothermic peak in the simultaneously recorded DSC curves. For the Ni(II) and Zn(II) complexes, the TGA/DTG curves display a large weight loss (estimated weight loss 49% and 41%, theoretical 45.3% and 44.8%) at 270.6 and 287.6 °C, respectively, which are in good agreement with the decomposition of one ligand molecule. This process appears in the DSC curves as a sharp exothermic peak at 270.7 °C ( $\Delta H$ , 249.2 J g<sup>-1</sup>) for Ni(II) complex and 296.1 °C( $\Delta H$ , 360.7 J g<sup>-1</sup>) for Zn(II) complex. Remarkably, the Ni(II) complex shows only a 13 °C temperature range of decomposition, which is more rapid than that of the Zn(II) complex. After the rapid loss of the two complexes, a gradual decomposition over a large temperature range (270-440 °C for Ni (II) complex and 300–500 °C for Zn(II) complex) occurs without any meaningful exothermic or endothermic peaks in the DSC curves, which may correspond to the degradation of the remaining ligand molecules. By comparison, the Co(II) and Cu(II) complexes display a steep weight loss at lower temperature of about 180–190 °C, and the weight loss rate (<20%) of the decomposition is much smaller than that of the former two complexes. This process is probably attributed to the decomposition of a 4,4dimethyl-3-oxopentanenitrile moiety, and, like the former two complexes, is associated with a sharp exothermic peak at 194.1 °C  $(\Delta H, 340.3 \text{ J g}^{-1})$  for Co(II) complex and 182.8 °C ( $\Delta H, 492.4 \text{ J g}^{-1}$ ) for Cu(II) complex. The following degradation of the Co(II) and Cu (II) complexes exhibits a progressive weight loss process in the rest of temperature range, and shows no obvious peak both in the DTG and DSC curves.

Measurements of the thermal properties on the synthesized Co (II) and Cu(II) complexes have shown a thermal decomposition at lower temperatures than required for recordable optical recording application (>250 °C). In contrast, the Ni(II) and Zn(II) complexes lead to a much better thermal stability than that of the former two complexes. However, although the peak temperature for Zn(II) complex is above 250 °C, its steepness of thermal decomposition is not so good, as required. An even more serious problem is, as discussed earlier, the poor photostability of the Zn(II) complex, which is also a critical parameter for this type of application. One of the promising aspects for this research is that the Ni(II) complex presents a unique combination of excellent solubility and photostability, suitable absorption band, desirable thermal stability and a steep decomposition threshold with high weight loss rate and, therefore, offers the potential to form a small, clear and durable information mark on the recording thin film [29]. Along with the rapid evolution of the high-density disc storage technology, this complex may ultimately prove to be a low-cost, but high-performance candidate for blu-ray recordable materials in the future.

# 4. Conclusions

In conclusion, we have synthesized a new hydrazone ligand and its four transition metal(II) complexes in good yields using a facile and efficient synthetic route. Due to the existence of tert-butyl and cyano substituents within the backbone, these materials exhibit excellent solubility in 2,2,3,3- tetrafluoro-1-propanol as well as most common organic solvents at room temperature. The free ligand crystallizes as keto-hydrazone form in the solid-state and exists as a tautomeric equilibrium of the keto-hydrazone and the azo-enol isomers in chloroform solution. The metal-to-ligand ratio of the metal(II) complexes was found to be 1:2, and thus, the metal (II) ions appear to be hexa-coordinated with the O,N,N'-monobasic tridentate ligands in azo-enol form. The metal(II) complexes show a typical electronic absorption spectra with blue-violet light absorption at 400-420 nm in solutions and in spin-coated films. The differences in the thermal stability and the photostability of the different metal(II) complexes were observed and evaluated in detail. Further research is underway to investigate the optical recording properties of these complexes.

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