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

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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.

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 ± 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 ± 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 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 ± 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 2,2,3,3-tetrafluoro-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_3-NH_4Cl solution) and calculated from the expression $X\ \% = C_{EDTA} \times V_{EDTA} \times M/m_s$, where X is the metal content of sample, C_{EDTA} is the concentration of EDTA titrant, 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^{-1} region. ^1H NMR spectra ($CDCl_3$ 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^{-1} 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-4,4-dimethyl-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 3-amino-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].

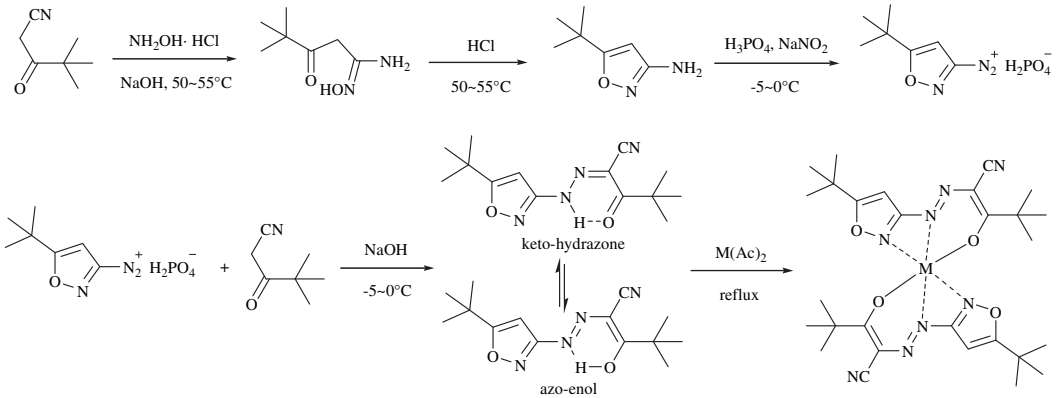

Fig. 1. Synthetical schemes of the free ligand (HL) and its four transition metal(II) complexes, $M(L)_2$ [M = Ni(II), Co(II), Cu(II), Zn(II)].