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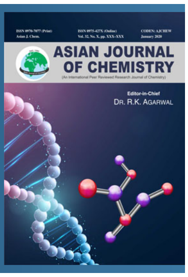

Synthesis, Spectral Characterization and Luminescent Properties of Ni(II) Complex Bearing 4,4'-dimethyl-2,2'-bipyridyl and Isothiocyanate Ligands for OLED Applications

THIPPESWAMY BASAVARAJA[1,2] and GIRIYAPURA R.VIJAYAKUMAR[1,*]

[1]Department of Studies and Research in Chemistry, University College of Science, Tumkur University, Tumkur-572103, India
[2]Department of Chemistry, Government Science College, Chitradurga-577501, India

*Corresponding author: E-mail: vijaykumargr18@gmail.com

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An octahedral Ni(II) complex *viz*. diisothiocyanatobis(dmbpy)nickel(II) (**3**) based on 4,4′-dimethyl-2,2′-bipyridine (dmbpy) ligand was prepared by conventional method under mild reaction conditions. Besides analyzing FT-IR spectrum and the determination of percentages of atoms of elements, a thorough investigation of thermal and photophysical properties of the present complex was carried out. Diffuse reflectance spectrum of the complex scanned in the range 200-1100 nm displayed a prominent peak at 455 nm, with exhibiting reflectance percentage of 45. The measured band gap energy of the complex obtained by following Kubelka-Munk (K-M) function was found to be 2.18 eV. The photoluminescence spectra that incorporated excitation and emission spectra exposed the likely possibility of emission of blue light by the complex, for which the Commission Internationale de l'Eclairage (CIE) coordinates of (0.3009, 0.2942) were calculated. A fairly high thermal stability of the synthesized complex with the incorporation of thiocyanate ligands, practically confirmed by simultaneous TG-DTA measurements, could be explored for application as an emissive layer in the fabrication of OLED devices.

Keywords: 4,4′-Dimethyl-2,2′-bipyridine, Thiocyanate, Nickel(II) complex, Photoluminescence, Diffuse reflectance.

INTRODUCTION

Development of light emitting devises purely based on organic ligands after the discovery of the first OLED [1] with efficient characterstics has been the subject of widespread research activity because of their ability to become better substitutes to conventional sources of light and displays [2-6]. It is worth noted that numerous metal complexes have been widely employed as emitting materials and electron-transporting materials in organic light emitting diode (OLED) applications. The OLED materials, displaying many advantages over conventional LED materials, are light weight and are known to demonstrate greater power efficiency and quicker response time. Scores of transition metal complexes with the exhibition of luminescent characters have been used in the development of economical, energy efficient, full colour and flat panel display applications [7,8]. Furthermore, several transition metal complexes with many chelating organic ligands are reported as robust electroluminescent materials for flat panel displays [9,10]. They are also identified as highly promising materials for optoelectronic applications owing to their excellent photo- and electroluminescent properties. Besides, these complexes are found to display proficient electron transport and light emission, high thermal stability and ease of sublimation. Complexes based on transition metals have also become promising candidates for use as hole-transporting materials, as the metal ions can assume variable oxidation states and are recognized to show small kinetic barries for self-exchange reactions [11].

Ichikawa *et al*. [12] investigated good performance of the materials with the incorporation of bipyridine and terpyridine derivatives as electron transporting layers in OLEDs because of their high electron mobility. Since 2,2′-bipyridine has been reported to demonstrate both σ-donor and π-acceptor abilities, its various disubstituted derivatives have been widely employed in supramolecular and coordination chemistry owing to their reasonably good redox stability [13,14]. They normally undergo chelation with soft metal ions, mostly transition metal ions in low oxidation states. Nozaki *et al*. [15] reported a theoretical study on the phosphorescence spectra of *tris*(2,2′-bipyridine) complexes of many transition metals by density functional theory (DFT). The synthesis of a novel distorted square-planar Pt(II) complex with bidentate 4,4′-diphenyl-2,2′-bipyridine ligand was reported by Shamaei *et al.* [16] with a prime objective of exploring its luminescent properties. Synthesis of a new distorted octahedral Ni(II) complex with 5,5′-dimethyl-2,2′-bipyridine had been reported by Abedi *et al.* [17] with a special focus on exploring its luminescent properties by undertaking a study on luminescence emission spectra . Rudmann *et al.* [18] preferably concentrated on various alkyl substituted bipyridyl ligands to synthesize Ru(II) complexes with the aim of preventing self-quenching of the excited state. The devices fabricated from the aforementioned Ru(II) complexes were observed to display rather high efficiency in relation to photoluminescence and electroluminescence when compared with the devices made from $Ru(bpy)_3^{2+}$.

Substitutions on the aromatic compounds in a symmetric manner have a greater impact on the electronic levels distribution and, as a result, regulation of luminescent properties of both the ligand and the metal complex obtained from it can be achieved [19]. Bathocuproine, a typical 1,10-phenanthroline derivative containing two methyl groups in 2,9- and two phenyl groups in 4,7-positions, has been widely used in OLED as well as in organic photovoltaics as a hole blocking material and in electron transporting layers [20,21]. Many organic ligands, possessing the ability to often undergo chelation with transition metal ions, are proved to be most essential for the synthesis of above mentioned metal complexes in order to explore their luminescent properties because the conduction in organic part of the complex is mainly attributed to complete or partial delocalization of π-electrons. The light-emitting properties of various complexes based on transition metal ions discussed as above have prompted us to report the synthesis, spectral characterization and thermal properties of Ni(II) complex bearing 4,4′-dimethyl-2,2′-bipyridine (dmbpy) and thiocyanate ligands so as to investigate it for possible OLED applications through diffuse reflectance and photoluminescence spectra.

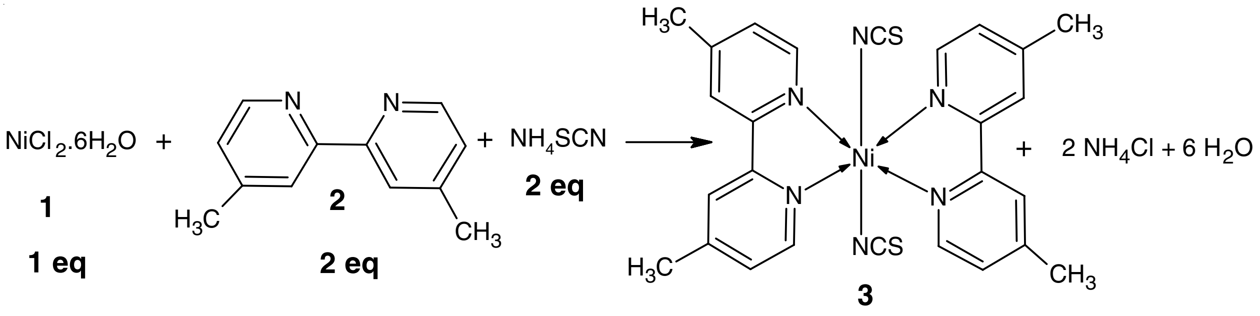
EXPERIMENTAL

Chemical & reagent samples accessible commercially were obtained from Sigma-Aldrich and employed for the synthesis of the complex compound. Solvent of reagent grade, requiring no further purification had been used for the synthesis. Thermo Nicolet, Avatar 370 FTIR spectrometer was used to scan the IR spectrum within the wavenumber range 4000-500 cm^{-1} by KBr pellet technique. The atoms of the elements C, H, N and S in terms of their percentages were found by using Elemental Vario EL III analyzer. Simultaneous TG-DTA technique by Perkin-Elmer, Diamond TG/DTA was adopted to investigate the thermal behaviour. Perkin-Elmer UV-visible spectrophotometer Lambda-35 for recording diffuse reflectance (DR) spectrum and spectrofluorimeter, Moriba operational with 450 W Xenon lamp as an excitation source for obtaining photoluminescence spectra were used.

Preparation of diisothiocyanatobis(dmbpy)nickel(II): The ligand, dmbpy (0.368 g, 2 mmol) in 3 mL ethanol was stirred on a magnetic stirrer at 50 ºC till the solution became clear. To the clear solution, nickel(II) chloride hexahydrate (0.237 g, 1 mmol) in 2 mL ethanol was added slowly and the resulting blue coloured solution was refluxed on a magnetic stirrer at 60 ºC for 1 h. The addition of ammonium thiocyanate solution (0.152 g, 2 mmol) in 3 mL water to the above solution was resulted in immediate precipitation. The precipitate was filtered, washed with alcohol and then triturated with toluene to afford a blue coloured Ni(II) complex, which was placed in a desiccator (**Scheme-I**). Yield: 89%. Elemental analysis of $[Ni(C_{12}H_{12}N_2)_2(NCS)_2]$ (m.w. = 543.33) calcd. (found) %: C: 57.47 (56.68); H: 4.45 (4.39); N: 15.46 (15.08); S: 11.80 (11.12). IR (KBr, cm^{-1}): 3064.36 (CH arom.), 2920.12 (CH of CH_3), 1614.08 (C=C arom.), 1411.27-1558.63 (C=N arom.), 2085.30 (C=N str. of Ni-NCS).

RESULTS AND DISCUSSION

The current work lays emphasis on one step synthesis, spectral characterization and luminescent properties of Ni(II) complex with a bidentate chelating ligand of organic nature such as dmbpy for use in the fabrication of OLED devices. The complex diisothiocyanato*bis*(dmbpy)nickel(II) (**3**) had been synthesized under mild conditions by the reaction of alcoholic solution of Ni(II) chloride hexahydrate with a previously stirred alcoholic solution of dmbpy ligand in a metal to ligand stochiometric ratio of 1:2. The precipitation of the above said complex took place only after the addition of two equivalents of NH_4SCN dissolved in alcohol. The synthesized complex was recovered from its alcoholic solution by filtering the precipitate through a Whatman filter paper. The complex, whose formation was confirmed primarily by colour change during the course of the reaction, was recovered in pure form on filtration, followed by trituration with toluene. The FT-IR spectrum, one of the main components of spectral characterization, was recorded for the synthesized complex. It was noticed from the IR spectrum of



Scheme-I: Reaction scheme for the formation of diisothiocyanatobis(dmbpy)nickel(II) (**3**) the complex that shift of absorption bands was pragmatic when compared with the IR spectrum of dmbpy ligand. A relatively greater stability has been accorded to the metal complex by the incorporation of thiocyanate ligands,which are supposed to exercise control over the absorption maximum and absorptivity [22]. As per HSAB principle, the nitrogen of thiocyanate has a tendency to become coordinated quite strongly to Ni^{2+}, owing to its small size and high electronegativity as compared to sulphur. Two NCS ligands in the aforesaid complex were possibly linked to Ni^{2+} through a bonding of anionic type. The octahedral coordination of Ni^{2+} to two N-bonded thiocyanate anions and four nitrogen atoms of dmbpy ligands is assumed to be similar to the one reported earlier [23].

TG-DTA analysis: The investigation of thermal properties of the synthesized complex (**3**) was performed simultaneously by thermogravimetry and differential thermoanalysis. The results of thermal analysis, summarized in Table-1, were in good agreement between the calculated and the experimental mass loss values. The commencement of mass loss for complex **3** (Fig. 1) was happened only at 350 ºC and a substantial amount of mass loss that was accompanied by a DTG peak at 416.89 ºC took place in a single step between 350 to 435 ºC. The mass loss in the above step was attributed to the loss of two moles of dmbpy ligand with an estimated mass loss of 67.8% (calcd. mass loss 68.50%). The formation of pure NiO was believed to be taken place above 520 ºC [24]. The presence of no coordinated water molecules or molecules of water of hydration was clearly evident from the TG-DTA curve. The high thermal stability of the complex could be conveniently employed as an emissive layer in OLED devices.

Diffuse reflectance spectrum: Diffuse reflectance (DR) spectrum of the synthesized complex 3 recorded in the wavelength range 200-1100 nm is depicted in Fig. 2. The emergence of a major peak peak with a diffuse reflectance percentage of 45 was observed at 455 nm in the DR spectrum. The peak appearance in the spectrum was mainly the result of transition between valence and conduction bands. The Kubelka-Munk (K-M) function was used for obtaining band gap energy of the complex. In the plot of $[F(R_\infty)h\nu]^{1/2}$ *versus* photon energy ($h\nu$), tangent drawn on the X-axis is shown in Fig. 2b. The K-M function $F(R_\infty)$ and photon energy ($h\nu$) were calculated by the following equations:

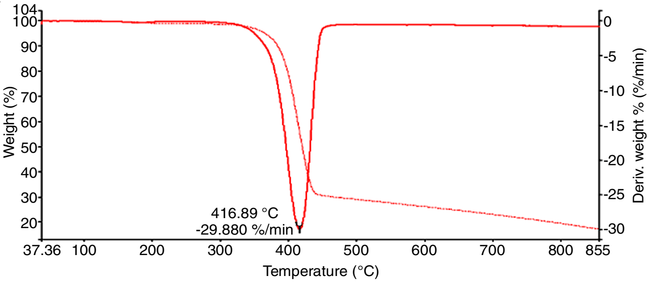


Fig. 1. TG-DTA of diisothiocyanatobis(dmbpy)nickel(II) (**3**)

$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} \quad (1)$$

$$h\nu = \frac{1240}{\lambda} \quad (2)$$

where R_∞ is the reflection coefficient of sample and λ is the absorption wavelength. The band gap energy obtained from the plot was found to be 2.18 eV [25]. There are certain reports to substantiate the possibility of accomplishing smaller band gap with the incorporation of electron-donating substituents that can destabilize the HOMO and electron-withdrawing substituents in order to destabilize the LUMO on the ancillary ligand [26,27].

TABLE-1
THERMAL DECOMPOSITION DATA FOR THE COMPLEX **3**

Complex formula	Temperature (°C)	DTG peak (°C)	Mass loss (%)		Intermediate compound
			Found	Calculated	
$Ni(dmbpy)_2(NCS)_2$	350-435	416.89	67.8	68.5	$Ni(SCN)_2$

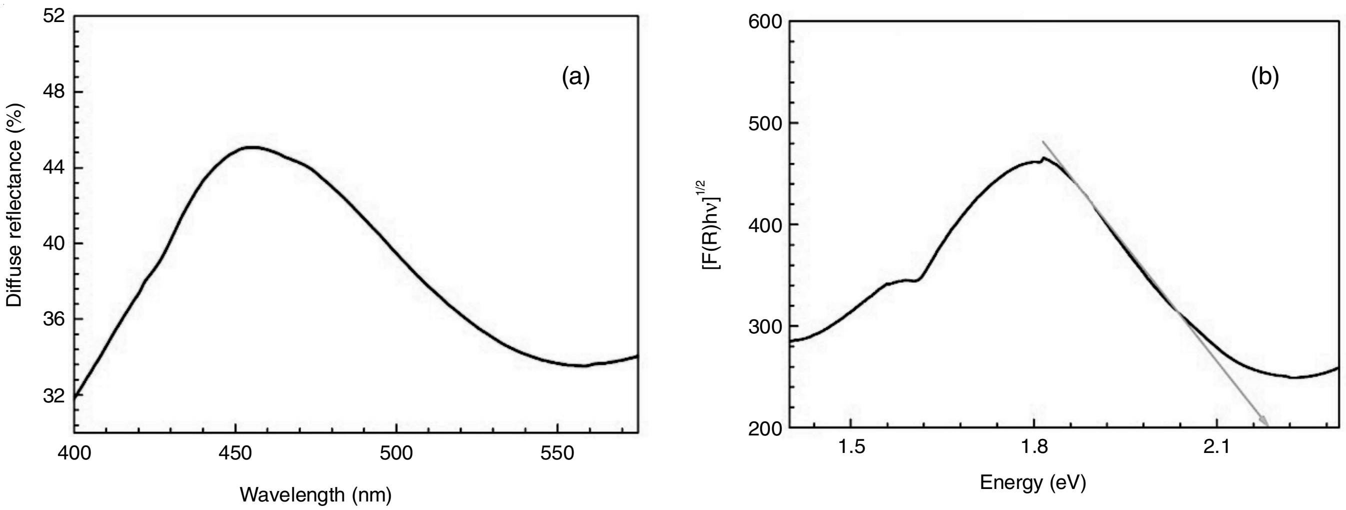


Fig. 2. (a) Diffuse reflectance spectrum (b) Plot of $[F(R_\infty)h\nu)]^{1/2}$ *versus* photon energy ($h\nu$) of complex (**3**)

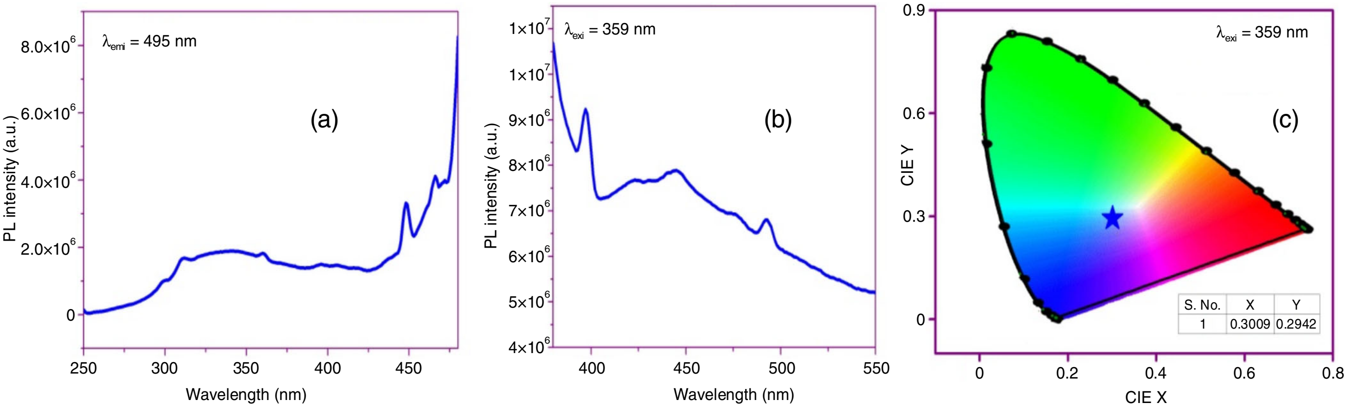


Fig. 3. (a) Photoluminescence excitation spectrum (b) Photoluminescence emission spectrum and (c) CIE graph of complex (**3**)

Photoluminescence spectra: The excitation and emission spectra scanned at room temperature and the CIE plot of the complex **3** are shown in Fig. 3. The excitation spectrum of the complex (Fig. 3a) at 495 nm emission wavelength displayed key excitations at 448 and 466 nm, thereby indicating that the phosphor could easily be excited by UV LED chip (360-400 nm). The emission spectrum of the complex (Fig. 3b) afforded three bands at 400, 445 and 493 nm. Estimation of Commission International De I-Eclairage (CIE) 1931 chromaticity coordinates [28,29] had been made possible at excitation wavelength 359 nm. The CIE values estimated at the aforementioned excitation wavelength are shown in Fig. 3c (inset). The likely possibility of emission colour of the material can be confirmed in the CIE chromaticity diagram by a star that is normally used in order to locate colour coordinates. One could notice from the CIE graph that emission colour of the complex was located in the blue region.

Conclusion

The present work focused on the ease of synthesis of Ni(II) complex of a bidentate chelating organic ligand (dmbpy) and thiocyanate ligands under moderate experimental conditions by the direct reaction of an alcoholic solution of Ni(II) chloride hexahydrate with the aforesaid ligands in an alcoholic medium. Inspite of spectral characterization and the determination of percentages of atoms of elements, simultaneous TG-DTA measurements had also been performed on the complex. The exhibition of exceptionally good thermal stability, an important prerequisite for a material to be employed in OLED devices, confirmed by TG-DTA and the display of fairly low band gap in accordance with diffuse reflectance (DR) spectrum by the synthesized complex could find suitable for use as an emissive layer in OLED applications. The blue colour of emission by the complex inferred by its CIE graph can further substantiate that the said phosphor could be used as blue light emitting material in the fabrication of OLED devices.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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