

# Synthesis, characterization, and photoluminescence properties of Cu(II), Co(II), Ni(II), and Zn(II) complexes of N-aminopyrimidine-2-thione

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This research concentrates on the preparation, characterization, and photoluminescence properties of new Co(II), Ni(II), Cu(II), and Zn(II) complexes of N-aminopyrimidine-2-thione. The ligand and metal complexes were characterized by elemental analysis and spectroscopic studies such as IR, UV/Vis, API-ES, NMR, fluorescence, and magnetic susceptibility measurements. The ligand and the resulting metal complexes gave intense emissions ( $\lambda_{\max} = 408$  nm) upon irradiation by ultraviolet light. The photoluminescence quantum yields and long excited-state lifetimes of the ligand and its complexes were calculated. The ligand had photoluminescence quantum yields of 36% and long excited-state lifetimes of 3.40 ns. The photoluminescence intensities and quantum yields of the metal complexes changed upon complexation with various metals. These novel complexes may be of interest as organic emitting material for electroluminescent devices.

**Key Words:** N-aminopyrimidine-2-thione, metal complex, characterization, photoluminescence

## Introduction

Pyrimidine is the parent heterocycle of a very important group of compounds that has been extensively studied due to their occurrence in living systems.<sup>1</sup> Considerable attention has been given to metal(II) complexes of the polydentate Schiff base ligands of N-aminopyrimidine because of their bioinorganic relevance, which has often

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been related to their chelating ability with trace metal ions.<sup>2–5</sup> Recent findings of the presence of metal-sulfur and metal-nitrogen bonds at the active sites of several oxidoreductases have stimulated an immense amount of interest in pyrimidine chemistry.<sup>6,7</sup>

New organic materials have attracted much attention over recent years for their light-emitting properties.<sup>8–10</sup> For example, organic polymers that exhibit strong luminescence at low driving voltages, particularly those that emit in the blue region, are of great interest for flat panel display applications.<sup>11,12</sup> Rare earth complexes with low-molecular-weight organic ligands have also been extensively studied to obtain highly fluorescent materials for application in electroluminescent devices<sup>13,14</sup> and laser systems.<sup>15</sup> Furthermore, luminescent materials from these low-molecular-weight organic ligands/rare-earth complexes have been prepared as polymer matrices due to the ease of processing polymers.<sup>16,17</sup> However, difficulty in dispersing the low-molecular-weight organic ligands/ rare-earth metal complexes into a polymer matrix has hindered progress.

Numerous aromatic amines and polymeric arylamines have also been developed as hole-transport layers in organic electroluminescent research.<sup>18,19</sup> The synthesis, luminescence, and cyclic voltammetric studies of novel binuclear ruthenium(II) complexes were reported by Yang et al.<sup>20</sup> These researchers investigated the single-photon fluorescence of synthesized ligands and their complexes. They concluded that the spectra of the ligands were similar because of their structural compatibility; however, for their respective complexes, the fluorescence emission was completely quenched. The synthesis and fluorescence of N-substituted 1- and 2-aminopyrenes have been studied, and their absorption and fluorescence spectra as well as fluorescence quantum yields in different solvents were measured and reported.<sup>21</sup> It was shown that the fluorescence quantum yield was dependent on both the structure and solvent polarity. The fluorescent *vic*-dioxime-type ligand and its mono- and dinuclear complexes have been studied.<sup>22</sup> It was noted that the fluorescence spectra of the probe showed a clear shift in excitation wavelength maxima upon metal binding, indicating its potential use as a ratiometric metal indicator. The fluorescence of the complexes was found to be highly sensitive to both polarity and the protic character of the solvent used. They allow for new fluorescent chemosensors for several transition metals, synthesized by conjugating 7-mercapto-4-methylcoumarin fluorophore and *vic*-dioxime as the metal-chelating moiety. It was further reported that the fluorescence emission intensity of the ligand decreased dramatically depending on the complex formation with transition metal ions. The decrease in emission intensities was due to the formation of the coordination complex of the N-atom on the ligand with the metal ions.

The aim of the present work was to synthesize and characterize Co(II), Ni(II), Cu(II), and Zn(II) complexes with N-aminopyrimidine-2-thione. An investigation of the optical properties of the ligand and its various complexes in solution was also carried out. The ligand and its various complexes were found to exhibit intense photoluminescence upon UV irradiation.

## Experimental procedure

### Materials and instrumentation

All of the chemicals, including 9,10-diphenylanthracene, dimethyl sulfoxide (DMSO), and methanol, were purchased from Aldrich Chemical Company and used as received.

Elemental analyses (C, H, N, S) were performed using a LECO CHNS model 932 elemental analyzer. IR

spectra were obtained using KBr disks of 4000-400  $\text{cm}^{-1}$  with a Bio-Rad-Win-IR spectrometer. The electronic spectra in the 200-900 nm range were obtained in dimethylformamide (DMF) on a Unicam UV2-100 UV/Vis spectrophotometer. Magnetic measurements were carried out by the Gouy method using  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as the calibrant. Molar conductance was determined in DMF at room temperature using a Jenway model 4070 conductivity meter.  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra were recorded with a Bruker 300-MHz UltraShield TM-NMR instrument. LC/MS-API-ES mass spectra were recorded using an Agilent model 1100 MSD mass spectrometer. The single-photon fluorescence spectra were collected on a PerkinElmer LS55 luminescence spectrometer. All of the samples were prepared in spectrophotometric-grade DMSO and analyzed in a 1 cm optical path quartz cuvette. The solution concentration of the ligands and the complexes in DMSO was  $1.0 \times 10^{-5} \text{ mol L}^{-1}$  and the samples were excited at a wavelength of 256 nm. The photoluminescence quantum efficiencies were calculated using 9,10-diphenylanthracene as the standard.<sup>23-25</sup>

### Preparation of the ligand (LH)

1-Amino-5-(4-methylbenzoyl)-4-(4-methylphenyl)-1*H*-pyrimidine-2-thione (LH, **1**) was prepared according to the literature method by a 2-step synthesis process.<sup>26,27</sup> 5-(4-Methylbenzoyl)-4-(4-methylphenyl)-1-(methylphenylmethylamino)-1*H*-pyrimidine-2-thione was obtained from acetophenonthiosemicarbazone with 4-(4-methylbenzoyl)-5-(4-methylphenyl)furan-2,3-dione. In acidic solution, from the hydrolysis of 5-(4-methylbenzoyl)-4-(4-methylphenyl)-1-(methylphenylmethylamino)-1*H*-pyrimidine-2-thione, 1-amino-5-(4-methylbenzoyl)-4-(4-methylphenyl)-1*H*-pyrimidine-2-thione was obtained. To a solution of 1 g of 5-(4-methylbenzoyl)-4-(4-methylphenyl)-1-(methylphenylmethylamino)-1*H*-pyrimidine-2-thione in 20 mL of butanol, 20 mL of water and 5 mL of acetic acid were added, and the mixture was heated under reflux for 45-50 min. Upon cooling, 0.46 g (58%) of **1** was recrystallized from butanol; mp 202 °C; IR (KBr):  $\nu = 3262$  (-NH<sub>2</sub>), 3069 (aromatic C-H), 2930 (aliphatic C-H), 1653 s (C=O), 1598-1462 m (C=C and C=N), 1160, 835  $\text{cm}^{-1}$  (C=S);  $^1\text{H-NMR}$  (DMSO):  $\delta = 7.71$ -6.99 (9H, ArH), 7.26 (s, 2H, N-NH<sub>2</sub>), 2.24 ppm (s, 3H, COArCH<sub>3</sub>), and 2.19 ppm (s, 3H, ArCH<sub>3</sub>). Anal. Calcd. for C<sub>19</sub>H<sub>17</sub>N<sub>3</sub>OS: C, 68.06; H, 5.11; N, 12.53; S, 9.56. Found: C, 67.93; H, 4.82; N, 12.24; S, 9.62%. UV/Vis [ $\lambda$  (nm)]: 266, 304.

### Preparation of the complexes

After 0.335 g (1.00 mmol) of LH (**1**) was dissolved in 25 mL of chloroform and 25 mL of methanol, a solution of 0.5 mmol  $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  (0.125 g),  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  (0.124 g),  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  (0.100 g), and  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (0.110 g) methanol was added dropwise with continuous stirring. The mixture was stirred further for 1 h at 60 °C. The precipitate was filtered off, washed with diethyl ether followed by cold methanol, and dried in a vacuum desiccator.

**[CoL<sub>2</sub>]·H<sub>2</sub>O (2)**: Yield was 306 mg (82%), mp 230 °C. Anal. Calcd. for C<sub>38</sub>H<sub>34</sub>CoN<sub>6</sub>O<sub>3</sub>S<sub>2</sub> (745.00 g mol<sup>-1</sup>): C, 61.20; H, 4.60; N, 11.27; S, 8.60. Found: C, 61.03; H, 4.34; N, 11.40; S, 9.00%. Selected IR data (KBr,  $\nu \text{ cm}^{-1}$ ): 3440  $\nu$ (OH/H<sub>2</sub>O), 3327  $\nu$ (NH), 3059 (C-H<sub>pyrimidine</sub>), 1646  $\nu$ (C=O), 1602-1521 (C=C and C=N), 1173, 873  $\nu$ (C=S), 476 (M-N). UV/Vis [ $\lambda$  (nm)]: 268, 274, 417.  $\mu_{\text{eff}}$ , 2.04 BM,  $\Lambda_{\text{o}}$  (S cm<sup>2</sup> mol<sup>-1</sup>) 13.11. API-ES: m/z 747.0 [<sup>59</sup>Co(L)<sub>2</sub>+2].

**[NiL<sub>2</sub>]<sub>2</sub>·H<sub>2</sub>O (3)**: Yield was 298 mg (88%), mp 263 °C. Anal. Calcd. for C<sub>38</sub>H<sub>32</sub>N<sub>6</sub>NiO<sub>3</sub>S<sub>2</sub> (735.71

g mol<sup>-1</sup>): C, 61.97; H, 4.52; N, 11.41; S, 8.71. Found: C, 61.70; H, 4.43; N, 11.61; S, 9.15%. Selected IR data,  $\nu$  (cm<sup>-1</sup>): 3412  $\nu$ (OH/H<sub>2</sub>O), 3325  $\nu$ (NH), 3059 (C-H<sub>pyrimidine</sub>), 1649  $\nu$ (C=O), 1602-1523 (C=C and C=N), 1169, 891  $\nu$ (C=S), 477 (M-N). UV/Vis [ $\lambda$  (nm)]: 268, 290, 370, 460, 556.  $\mu_{\text{eff}}$ , Dia,  $\Lambda_{\text{o}}$  (S cm<sup>2</sup> mol<sup>-1</sup>) 3.50. API-ES: m/z 1475.1 [<sup>58</sup>Ni<sub>2</sub>L<sub>4</sub>+H<sub>2</sub>O+3]; 726.9 [<sup>58</sup>NiL<sub>2</sub>]<sup>+</sup>.

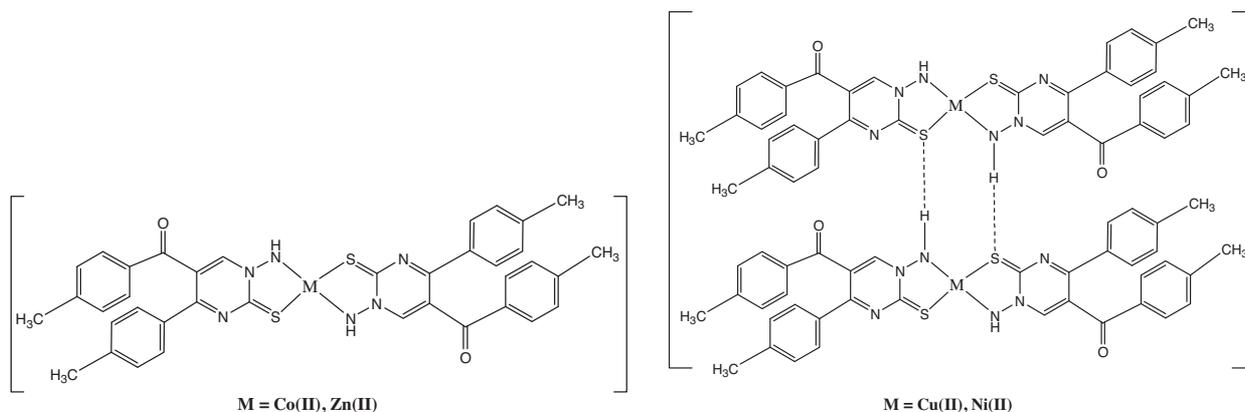
[CuL<sub>2</sub>]<sub>2</sub> (**4**): Yield was 355 mg (49%), mp 227 °C. Anal. Calcd. for C<sub>76</sub>H<sub>64</sub>Co<sub>2</sub>N<sub>12</sub>O<sub>6</sub>S<sub>4</sub> (1462.2 g mol<sup>-1</sup>): C, 62.32; H, 4.40; N, 11.48; S, 8.76. Found: C, 62.49; H, 4.47; N, 11.62; S, 9.22%. Selected IR data,  $\nu$  (cm<sup>-1</sup>): 3327  $\nu$ (NH), 3059 (C-H<sub>pyrimidine</sub>), 1657  $\nu$ (C=O), 1603 (C=N<sub>pyrimidine</sub>), 1169, 890  $\nu$ (C=S), 486 (M-N). UV/Vis [ $\lambda$  (nm)]: 282, 310, 378, 432, 678.  $\mu_{\text{eff}}$ , 1.81 BM,  $\Lambda_{\text{o}}$  (S cm<sup>2</sup> mol<sup>-1</sup>) 11.12. API-ES: m/z 1463.1 ([CuL<sub>2</sub>]<sub>2</sub>+1); m/z 733.2 [CuL<sub>2</sub>+1].

[ZnL<sub>2</sub>] (**5**): Yield was 225 mg (61%), mp 251 °C. Anal. Calcd. for C<sub>38</sub>H<sub>32</sub>N<sub>6</sub>O<sub>3</sub>S<sub>2</sub>Zn (732.00 g mol<sup>-1</sup>): C, 62.16; H, 4.39; N, 11.45; S, 8.73. Found: C, 61.76; H, 4.40; N, 11.46; S, 9.00%. Selected IR data,  $\nu$  (cm<sup>-1</sup>): 3309  $\nu$ (NH), 3058 (C-H<sub>pyrimidine</sub>), 1642  $\nu$ (C=O), 1601 (C=N<sub>pyrimidine</sub>), 1169, 875  $\nu$ (C=S), 492  $\nu$ (M-N). <sup>1</sup>H-NMR (DMSO, ppm):  $\delta$  = 8.55 (s, 2 H, C-H<sub>pyrimidine</sub>), 7.13 (d,  $J$  = 8.06 Hz, 4H, (Pym)Ph-*Hm*), 7.25 (d,  $J$  = 8.06 Hz, 4H, (CO)Ph-*Hm*), 7.34 (d,  $J$  = 8.07 Hz, 4H, (Pym)Ph-*Ho*), 7.67 (d,  $J$  = 8.10 Hz, 4H, (Pym)Ph-*Ho*), 2.51, 2.23 ppm (s, 12H, 4 × CH<sub>3</sub>). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>, ppm),  $\delta$  191.62 (OC-Ar), 174.85 (C=S, pyrimidine), 161.42 (-C6, pyrimidine), 145.22-120.64 (C, aromatic), 21.64, 21.32 (CH<sub>3</sub>). UV/Vis [ $\lambda$  (nm)]: 266, 304, 356.  $\mu_{\text{eff}}$ , Dia,  $\Lambda_{\text{o}}$  (S cm<sup>2</sup> mol<sup>-1</sup>) 4.56. API-ES: m/z 733.8 [ZnL<sub>2</sub>+1].

## Results and discussion

### Synthesis

1-Aminopyrimidine-2(1*H*)-thione (LH, **1**) was prepared according to the literature method by a 2-step synthesis process.<sup>26,27</sup> The ligand and its complexes were very stable at room temperature in the solid state. The ligand is soluble in common organic solvents, but its metal complexes are generally only soluble in DMF and DMSO. The microanalytical data of the complexes revealed a metal:ligand stoichiometry of 1:2, corresponding to a square planar geometry of [M(L)<sub>2</sub>] or [M(L)<sub>2</sub>]<sub>2</sub>·nH<sub>2</sub>O (Figure 1). These analytical data are in good agreement with the proposed stoichiometry of the complexes. The molar conductivities of compounds **2-5** in DMF at 25 °C are in the range of 3.50-13.11 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>, indicating nonelectrolytes.<sup>28</sup>



**Figure 1.** Proposed chemical structure of the metal complexes.

## Structural study

Characteristic IR bands of the ligand were assigned at  $3262\text{ cm}^{-1}$   $\nu(\text{NH}_2)$ ,  $3069\text{ cm}^{-1}$   $\nu(\text{C-H pyrimidine ring})$ ,  $1652\text{ cm}^{-1}$   $\nu(\text{C=O benzoyl})$ ,  $1602\text{ cm}^{-1}$  ( $\text{C=N}_{\text{pyrimidine}}$ ),  $1160$ , and  $835\text{ cm}^{-1}$   $\nu(\text{C=S})$  vibrations.<sup>29,30</sup> IR spectra of the complexes were compared with that of the free ligand to show changes during complexation. Co(II), Ni(II), Cu(II), and Zn(II) complexes of the ligand at  $3241\text{ cm}^{-1}$  for  $\nu(\text{NH})$  primer amine asymmetric-symmetric stretching vibration bands vanished, and the sec-amine peak was observed at  $3309\text{-}3423\text{ cm}^{-1}$ . The  $\nu(\text{C=S})$  vibration at  $1160$  and  $835\text{ cm}^{-1}$  in the free ligand shifted to a higher frequency, to approximately  $1170$  and  $870\text{ cm}^{-1}$ , after complexation, due to coordination with the sulfur atom of the thione group to the metal ion.<sup>29-31</sup> This situation indicated coordination of sulfur and nitrogen to the metal(II) ion.<sup>32</sup> Thus, a metal-ligand bond formed over the  $\text{NH}_2$  group, which lost one proton of the ligand.<sup>33</sup> The low frequency region of the spectra revealed the presence of a new medium-intensity band between  $470$  and  $490\text{ cm}^{-1}$  due to  $\nu(\text{M-N})$  vibrations.<sup>33</sup>

The UV/Vis spectral data of the compounds in DMF are presented in the experimental section. There were 2 absorption bands, assigned to  $n-\pi^*$  and  $\pi-\pi^*$  transitions, in the electronic spectrum of the ligand. These transitions were also observed in the spectra of the complexes, but they were shifted toward lower and higher frequencies, confirming the coordination of the ligand to the metallic ions.<sup>34</sup>

The electronic absorption spectrum of the Ni(II) complex showed 2 bands, at  $565$  and  $650\text{ nm}$ , which were attributed to the  $^1\text{A}_{1g} \rightarrow ^1\text{A}_{2g}$  and  $^1\text{A}_{1g} \rightarrow ^1\text{B}_{2g}$  transitions.<sup>35</sup> These transitions, as well as the measured value of the magnetic moment ( $\mu_{\text{eff}} = 0$ ), suggested a square-planar stereochemistry for the compound.

Since the zinc ion has a  $d^{10}$  configuration, the absorption at  $390\text{ nm}$  could be assigned to a charge-transfer transition. However, taking into account the spectrum and the configuration of the zinc(II) ion, a tetrahedral geometry may be assumed for its complex.<sup>34,36</sup>

The electronic absorption spectrum of the copper complex exhibited bands at  $440$  and  $645\text{ nm}$ , which could be assigned to the  $^2\text{B}_{1g} \rightarrow ^2\text{A}_{1g}$  and  $^2\text{B}_{1g} \rightarrow ^2\text{E}_{1g}$  transitions. These transitions, together with the measured value of the magnetic moment ( $\mu_{\text{eff}} = 1.88\text{ BM}$ ), suggested a square-planar stereochemistry for this compound. The values for the effective magnetic moment obtained from the measurements of magnetic susceptibility ( $1.77\text{-}1.80\text{ BM}$ ) were characteristic for copper(II) ions of a square-planar local configuration.<sup>37</sup>

DMSO- $d_6$  was used as a solvent for  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra. In the  $^1\text{H-NMR}$  spectrum of 1-amino-5-(4-methylbenzoyl)-4-(4-methylphenyl)-1*H*-pyrimidine-2-thione, a singlet signal at  $\delta 7.26\text{ ppm}$  assigned to the  $\text{NH}_2$  band on the pyrimidine molecule was observed.<sup>27</sup> The  $^1\text{H-NMR}$  spectrum of the Zn(II) complex is shown in Figure 2. In the spectra of the diamagnetic Zn(II) complexes, the low field signals due to the  $\text{NH}_2$  protons disappeared, indicating the replacement of these protons by the metal ion. The multiplets in the region of  $\delta 7.74\text{-}7.11\text{ ppm}$  were due to aromatic protons, and singlets in the region of  $2.51$  and  $2.23\text{ ppm}$  were due to the methyl protons in the free ligand.<sup>27</sup> On the basis of the above discussion, a square-planar structure can be suggested for the Zn(II) complex (Figure 1).

The  $^{13}\text{C-NMR}$  spectrum of the Zn(II) complex is shown in Figure 3. It displayed characteristic signals at  $191.62$ ,  $174.85$ , and  $161.42\text{ ppm}$  due to the (OC-Ar), (C=O, pyrimidine), and (-C6, pyrimidine ring) of the Zn(II) complexes, respectively. The singlets at  $\delta 145.22\text{-}120.64$  and  $21.64$  and  $21.32\text{ ppm}$  were due to the aromatic and methyl carbons of the complex.<sup>38</sup>

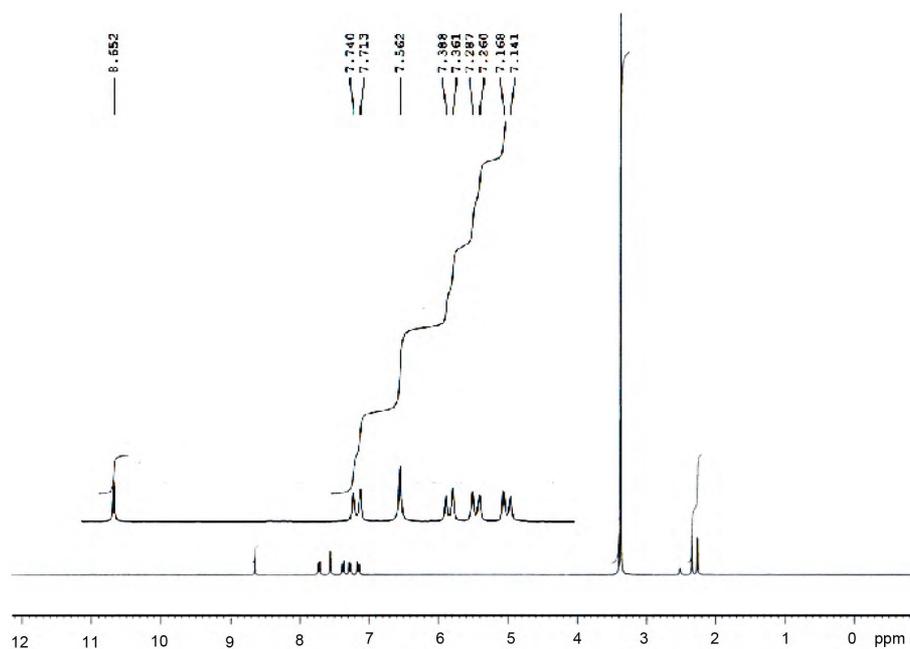


Figure 2. <sup>1</sup>H-NMR spectrum of Zn(II) complex.

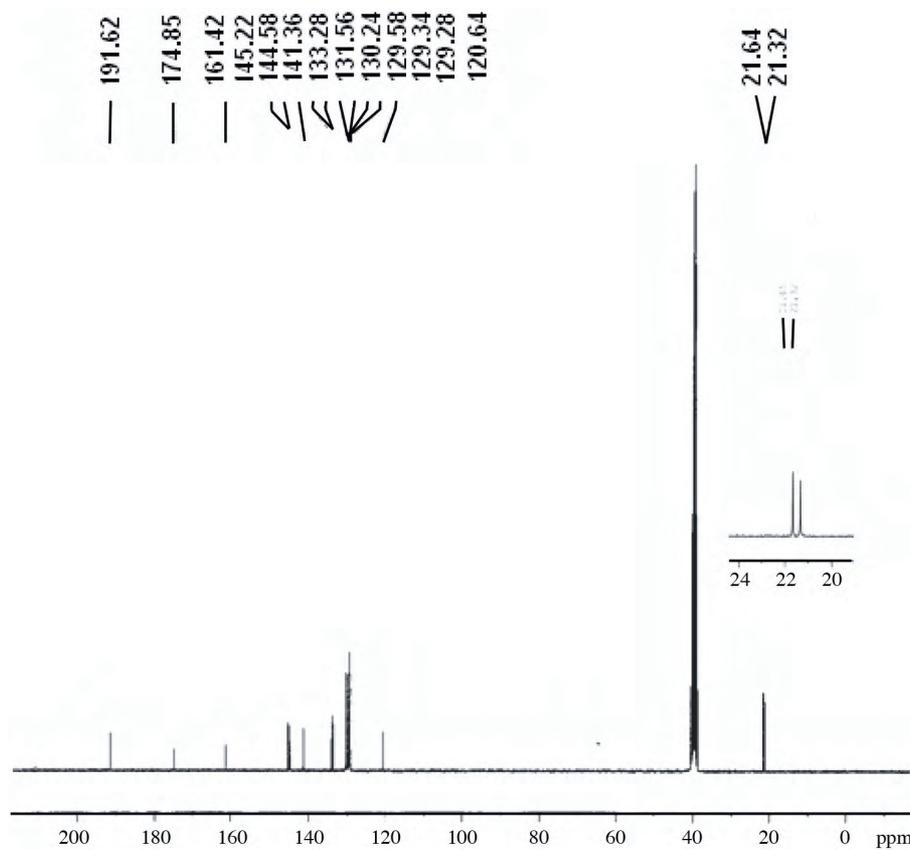
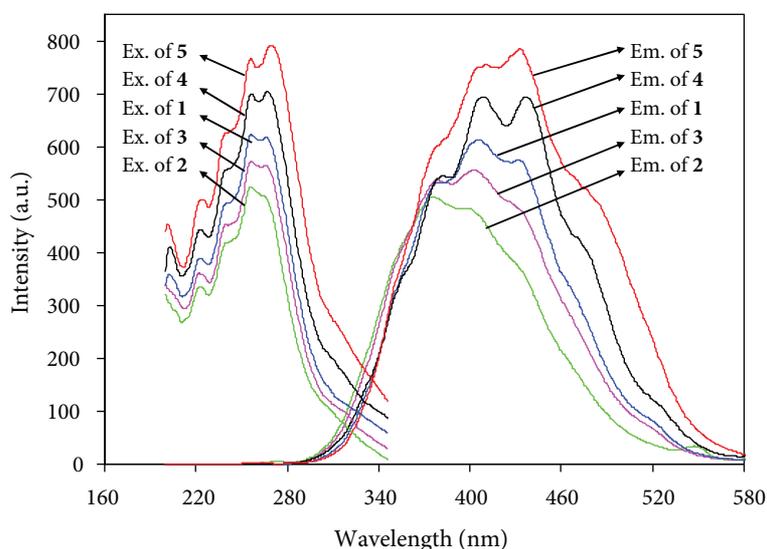


Figure 3. <sup>13</sup>C-NMR spectrum of Zn(II) complex.

The LC/MS-API-ES spectra of the  $[\text{CoL}_2] \cdot \text{H}_2\text{O}$ ,  $[\text{NiL}_2]_2 \cdot \text{H}_2\text{O}$ ,  $[\text{CuL}_2]_2$ , and  $[\text{ZnL}_2]$  complexes showed molecular ion peaks  $[\text{}^{59}\text{Co}(\text{L})_2+2]$ ,  $[\text{}^{58}\text{Ni}_2\text{L}_4+\text{H}_2\text{O}+3]$ ,  $[[\text{CuL}_2]_2+1]$ , and  $[\text{ZnL}_2+1]$  at  $m/z$  747.0, 1475.1, 1463.1, and 733.8, respectively. All of the compounds were consistent with the molecular ion fragment and support the proposed structure of the complexes. The Co(II) and Ni(II) complexes had one additional water of crystallization. Single crystals of the compounds could not be isolated.

## Fluorescence measurements

The optical properties of the ligand and its various complexes were explored using UV/Vis and photoluminescence. Absorption and photoluminescence spectra were studied for solutions of the ligand excited at 256 nm. The most striking feature was that the ligand gave an intense emission upon irradiation by UV light. The photoluminescence spectrum of the ligand in DMSO is shown in Figure 4. Maximum luminescent intensity was observed at 408 nm, and the full width at half maximum was 116 nm. The ligand exhibited a photoluminescence quantum yield of 36% and a long excited-state lifetime of 3.40 ns. The high quantum yields resulted from the  $\pi$ -electron's extensive delocalization, forming a large conjugated system in the ligand structure.



**Figure 4.** Photoluminescence spectra of the ligand and its various complexes in DMSO; samples were excited at 256 nm.

Figure 4 also shows the comparison of excitation and emission spectra of the ligand and its various complexes in the solvent DMSO. The complexes, the preparation of which is described in the experimental section, were used for the luminescent measurements. The photoluminescence intensities and quantum yields of the metal complexes changed with respect to that of the ligand upon complexation with various metals. As seen in Figure 4, the ligand exhibited an excitation maximum wavelength at 260 nm, which shifted to 272 nm upon binding to the transition metal ions. Furthermore, a decrease in the excitation intensity of the ligand was observed depending on complex formation with Co and Ni transition metal ions. However, an increase in excitation intensity of the ligand was observed depending on complex formation with  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  metal

ions. When excited at 260 nm, the ligand showed an emission maximum at 408 nm, which shifted to 439 nm upon binding to the transition metal ions (Figure 4). Thus, it is evident that the fluorescence emission intensity of the ligand decreases dramatically depending on the complex formation with the transition metal ions. The decrease of emission intensities is due to the formation of the coordination complex of the S and N atom in the ligand with the metal ions. These coordination complexes make the energy transfer possible from the excited state of the ligand to the metal ions, thus increasing the nonradiated transition of the ligand excited state and decreasing the fluorescence emission. However, the degree of the fluorescence quenching increases upon complex formation with metal ions, which have lower d-orbital electron numbers. The decreases in emission maxima were in the order of  $Zn^{2+} < Cu^{2+} < Ni^{2+} < Co^{2+}$  for the synthesized complexes (Figure 4). This clearly implicates an interaction between the metal and the ligand.

The emission of the ligand, being inhibited in this case, is dependent on the presence of a metal ion, and the ligand photoluminescence in DMSO is regarded as being dependent on the d-block metals that are effective in DMSO solutions. Quenching of fluorescence of the ligand by transition metal ions during complexation is a rather common phenomenon, which can be explained by processes including magnetic perturbation, redox-activity, and electronic energy transfer.<sup>39,40</sup> Enhancement of fluorescence through complexation is, however, of much interest, as it opens up the opportunity for photochemical applications of these complexes.<sup>41,42</sup> It can be seen in Figure 4 that upon complexation of the ligand, the photoluminescence intensities and quantum yields of the  $Cu^{2+}$  and  $Zn^{2+}$  metal complexes increase. The increase in intensity is due to the formation of a metal-to-ligand ratio of 1:2, resulting in larger molecule formation. There are 2 driving forces competing here: the interaction between the metal and ligand due to complexation results in a reduction of photoluminescence intensities, while the formation of the metal-to-ligand ratio of 1:2 leads to an increase in photoluminescence intensities and thus the formation of larger molecules. The first instance, where there is a reduction of photoluminescence, is greater for the Co and Ni complexes, while the second case applies for the Cu and Zn complexes. Additionally, upon

**Table.** Photoluminescence data for the ligand and its various complexes.

Entity	$\lambda_{\max}$ Ex (nm)	In Ex	$\lambda_{\max}$ Em (nm)	In Em	$\phi_f$ (%)	$\tau_f$ (ns)
LH (1)	260 (226, 241, 269)	615	408 (355, 379, 435, 471)	608	36	3.40
L-Co (2)	258 (219, 236, 267)	520	374 (353, 402, 433, 465)	515	32	2.99
L-Ni (3)	259 (225, 242, 268)	563	405 (354, 379, 436, 468)	557	34	3.17
L-Cu (4)	269 (226, 242, 259)	699	439 (359, 384, 411, 476)	691	40	3.75
L-Zn (5) L-Zn (5)	272 (226, 242, 258)	787	436 (359, 379, 413, 486)	778	44	4.10

$\lambda_{\max}$  Ex: maximum excitation wavelength, In Ex: maximum excitation intensity,

$\lambda_{\max}$  Em: maximum emission wavelength, In Em: maximum emission intensity,

$\phi_f$ : quantum yield,  $\tau_f$ : excited-state lifetime; L: ligand.

complexation of the ligand, the maximum photoluminescence peak shifted from 408 to 439 nm, and other peaks and shoulder peaks became more intense and obvious. Some electrons of the atoms or moieties of this ligand become affected by the inserted metal ions. This emission wavelength difference can probably be used for tuning in photoluminescent devices. The photoluminescence data for the ligand and its various complexes are summarized in the Table. The photoluminescent properties of these compounds may indicate a great deal of potential for numerous optical and electronic applications.

## Conclusion

In this study, the synthesis, spectroscopic characterization, and photoluminescence properties of a N-aminopyrimidine-2-thione ligand and its various complexes were presented. The structures of the metal complexes were characterized with UV/Vis, FT-IR,  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR, and magnetic susceptibility and electrolytic measurement techniques. The ligand was found to exhibit an intense photoluminescence at 408 nm, and the complexes showed great changes in maximum luminescence intensities and quantum efficiencies. Upon complexation, the luminescence peak shifted from 408 to 439 nm. These compounds may be interesting materials for application in electroluminescent devices.

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## References

1. Kandil, S. S.; Katib, S. M. A.; Yarkandi, N. H. M. *Trans. Met. Chem.* **2007**, *32*, 791-798.
2. Baraldi, P. G.; Pavani, M. G.; Nunez, M.; Brigidi, P.; Vitali, B.; Gambari, R.; Romagnoli, R. *Bioorg. Med. Chem.* **2002**, *10*, 449-456.
3. Nasr, M. N.; Gineinah, M. M. *Arch. Pharm.* **2002**, *335*, 289-295.
4. Leistner, S.; Wagner, G.; Guetscharo, M.; Glusa, E. *Pharmazie* **1986**, *41*, 54-55.
5. Bousquet, E.; Romero, G.; Guerrero, F.; Caruso, A.; Roxas, M. A. *Farmaco Ed. Sci.* **1985**, *40*, 869-874.
6. Kumar, N.; Singh, G.; Yadav, A. K. *Heteroat. Chem.* **2001**, *12*, 52-56.
7. Mangalagiu, G.; Ungureanu, M.; Grosu, G.; Mangalagiu, I.; Petrovanu, M. *Ann. Pharm. Fr.* **2001**, *59*, 139-140.
8. Chen, T. R.; Chen, J. D.; Keng, T. C.; Wang, J. C. *Tetrahedron Lett.* **2001**, *42*, 7915-7917.
9. Akcelrud, L. *Prog. Polym. Sci.* **2003**, *28*, 875-962.
10. Wang, H.; Song, N.; Li, H.; Li, Y.; Li, X. *Synthetic Met.* **2005**, *151*, 279-284.
11. Carrard, M.; Goncalves-Conto, S.; Si-Ahmed, L.; Ades, D.; Siove, A. *Thin Solid Films* **1999**, *352*, 189-194.
12. Feng, L.; Chen, Z. *Polymer* **2005**, *46*, 3952-3956.
13. Fang, Q.; Tanimoto, A.; Yamamoto, T. *Synthetic Met.* **2005**, *150*, 73-78.

14. Qin, C.; Wang, X.; Wang, E.; Hu, C.; Xu, L. *Inorg. Chim. Acta* **2004**, *357*, 3683-3688.
15. Heller, A.; Wasserman, E. *J. Chem. Phys.* **1965**, *42*, 949-956.
16. Granstrom, M.; Inganas, O. *Appl. Phys. Lett.* **1996**, *68*, 147-149.
17. Chou, H. L.; Hsu, S. Y.; Wei, P. K. *Polymer* **2005**, *46*, 4967-4970.
18. Chen, C. H.; Shi, J.; Tang, C. W. *Macromol. Symp.* **1998**, *125*, 1-48.
19. Abkowitz, M.; Facci, J. S.; Stolka, M. *Chemical Physics* **1993**, *177*, 783-792.
20. Yang, L.; Zhao, X. H.; Zhou, H. P.; Wu, J. Y.; Yang, J. X.; Shao, G. Q.; Tian, Y. P. *Trans. Met. Chem.* **2008**, *33*, 431-437.
21. Soustek, P.; Michl, M.; Almonasy, N.; Machalicky, O.; Dvorak, M.; Lycka, A. *Dyes Pigments* **2008**, *78*, 139-147.
22. Ozer, M.; Kandaz, M.; Ozkaya, A. R.; Bulut, M.; Guney, O. *Dyes Pigments* **2008**, *76*, 125-132.
23. Guilbault, G. G., Ed. *Practical Fluorescence*, Marcel Dekker, New York, 1990.
24. Gilbert, A.; Bagott, J. *Essentials of Molecular Photochemistry*, CRC Press, Boca Raton, Florida, 1991.
25. (a) Osaheni, J. A.; Jenekhe, S. A. *J. Am. Chem. Soc.* **1995**, *117*, 7389-7398. (b) Jenekhe, S. A.; Osaheni, J. A. *Chem. Mater.* **1994**, *6*, 1906-1909.
26. Yıldırım, I.; Koca, I. *Kuwait J. Sci. Eng.* **2005**, *32*, 49-60.
27. Önal, Z.; Yıldırım, İ. *Heterocycl. Commun.* **2007**, *13*, 113-120.
28. Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81-122.
29. Nakamoto, K. *Infrared Spectra and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons, New York, 1997.
30. Sönmez, M.; Şekerci, M. *Synth. React. Inorg. Met.-Org. Chem.* **2003**, *33*, 1689-1700.
31. Ashok, K.; Mishra, J.; Jacob, K. M. *Dyes Pigments* **2007**, *75*, 1-10.
32. Baqi, Y.; Weyler, S.; Iqbal, J.; Zimmermann, H.; Muller, C. E. *Purinergic Signalling* **2009**, *5*, 91-106.
33. Yildiz, E.; Keles, T. *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.* **2009**, *39*, 455-461.
34. Lever, A. B. P. *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 1984.
35. Sönmez, M.; Bayram, R.; Çelebi, M. *J. Coord. Chem.* **2009**, *62*, 2728-2735.
36. Sönmez, M. *Turk. J. Chem.* **2001**, *25*, 181-185.
37. Masoud, M. S.; Amira, M. F.; Ramadan, A. M.; El-Ashry, G. M. *Spectrochim. Acta A* **2008**, *69*, 230-238.
38. Sönmez, M.; Çelebi, M.; Berber, İ. *Eur. J. Med. Chem.* **2010**, *45*, 1935-1940.
39. Varnes, A. W.; Dodson, R. B.; Wehry, E. L. *J. Am. Chem. Soc.* **1972**, *94*, 946-950.
40. Kemlo, J. A.; Sheperd, T. M. *Chem. Phys. Lett.* **1977**, *47*, 158-162.
41. Chattopadhyay, N.; Mallick, A.; Sengupta, S. *J. Photochem. Photobiol. A* **2006**, *177*, 55-60.
42. Purkayastha, P.; Patra, G. K.; Datta, D.; Chattopadhyay, N. *Indian J. Chem. A* **2000**, *39*, 375-379.