



## Schiff bases of 1,5-diarylpent-4-ene-1,3-diones and their metal complexes: Synthesis, characterization and fluorescent studies

MUHAMMED BASHEER UMMATHUR<sup>1\*</sup>, RADHIKA PALLIKKAVIL<sup>2</sup>  
and KRISHNANNAIR KRISHNANKUTTY<sup>2</sup>

<sup>1</sup>Department of Chemistry, KAHM Unity Women's College, Manjeri, Kerala-676122, India  
and <sup>2</sup>Department of Chemistry, University of Calicut, Kerala-673635, India

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**Abstract:** Four Schiff bases ( $H_2L^1$  to  $H_2L^4$ ) were synthesized by the condensation of *o*-aminophenol and unsaturated diketones (1,5-diarylpent-4-ene-1,3-diones). Analytical, IR, <sup>1</sup>H-NMR and mass spectral data revealed their existence in the imine–enamine form. Dibasic tetradentate coordination of the Schiff bases in their ML complexes (M = Cu(II), Ni(II), Co(II), Zn(II), Cd(II), and Hg(II)) was established based on physical, analytical and spectral data. The fluorescent studies of  $H_2L^4$  showed that the fluorescence emission maxima shifted with increasing polarity and hydrogen bonding ability of the solvent. Paramagnetic Cu(II), Ni(II) and Co(II) ions decrease the fluorescence intensity with increasing concentration of the metal ion while diamagnetic Zn(II), Cd(II) and Hg(II) ions have very little influence on the fluorescence intensity of the Schiff base  $H_2L^4$ .

**Keywords:** *o*-aminophenol; imine–enamine form; tetradentate coordination; spectral data.

### INTRODUCTION

In polycarbonyl compounds, Schiff base condensation can occur with more than one carbonyl function that normally results in the formation of polydentate chelating ligand systems having interesting properties.<sup>1,2</sup> Metal complex formation of these Schiff's bases depends on the type and nature of functional groups present in the vicinity of the azomethine group.<sup>3,4</sup> Most of the reported Schiff's bases of 1,3-diketones are based on compounds in which the diketo function is directly attached to alkyl/aryl functions.<sup>5–7</sup> Only very few reports are available on Schiff's bases of unsaturated 1,3-diketones.<sup>8–10</sup> Many naturally occurring and synthetic unsaturated 1,3-diketones and their metal complexes are known to exhi-

\* Corresponding author. E-mail: mbummathur@gmail.com  
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bit anticancer, antitumor, antioxidant, anti-inflammatory, antiviral and immunomodulatory activities.<sup>11–14</sup>

The photochemical properties of various unsaturated 1,3-diketones have been well studied by many research groups and the behaviour of these molecules in the excited states explained.<sup>15</sup> Curcuminoids, a group of unsaturated 1,3-diketones, are generally less stable to UV radiation and hence the yellow colour of turmeric products fades considerably when exposed to light. The formation of cyclic products on exposure to light has been reported.<sup>16</sup> The reaction mechanism and kinetics of the overall photochemical degradation of curcuminoids suggest that they act as photosensitizer of singlet oxygen. The possibility that curcumin itself could act as a photosensitizing agent is an interesting aspect in many drug formulations.<sup>17</sup> Studies have shown that the antibacterial activity of curcumin is generally enhanced by visible radiation.<sup>18</sup> The photophysical properties of curcumin were studied using time resolved fluorescence spectra.<sup>19</sup> Studies on the steady state absorption and fluorescence of curcumin showed that absorption/emission maxima are solvent dependent.<sup>20</sup>

In the present investigation, four Schiff bases derived from unsaturated 1,3-diketones (1,5-diarylpent-4-ene-1,3-diones) and *o*-aminophenol were synthesized and characterized. Typical metal complexes of these polydentate ligand systems were also studied. The effects of different solvents, water and various metal ions on the fluorescence behaviour of a typical Schiff's base ( $H_2L^4$ ) were also investigated.

## EXPERIMENTAL

### *Instruments, materials and methods*

The carbon, hydrogen and nitrogen contents were determined by microanalyses (Heraeus elemental analyzer) and the metal contents of the complexes by AAS (Perkin Elmer 2380). The electronic spectra of the compounds in methanol ( $10^{-6}$  M) were recorded on a JASCO V-550 UV-Vis spectrophotometer, IR spectra (KBr disks) on a JASCO FT/IR 4100 instrument,  $^1H$ -NMR spectra ( $CDCl_3$  or  $DMSO-d_6$ ) on a JEOL 400 NMR spectrometer and mass spectra on a JEOL-JMS 600H FAB mass spectrometer. Fluorescence spectra were recorded using solutions of  $10^{-3}$  to  $10^{-6}$  M concentration on an Elico SL 174 spectrophotofluorometer. Ground state absorption measurements were realised with a Systronics UV-Vis double beam spectrophotometer. Molar conductance of the complexes was determined in DMF ( $\approx 10^{-3}$  mol  $L^{-1}$ ) at  $28 \pm 1$  °C. Magnetic susceptibilities were determined at room temperature on a Sherwood Scientific magnetic susceptibility balance at room temperature ( $28 \pm 1$  °C) using  $Hg[Co(NCS)_4]$  as the standard. The chemicals used were from Merck and Aldrich or of chemically pure grade. The metal salts used for the synthesis of metal chelates were  $Cu(OAc)_2 \cdot H_2O$ ,  $Ni(OAc)_2 \cdot 4H_2O$ ,  $Co(OAc)_2 \cdot 4H_2O$ ,  $Zn(OAc)_2$ ,  $Cd(OAc)_2$  and  $Hg(OAc)_2$ .

### *Synthesis*

*Synthesis of unsaturated 1,3-diketones.* The unsaturated 1,3-diketones were synthesized by the reaction of aromatic aldehydes with benzoyl acetone in presence of boric oxide and tri(*sec*-butyl)borate using *n*-butylamine as the condensing agent as reported earlier.<sup>21–23</sup> The

aldehydes used for the condensation reaction were benzaldehyde, *p*-anisaldehyde, cinnamaldehyde and vanillin.

*Synthesis of Schiff bases (H<sub>2</sub>L).* A methanolic solution of *o*-aminophenol (0.02 mol, 2.18 g) was mixed with a methanolic solution of an unsaturated 1,3-diketone (0.01 mol) and refluxed for  $\approx$ 5 h. The resulting solution was poured into ice-cold water under vigorous stirring. The dark brown coloured precipitate formed was filtered and recrystallized from methanol.

*Synthesis of metal complexes.* Cu(II), Ni(II), Co(II), Zn(II), Cd(II) and Hg(II) complexes were prepared by the following method. To a refluxing ethanolic solution of the ligand (0.01 mol, 30 mL), an ethanolic solution of the metal(II)acetate (0.01 mol, 30 mL) was added. A pinch of sodium acetate was also added to maintain the pH of the solution at around 6. The mixture was refluxed for  $\approx$ 5 h on a boiling water bath. The complex that precipitated on cooling to room temperature was filtered, washed with ethanol, and then with water and dried under vacuum. The complexes were recrystallized from hot benzene.

#### *Absorption and fluorescence spectroscopy*

*Effect of solvents on the maxima.* Solutions (1  $\mu$ M of the Schiff base, H<sub>2</sub>L<sup>4</sup>, in different solvents (methanol, ethanol, acetone and DMSO) were prepared. The absorption and fluorescence spectra were recorded. The fluorescent emission was measured at 400 V.

*Effect of water on fluorescence.* The effect of various concentrations of water on fluorescence was studied by measuring the fluorescence intensity of the compound in different ratio of methanol and water. For this, a different volume of water was added to a methanolic solution of the compound (2  $\mu$ M) and in each case fluorescence intensity was measured at 500 V. The intensity of fluorescence of the compound in pure anhydrous methanol was also determined.

*Effect of metal ions on fluorescence.* Different concentrations of methanolic solutions of metal salts were added to 1 mL of 1  $\mu$ M solution of the Schiff base in methanol. The total volume was then made up to 10 mL and the spectra were recorded. The excitation wavelength was 402 nm.

*Emission maxima of the metal complexes.* Solutions of the metal chelates (1  $\mu$ M) in DMSO were prepared. The absorption and emission spectra were recorded. The fluorescent emission was measured at 550 V.

*Selection of the standard.* A solution (10 ppm) of quinine sulphate in 0.1 M H<sub>2</sub>SO<sub>4</sub> was taken as the standard, the quantum yield of which is 0.54. Standard 10 mm path length fluorescence cuvettes were used for the fluorescence measurements.

The spectral data of the synthesized Schiff bases (H<sub>2</sub>L) and the synthesized metal complexes are given in the Supplementary material to this paper.

## RESULTS AND DISCUSSION

### *Characterization of Schiff bases and their metal complexes*

The elemental analytical data of the Schiff bases indicated that the reaction between unsaturated 1,3-diketone and *o*-aminophenol occurred in 1:2 ratio. All the compounds (H<sub>2</sub>L) were crystalline in nature and soluble in common organic solvents. Attempts to prepare a single crystal of the ligands failed. The Schiff bases formed stable complexes with Cu(II), Ni(II), Co(II), Zn(II), Cd(II) and Hg(II) ions. The analytical data together with their non-electrolytic nature in DMF (specific conductance < 10  $\Omega^{-1}$  cm<sup>-1</sup>; 10<sup>-3</sup> M solution) suggested ML

stoichiometry. The Zn(II), Cd(II), and Hg(II) chelates were diamagnetic while the Cu(II), Ni(II), and Co(II) complexes showed normal paramagnetic moment. The observed UV, IR,  $^1\text{H-NMR}$  and mass spectral data were in conformity with the proposed structural formulas of the Schiff bases and their metal complexes given in Fig. 1.

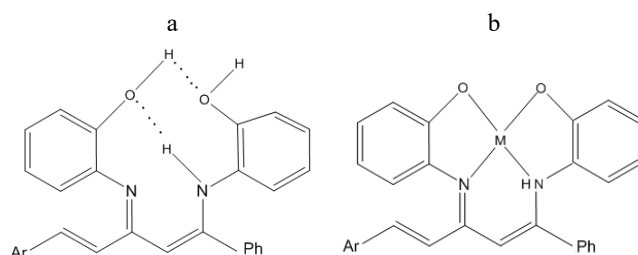


Fig. 1. The proposed structural formulas of: a) the Schiff bases,  $\text{H}_2\text{L}$  and b) their metal complexes,  $\text{ML}$ ; Ar = phenyl ( $\text{H}_2\text{L}^1$  and  $\text{ML}^1$ ); 4-methoxyphenyl ( $\text{H}_2\text{L}^2$  and  $\text{ML}^2$ ); styryl ( $\text{H}_2\text{L}^3$  and  $\text{ML}^3$ ); 4-hydroxy-3-methoxyphenyl ( $\text{H}_2\text{L}^4$  and  $\text{ML}^4$ ); M = Cu(II), Ni(II), Co(II), Zn(II), Cd(II) and Hg(II); Co(II) and Ni(II) complexes also contain two coordinated  $\text{H}_2\text{O}$  molecules.

*Infrared spectra.* The two important functional groups present in the unsaturated 1,3-diketones considered in this investigation are the benzoyl and cinnamoyl carbonyls. The stretching frequency of the former appears<sup>21-24</sup> at  $\approx 1650\text{ cm}^{-1}$  and the later at  $\approx 1630\text{ cm}^{-1}$ . The IR spectra of the Schiff bases are characterized by the absence of both bands in these regions. Thus, it could be concluded that the compounds do not contain free benzoyl or cinnamoyl functions and both the carbonyl groups were involved in the condensation of the Schiff's bases.

The IR spectra of all the Schiff bases exhibited two strong bands at  $\approx 1610$  and  $\approx 1580\text{ cm}^{-1}$  due to the stretching of the highly conjugated  $\nu_{\text{C}=\text{N}}$  and  $\nu_{\text{C}=\text{C}}$  functions,<sup>9,24</sup> respectively, seen in Fig. 1. The IR spectra of the compounds showed prominent bands at  $\approx 1540$  and  $\approx 1280\text{ cm}^{-1}$  due to NH deformation vibrations and  $\nu_{\text{C}-\text{N}}$ . These, together with the  $\nu_{\text{C}=\text{N}}$  band, suggested the existence of the compounds in the imine-enamine form rather than in the di-imine or di-enamine form. The broad band observed in the range  $3000\text{--}3500\text{ cm}^{-1}$  in the spectra are due to the intramolecularly hydrogen bonded phenolic and NH groups,<sup>24</sup> seen in Fig. 1.

The most important feature of the IR spectra of all the metal complexes was the disappearance of the free ligand band at  $\approx 1610\text{ cm}^{-1}$  due to  $\nu_{\text{C}=\text{N}}$ . Instead, a prominent band appeared at  $\approx 1550\text{ cm}^{-1}$  assignable to the stretching of the metal bonded C=N function,<sup>9,25</sup> seen in Fig. 1. The prominent band observed in the ligands at  $\approx 1540\text{ cm}^{-1}$  due to NH deformation vibrations remained almost unaffected and the band at  $\approx 1280\text{ cm}^{-1}$  due to  $\nu_{\text{C}-\text{N}}$  shifted to lower wave numbers in

the spectra. These indicate that the NH proton was not replaced by a metal ion during coordination involving nitrogen.<sup>25</sup> The broad band in the region 3000–3500  $\text{cm}^{-1}$  of the ligands was absent in the spectra of all the metal complexes, indicating deprotonation of phenolic oxygen atoms prior to complexation.<sup>25</sup> The spectra of the Ni(II) and Co(II) complexes showed bands due to coordinated water at  $\approx 3450 \text{ cm}^{-1}$ . That the two phenolic oxygens along with the imino and amino nitrogens were involved in complexation is further supported by the appearance of additional medium intensity bands in the range 520–580  $\text{cm}^{-1}$  and 420–480  $\text{cm}^{-1}$  due to the stretching of  $\nu_{\text{M-N}}$  and  $\nu_{\text{M-O}}$ , respectively.<sup>25</sup>

*<sup>1</sup>H-NMR spectra.* The <sup>1</sup>H-NMR spectra of all the Schiff bases displayed three low field one proton signals at  $\delta \approx 8.6$ , 9.5 and 10.7 ppm due to amino and intramolecularly hydrogen bonded phenolic protons.<sup>26</sup> Since the two phenolic protons are in different electronic environments, the signal at  $\delta \approx 10.7$  ppm can be assigned to phenolic proton associated with the olefinic group. The methine proton signal was located at  $\delta \approx 5.8$  ppm. The trans orientation of the –CH=CH– group is evident<sup>13</sup> from their observed *J* values ( $\approx 16$  Hz). The integrated intensities of all the protons agree well with the formulation of the compounds as in Fig. 1.

In the <sup>1</sup>H-NMR spectra of the diamagnetic Zn(II) complexes, the phenolic proton signals of the ligands disappeared, indicating the replacement of these protons with a metal ion during complexation.<sup>23</sup> The N–H proton signal of the ligands remain unaltered, which indicated that this proton was not replaced during coordination. The methine proton signal shifted appreciably to a lower field compared to the shift in the olefinic and aromatic protons. This may be due to the aromatic character imparted to the C<sub>3</sub>N<sub>2</sub>M ring system of the chelates by the attachment of highly conjugated groups. That the aryl substituents of H<sub>2</sub>L<sup>2</sup> and H<sub>2</sub>L<sup>4</sup> were not involved in bonding with the metal ion was clearly indicated in the spectra of the complexes in which the signals remain unaltered.<sup>23</sup> Aryl protons appeared in the  $\delta$  range 6.8–7.5 ppm as a complex multiplet. The integrated intensities of the various signals agree well with the proposed ML stoichiometry of the complexes as shown in Fig. 1.

*Mass spectra.* The mass spectra of all the Schiff bases displayed intense parent ion peak, P<sup>+</sup>/(P+1)<sup>+</sup>, thereby confirming the formulation of the compounds.<sup>27</sup> Other prominent peaks were due to the elimination of aryl substituents, Ar–CH=CH, Ph, Ar, etc. from the parent ion. The FAB mass spectra of the Cu(II) complexes showed a molecular ion peaks, P<sup>+</sup>/(P+1)<sup>+</sup>, corresponding to CuL stoichiometry. Peaks correspond to L<sup>+</sup> and fragments of L<sup>+</sup> were also present in the spectra. The spectra of all the chelates contained a number of fragments containing copper in the 3:1 natural abundance of <sup>63</sup>Cu and <sup>65</sup>Cu isotopes.<sup>9,12</sup>

*Electronic spectra.* The UV spectra of the Schiff bases showed two broad bands with maxima at  $\approx 360$  and 260 nm due to various n→ $\pi^*$  and  $\pi$ → $\pi^*$  transitions. The absorption maxima of the metal chelates bear close resemblance with

the free ligands, which indicates that no structural alteration of the ligand occurred during complexation. However, the values shifted to longer wavelength. The shift was more prominent for the band at  $\approx 360$  nm of the free ligand due to the  $n \rightarrow \pi^*$  transition of the azomethine function;<sup>28</sup> This clearly indicated the involvement of the group in metal coordination as shown in Fig. 1.

The Cu(II) complexes showed a broad visible band with  $\lambda_{\max}$  at  $\approx 14,800$   $\text{cm}^{-1}$ . This, together with the measured  $\mu_{\text{eff}}$  values ( $\approx 1.75$  BM), suggests their square-planar geometry.<sup>4</sup> The spectra of the paramagnetic Ni(II) chelates ( $\mu_{\text{eff}} \approx 2.80$  BM) showed three bands at  $\lambda_{\max} \approx 8,500$ ,  $\approx 14,000$  and  $\approx 24,500$   $\text{cm}^{-1}$ , corresponding to the transitions  ${}^3A_{2g} \rightarrow {}^3T_{2g}(\text{F})$ ;  ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{F})$  and  ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{P})$ , respectively, confirming their octahedral geometry along with two coordinated water molecules.<sup>29</sup> The spectra of the Co(II) chelates showed three bands at  $\lambda_{\max} \approx 9,500$ ,  $\approx 12,000$  and  $\approx 20,000$   $\text{cm}^{-1}$ , corresponding to the transitions  ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}$ ;  ${}^4T_{1g}(\text{F}) \rightarrow {}^4A_{2g}$ ;  ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$ , respectively. The transition to  ${}^4A_{2g}$  is very weak and appears as a shoulder. This, together with the measured  $\mu_{\text{eff}}$  values ( $\approx 4.80$  BM), suggest their octahedral geometry with two coordinated water molecules.<sup>30</sup> In most of the cases, interpretation was difficult as the d-d bands were masked by intense charge transfer transitions.

#### *Studies on the fluorescence characteristics of the Schiff base ( $\text{H}_2\text{L}^4$ )*

*Effect of solvents.* The unsaturated 1,3-diketones are insoluble in water but soluble in many organic solvents and are readily soluble in polar organic solvents.<sup>12,14</sup> The absorption and emission spectra are highly dependent on the nature of the solvent. Absorption maxima of  $\text{H}_2\text{L}^4$  showed a red shift with increasing solvent polarity (Table I). The absorption band was very broad and consisted of a shoulder. All these features indicated the presence of more than one species of the compound in solution.

TABLE I. Absorption and emission maxima of  $\text{H}_2\text{L}^4$  in different organic solvents

Solvent	$\lambda_{\text{ab}} / \text{nm}$	$\lambda_{\text{fl}} / \text{nm}$
Acetone	392	773
Ethanol	400	792
Methanol	402	795
DMSO	498	822

The fluorescence maxima also showed solvent dependence. A large red shift from 773 nm in acetone to 822 nm in DMSO, the most polar among the solvents used. As the polarity of the solvent increased, the broadening of the spectral band also increased. This suggests that the excited singlet state has a large intramolecular charge transfer character.<sup>31</sup> This is possible in these types of molecules in which a reasonable amount of energy from the aromatic ring can be transferred to the enamine tautomer of the Schiff base. Similarly, hydrogen bonding with the solvent may also be involved in this process. Thus, it appears that polarity and

hydrogen bonding ability of the solvents have significant influence on the absorption and emission spectra of the compound.

*Effect of water.* Earlier reports showed that water quenches the fluorescence intensity of curcuminoids.<sup>32</sup> The results obtained for H<sub>2</sub>L<sup>4</sup> also agreed with this observation. The effect of water on the fluorescence intensity of the compound is given in Table II. The fluorescence intensity decreased with increasing water content.

TABLE II. Effect of various concentrations of water on the fluorescence of H<sub>2</sub>L<sup>4</sup> in methanol

$c_{\text{H}_2\text{O}} / \%$	Emission maxima, nm	Fluorescence intensity	$\eta^0/\eta$	$I_{\text{fl}}^0/I_{\text{fl}}$	$(\eta^0/\eta) \times (I_{\text{fl}}^0/I_{\text{fl}})$
0	796	369	1.00	1.00	1.00
3	796	326	0.99	1.1366	1.1252
5	796	286	0.96	1.2991	1.2871
7	795	273	0.95	1.3696	1.3011
10	797	241	0.92	1.5435	1.4200
20	796	215	0.85	1.7317	1.4719
30	795	207	0.79	1.7842	1.799
40	797	173	0.66	2.1462	1.986

It was reported that the fluorescence quenching could be attributed to the interaction of the lone pair electrons of H<sub>2</sub>O with the excited state of the compound, resulting in the formation of a non-fluorescent associated species.<sup>33</sup> The effect of water could be studied with the help of a modified Stern–Volmer equation:<sup>34</sup>

$$I_{\text{fl}}^0/I_{\text{fl}} = (1 + K_q \tau c_{\text{H}_2\text{O}})/(\eta^0/\eta)$$

where  $K_q$  is the rate constant for quenching,  $\tau$  is the life time of the excited singlet state, and  $I_{\text{fl}}^0$  is the fluorescence intensity in the absence of water,  $\eta^0$  and  $\eta$  are the viscosity of pure methanol and methanol–water mixture, respectively.

From the modified Stern–Volmer plot of  $(I_{\text{fl}}^0/I_{\text{fl}}) \times (\eta^0/\eta)$  vs.  $c_{\text{H}_2\text{O}}$  on the fluorescence quenching, it is clear that fluorescence quenching by water is dependent on the viscosity of the solvent. The slope of the plot is  $1.29 \times 10^{-2} \text{ M}^{-1}$ . However, the reported value for curcumin<sup>34</sup> is  $1.38 \times 10^{-2} \text{ M}^{-1}$ , which indicates that the effect of water quenching on the fluorescence of H<sub>2</sub>L<sup>4</sup> is slightly less than that of curcumin.

*Effect of metal ions.* Metal ions generally influence the fluorescent intensity and fluorescent maxima of organic molecules. In the present study, the effect of Cu(II), Ni(II), Co(II), Zn(II), Cd(II) and Hg(II) ions on the fluorescent intensity and fluorescent maxima of H<sub>2</sub>L<sup>4</sup> were measured. The results are summarized in Tables III and IV. The observed data revealed that in all the cases, the fluorescent maxima showed only marginal shift ( $\pm 5$  nm) with increasing concentration of metal ions, whereas the fluorescent intensity was highly dependent on the metal ion concentration. Thus the presence of Cu(II), Ni(II) and Co(II) ions decreased



the fluorescent intensity of the Schiff base. In the case of Zn(II), Cd(II) and Hg(II) ions, the decrease in the intensity was very small.

TABLE III. Effect of Cu(II), Ni(II) and Co(II) ions on the fluorescence intensity of H<sub>2</sub>L<sup>4</sup>; concentration of H<sub>2</sub>L<sup>4</sup> was 1 μM

Concentration of metal(II) solution, μM	Cu(II)		Ni(II)		Co(II)	
	λ <sub>fl max</sub> nm	Fluorescence intensity	λ <sub>fl max</sub> nm	Fluorescence intensity	λ <sub>fl max</sub> nm	Fluorescence intensity
0	792	322	800	174	796	491
1	792	298	802	139	796	457
2	791	270	805	135	795	415
3	796	195	803	128	796	364
4	792	141	804	120	797	352
5	797	120	801	93	796	308
6	796	100	802	86	795	276
7	796	88	801	76	795	247
8	799	66	801	55	794	221

From the measurements, it is clear that whether or not the metal ion form a complex with the organic molecule in its ground state, they have significant influence on the fluorescence.

Table IV. Effect of Zn(II), Cd(II) and Hg(II) ions on the fluorescence intensity of H<sub>2</sub>L<sup>4</sup>; concentration of H<sub>2</sub>L<sup>4</sup> was 1 μM

Concentration of metal(II) solution, μM	Zn(II)		Cd(II)		Hg(II)	
	λ <sub>fl max</sub> nm	Fluorescence intensity	λ <sub>fl max</sub> nm	Fluorescence intensity	λ <sub>fl max</sub> nm	Fluorescence intensity
0	795	372	799	258	798	243
1	795	369	798	243	797	242
2	795	366	797	239	797	240
3	794	364	797	238	797	229
4	796	368	797	238	796	228
5	795	361	797	237	798	222
6	795	368	799	232	798	222
7	794	363	797	233	797	209
8	795	362	797	230	797	205

Generally, paramagnetic metal ions influence the intensity of fluorescence because paramagnetic spectrum enhances the rate of intersystem crossing in organic molecules.<sup>35</sup> This may be due to the influence of the unpaired electron on the excited state of the ligand.

In the presence of metal ions, the changes in the fluorescent intensity of an organic metal chelating ligand molecule may be due to several factors. The metal ion form complexes with the ligand. Then the complex may be fluorescent or non-fluorescent. If the complex is fluorescent, it may emit at different wave-



lengths. When the complex is non-fluorescent, the emission profile depends only on the ligand concentration. Another factor that may affect the fluorescence intensity is the magnetic properties of the metal ion. Most of the paramagnetic metal ions are effective quenchers of fluorescence and cause a reduction in the fluorescence intensity. An excited state charge transfer process occurs between the fluorescent molecule and the metal ion. Spin-orbit coupling between the unpaired electron on the metal ion and the excited state of the molecule also increases the rate of intersystem crossing.<sup>35</sup> Hence, the decrease in the fluorescence intensity in the presence of Cu(II), Ni(II), and Co(II) ion was due to the formation of non-fluorescent complexes. The emission profile was due to the free ligand molecules that were not involved in the chelation process.<sup>35</sup>

#### CONCLUSIONS

Four new Schiff bases ( $H_2L^1$  to  $H_2L^4$ ) were synthesized by condensing both the carbonyl groups of four unsaturated 1,3-diketones (1,5-diarylpent-4-ene-1,3-diones) with the amino group of *o*-aminophenol. The existence of these Schiff bases in the intramolecularly hydrogen bonded imine-enamine form has been well demonstrated from their physical, analytical and various spectral data. Spectral and analytical data of the metal complexes are in agreement with the dibasic tetradentate coordination of the Schiff bases with ML stoichiometry ( $M = Cu(II), Ni(II), Co(II), Zn(II), Cd(II),$  and  $Hg(II)$ ) in which both the phenolic protons of the ligand are replaced by the divalent metal cations. The fluorescent studies of the typical Schiff base  $H_2L^4$  showed that fluorescence emission maxima shift with increasing polarity and hydrogen bonding ability of the solvent. As the concentration of metal ion increases, a decrease in fluorescence intensity was observed for paramagnetic Cu(II), Ni(II) and Co(II) ions. The results revealed that the intensity of fluorescence of the Schiff base  $H_2L^4$  is not significantly affected by diamagnetic Zn(II), Cd(II) and Hg(II) ions.

#### SUPPLEMENTARY MATERIAL

Spectral data of the synthesized Schiff bases ( $H_2L$ ) are available electronically at the pages of journal website: <https://www.shd-pub.org.rs/index.php/JSCS/index>, or from the corresponding author on request.

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## ИЗВОД

1,5-ДИАРИЛПЕНТ-4-ЕН-1,3-ДИОН ШИФОВЕ БАЗЕ И ЊИХОВИ КОМПЛЕКСИ  
МЕТАЛА: СИНТЕЗА, КАРАКТЕРИЗАЦИЈА И ФЛУОРЕСЦЕНТНА ИСПИТИВАЊА

MUHAMMED BASHEER UMMATHUR<sup>1</sup>, RADHIKA PALLIKKAVIL<sup>2</sup> и KRISHNANNAIR KRISHNANKUTTY<sup>2</sup>

<sup>1</sup>Department of Chemistry, KAHM Unity Women's College, Manjeri, Kerala-676122, India и

<sup>2</sup>Department of Chemistry, University of Calicut, Kerala-673635, India

Кондензационом реакцијом између *o*-аминофенола и незасићених дикетона (1,5-диарилпент-4-ен-1,3-дион) синтетисана су четири лиганда типа Шифових база ( $H_2L^1$ – $H_2L^4$ ). На основу IR и <sup>1</sup>H-NMR спектроскопских и масених спектрометријских мерења потврђено је да све синтетисане Шифове базе садрже имин–енаминску структурну јединицу. Тетраденатна координација ових Шифових база (L) у одговарајућим ML комплексима (M = Cu(II), Ni(II), Co(II), Zn(II), Cd(II) и Hg(II)) потврђена је на основу физикохемијских, аналитичких и спектроскопских испитивања. Флуоресцентна испитивања  $H_2L^4$  Шифове базе су показала да се емисиони максимум помера са повећањем поларности растварача и његове способности за формирање водоничних веза. Парамагнетични Cu(II), Ni(II) и Co(II) јони смањују флуоресцентни интензитет са повећањем концентрације ових јона метала, док дијамагнетични Zn(II), Cd(II) и Hg(II) јони имају врло мали утицај на интензитет флуоресценције  $H_2L^4$  Шифове базе.

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