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A novel azo-azomethine based fluorescent dye and its Co(II) and Cu(II) metal chelates

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ABSTRACT

Cobalt(II) and copper(II) complexes of a novel Schiff base ligand containing two –N==N– chromophore groups, derived from the condensation of 2-hydroxy-5-[(*E*)-phenyldiazenyl]benzaldehyde with *p*-aminoazobenzene were synthesized and characterized by analytical and spectroscopic methods. The X-ray powder diffraction analysis was used to determine the unit cell parameters of the synthesized ligand and its metal complexes. Self-isomerization via intramolecular proton transfer was investigated by UV–Vis and theoretical calculations. The effect of solvent polarity on UV–Vis was examined. The electronic structures of compounds were also predicted with computational chemistry methods. Theoretical vibrational and electronic spectra of the metal complexes were obtained from these structures. Binding energies of the metal complexes were obtained by quantum chemical calculations. Upon irradiation the ligands and their metal complexes were blue light. The (1*a*) azo-aldehyde and (2*a*) azo-azomethine ligands revealed quantum yields of 35 and 41% and their excited-state lifetimes were 3.26 and 3.86 ns, respectively. Decreases in photoluminescence intensity and quantum yield upon complexation with metal lons were noted. The thermal behavior to include activation energy (*E*), entropy (ΔS^*), enthalpy (ΔH^*) and Gibbs free energy change (ΔG^*), using Coats–Redfern (CR) and Horowitz–Metzger (HM) methods, were examined.

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1. Introduction

Schiff bases derived from aromatic amines and aromatic aldehydes and their metal complexes have a wide variety of applications in the fields of biology [1], catalysis [2], materials [3] and inorganic [2] and analytical chemistry [4]. These compounds have been found to possess a wide range of biological activities such as antibacterial [5], antifungal [6], antimalarial [7], anticancer [8], antitubercular [9], anti-inflammatory [10], and antiviral [11].

Azo dyes are key chromophores in the chemical industry as dyes and pigments [12], food additives [13], indicators [14], radical reaction initiators [15] and therapeutic agents [16]. The azo azomethine compounds are commonly prepared by the condensation between primary amine or hydrazine and aromatic aldehyde or ketone-linked – N=N– chromophore group. Recent years have a great deal of interest in the preparation and characterization of azo azomethines and their metal complexes [17–22].

Research and development for new organic materials as light emitting devices continue [23–25]. Organic polymers having strong luminescence

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http://dx.doi.org/10.1016/j.molliq.2014.10.012 0167-7322/© 2014 Elsevier B.V. All rights reserved. and using insignificant voltages, for flat panel displays prove to be important [26,27]. Aromatic amines and polymeric arylamines have been used as hole transport layers for electroluminescent technology [28,29]. A fluorescent dioxime-type ligand and its complexes have been reported in the literature [30]; fluorescence emission intensity of the ligand decreased with metal ion complex formation, where decreases in emission intensities were reported to be a result of the coordination complex of *N*-atom of the ligand with the metal ions. Further, fluorescent studies using metal complexes have been explored, for example, metal complexes in excited states have been studied as components of luminescent sensors and switches [31,32]. Developments in photochemistry and photophysics using Ru(II)-polypyridine complexes have been reported by Balzani and Juris, where these complexes helped to explain important electronic phenomena and interactions [33]. Balzani et al. have also given a detailed discussion of photoactive dendrimers containing metal complexes [34]. A multitude of research have been carried out on fluorescent sensors and metal ions, for example, the transduction mechanisms for metal ion detection by fluorescence were outlined by Formic et al. [35]. Small molecule fluorescent sensors for the detection of several molecular components of oxidative stress have also been reviewed by Hyman [36], where design, function and application of probes to detect metal cations, reactive oxygen species, and intracellular thiol-containing compounds were addressed. Also the development of luminescent transition metal

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complexes as chemosensors for cations and anions is presented in the literature [37].

As part of our continuing interest in azo-azomethine chemistry, we synthesized numbers of such compounds [38–40]. We now report on the successful synthesis of a novel azomethine ligand containing – N=N– moiety and its Co(II) and Cu(II) metal chelates and their photoluminescence properties were investigated. The structures of the prepared compounds were confirmed by spectroscopic techniques to include UV–Vis, FT-IR, ¹H and ¹³C NMR data and elemental analysis. The theoretical study of the synthesized compound and its metal complexes was carried out by using different programs and methods. The crystallinity of the prepared compound and its metal complexes was studied by X-ray powder diffraction. The thermal stability of the prepared ligands and its metal complexes was also investigated using a thermogravimetric analysis (TGA), along with the kinetics and thermodynamic data evaluation.

2. Experimental

2.1. Reagents

Salicylaldehyde was purchased from Merck and used as received. Dimethylformamide (DMF), chloroform (CHCl₃), dichloromethane (CH₂Cl₂), carbon tetrachloride (CCl₄), hexane, toluene, methanol, ethanol, 9,10-diphenylanthracene, acetone and diethyl ether were purchased from Aldrich Chem. Co. and Merck and used as received. Reagents used were purchased from Aldrich, Fluka and Merck and used without further purification. The azo-aldehyde compound, 2-hydroxy-5-[(*E*)-phenyldiazenyl]benzaldehyde (**1***a*) was prepared according to the published paper [38].

2.2. Techniques

The melting points of the azo-azomethine compounds were determined with an Electrothermal LDT 9200 apparatus. Infrared spectra were recorded on a PerkinElmer FT-IR spectrophotometer using KBr discs. ¹H and ¹³C NMR spectra were collected using Bruker AC spectrometer 600 MHz, with samples dissolved in CDCl₃, and chemical shifts expressed in δ with TMS as an internal standard. Elemental analysis for C, H and N was performed on a PerkinElmer 240 elemental analyzer in Inonu University, Malatya, Turkey. The synthesized azo-azomethine ligand and its Co(II) and Cu(II) complexes were examined in spectrophotometric grade different solvents. The UV-Vis spectra were recorded from 190 to 1100 nm using a PG Instruments Ltd T80 + UV/VIS scanning spectrophotometer on 2.0×10^{-5} mol/L sample concentrations, prepared in spectrophotometric grade different solvents, and contained in 1 cm optical path quartz cuvette. The X-ray powder diffraction patterns were recorded on a vertical type Rigaku D-max/B diffractometer with CuK α radiation generated at 30 kV and 30 mA. Samples were measured from 20° to 50° (2 θ) with a step size of 0.02 1 and a count time of 1 s per step. Ligand and complex fluorescence spectra were obtained using a PerkinElmer LS55 spectrometer. Samples were prepared in spectrophotometric grade DMF, where solution concentrations were 1.0×10^{-5} mol/L and excitation was achieved at 338 nm. The standard 9,10-diphenylanthracene was used for quantum efficiency calculations [41,42]. Thermogravimetric analysis (TG and DTG) and differential thermal analysis (DTA) experiments were performed using a SII Exstar TG/DTA 6200 in the temperature range of 25–1000 °C with a heating rate of 20 °C min⁻¹ under flowing dry air atmosphere (30 mL/min).

2.3. Preparation of 4-[(E)-phenyldiazenyl]-2-[(E)-({4-[(E)-phenyldiazenyl] phenyl}imino) methyl]phenol (**2a**)

A hot solution (60 °C) of *p*-aminoazobenzene (0.197 g, 1 mmol) in 10 mL of MeOH + 10 mL of CHCl₃ mixture was mixed with a hot

solution (60 °C) of 2-hydroxy-5-[(*E*)-phenyldiazenyl]benzaldehyde (**1a**) (0.226 g, 1 mmol) in the same solvent. The reaction mixture was then refluxed for 2 h. A solid product was obtained and separated by filtration, then purified by crystallization from EtOH, washed with Et₂O, and then dried. Yield, 0.259 g (64%). m.p.: 188–189 °C. \wedge_m : 2.70 Ω^{-1} cm² mol⁻¹. Elemental analyses for C₂₅H₁₉N₅O (405.45 g/mol): Found: C, 74.15; H, 5.096; N, 17.06%. Calcd.: C, 74.06; H, 4.72; N, 17.27%. IR (KBr, cm⁻¹): 3450 v(O–H), 3049 v(aromatic C–H), 1616 v(C=N), 1480 v(N=N). ¹H NMR (ppm, in CDCl₃): 13.672 (s, 1H, OH), 8.846 (s, 1H, CH=N), 8.121 (s, 1H, Ar–H), 7.204–7.189 (m, 1H, Ar–H). ¹³C NMR (ppm, in CDCl₃): 164.045, 162.78, 152.67, 152.59, 151.51, 149.92, 145.70, 131.19, 130.68, 129.16, 129.13, 128.15, 127.92, 124.32, 122.94, 122.66, 122.04, 118.86, 118.28.

2.4. Preparation of copper(II) complex (2b)

Cu(CH₃COO)₂·H₂O (0.10 g, 0.5 mmol) in 10 mL of hot MeOH–CHCl₃ (1:1) was added to 20 mL of the azo-azomethine ligand (**2a**) (0.405 g, 1.0 mmol) in CHCl₃. The mixture was refluxed for 3 h on water bath. The volume of the solution was reduced to one-third of its original volume and left overnight. The dark green precipitate was filtered off, washed with cold MeOH and Et₂O and dried. Yield, 0.62 g (79%). m.p.: 275 °C. \wedge_m : 3.10 Ω^{-1} cm² mol⁻¹. μ_{eff} = 1.78 B.M. Elemental analyses for C₅₀H₃₆CuN₁₀O₂ (872.43 g/mol): Found: C, 68.21; H, 4.42; N, 15.58%. Calcd.: C, 68.83; H, 4.16; N, 16.05%. IR (KBr, cm⁻¹): 3049 υ (aromatic C–H), 1611 υ (C=N), 1472 υ (–N=N–), ~556 υ (M–O), 513 υ (M–N).

2.5. Preparation of cobalt(II) complex (2c)

To a solution of (0.202 g, 0.5 mmol) 4-[(*E*)-phenyldiazenyl]-2-[(*E*)-({4-[(*E*)-phenyldiazenyl]phenyl}imino)methyl]phenol (*2a*) in 20 mL CHCl₃, 10 mL of CoCl₂·6H₂O (0.0059 g, 0.25 mol) was added. The solution was refluxed at 40–50 °C with stirring for 2 h, and the resulting mixture was kept in the refrigerator for one day. The reddish brown complex was filtered and washed with cold MeOH and dried under vacuum. Yield, 0.309 g (70%). m.p.: 254 °C. \wedge_m : 51 Ω^{-1} cm² mol⁻¹. μ_{eff} = 3.33 B.M. Elemental analyses for C₅₁H₄₆ClCoN₁₀O₆ (989.36 g/mol): Found: C, 61.86; H, 4.960; N, 14.08%. Calcd.: C, 61.91; H, 4.696; N, 14.16%. IR (Kr, cm⁻¹): 3320 v(O–H-hydrated and methanol), 3058 v(aromatic C–H), 2930 (Me–H), 1612 v(C=N), 1480 v(–N=N–), 826 (coordinated water), 549 v(M–O), 510 v(M–N).

2.6. Computational method

All calculations were made by Gaussian 09 package programs [43–45]. Hartree–Fock (HF) and density functional theory (DFT/B3LYP) methods with 3-21G and LANL2DZ basis sets were used for obtaining the optimized structure of tautomers and copper(II) and cobalt(II) complexes. The calculated vibrational frequencies were scaled by 0.9, 0.9393, 0.964 [46] and 0.9978 [47] for HF/3-21G, HF/LANL2DZ, B3LYP/3-21G and B3LYP/LANL2DZ, respectively. The best level was found as HF/3-21G level from the correlation of experimental and calculated vibrational frequencies. Tautomer interacting with metal cation was determined by calculating the orbital character of HOMO and HOMO-1. Time dependent-HF (TD-HF) method was used for UV–Vis spectra calculations. The UV–Vis spectra were calculated in vacuum, water and chloroform. Solute–solvent interactions were taken into account by the conductor-like polarizable continuum model (CPCM) [48].

3. Results and discussion

3.1. Synthesis and solubility

The synthesized ligand and its metal complexes were characterized by IR, UV–Vis, NMR spectra, magnetic susceptibility measurements and

molar conductance. The analytical data of the ligand, Co(II) and Cu(II) metal chelation along with their physical properties are given in the Experimental section. It was noted that the metal(II) complexes are air stable in the solid state and completely soluble in CHCl₃, DMF, and DMSO and partially soluble in MEOH and EtOH. Elemental analysis data are given in the Experimental section and are in well agreement with theoretical values. The synthesized complexes showed 1:2 metal-ligand stoichiometry. The ligand acts as a bidentate ligand, with the metals coordinating via phenolic oxygen and azomethine nitrogen donor atoms. Single crystals of the new azo-azomethine ligand and its transition metal chelates could not be isolated from organic solvents, and so no definite structures are available. However, structures of the ligand and Co(II) and Cu(II) compounds were proposed by the analytical and spectroscopic data as shown in Scheme 1, and Fig. 1, respectively.

The molar conductance of 10^{-3} M solutions of the ligand and its metal complexes in dimethylsulfoxide (DMSO) solvent were measured on a Mettler Toledo Seven Multi conductivity meter. The reported values are averages of triplicate measurements. All the measurements were taken at room temperature for freshly prepared solutions. The molar conductance values of Cu(II) and Co(II) complexes were found to be 3.10 and 51 Ω^{-1} cm² mol⁻¹, respectively. The low molar conductivity value of Cu(II) complex indicates that it is non-electrolyte in DMSO, however Co(II) complex behaves as 1:1 electrolyte. The molar conductance value suggests that in the Co(II) complex the phenolic group of one of the ligand remained protonated and the complex contains a chloride counter ion. Suggested formulation of the Co(II) complex is in good agreement with spectral and analytical data.

Magnetic susceptibility measurements were carried out on a Sherwood Scientific magnetic balance according to the Gouy method and Hg[Co(SCN)₄] was used as a calibrant. The effective magnetic moments were calculated using the relation $\mu_{eff} = 2.828 \sqrt{\chi_m T}$, where *T* is the absolute temperature and χ_m is the molar susceptibility corrected using Pascal's constants for diamagnetism of all atoms in the compounds. The magnetic measurement studies suggest that the Cu(II) and Co(II) complexes exhibit paramagnetic behaviors with μ_{eff} values of 1.78 and 3.33, respectively. The magnetic moment of the Cu(II) complex (1.78 μ_B) indicates the presence of one unpaired electron. The Co(II) complex shows a value of 3.33 μ_B indicating octahedral geometry.

3.2. ¹H and ¹³C NMR spectra

The ¹H and ¹³C NMR spectra of azo-azomethine ligand (**2***a*) were recorded in CDCl₃. The ¹H NMR spectrum of the ligand presents the signal at 13.67 ppm, assigned to the phenolic OH proton. The data of the ligand (**2***a*) showed a sharp singlet at 8.85 ppm assigned to the azomethine group proton (CH=N) [18]. Furthermore, the signals in the range of δ 8.06–7.28 ppm were attributed to the aromatic protons [40] (Fig. S1).

In ¹³C NMR spectrum of the ligand, the signals at δ 164 and 162 ppm were assigned to the carbon shifts of C=N and C-OH groups, respectively [22] (Fig. S2). All the other aromatic carbon shifts were observed in the range of δ 118–152 ppm. Both ¹H and ¹³C NMR spectra of the ligand showed that there was no significant organic impurity in the sample.

3.3. IR spectra

The infrared spectral data of the bidentate ligand and its metal complexes are presented in the Experimental section. The spectra of the Co(II) and Cu(II) complexes of the azo-azomethine ligand are shown in Fig. S3. The azo-azomethine ligand (2a) exhibits a medium intense band at 3450 cm⁻¹ due to the intramolecular hydrogen bonded (O-H), where its absence in the spectra of the Co(II) and Cu(II) complexes indicates deprotonation of the phenolic group and coordination of the oxygen atom to the metal ion. Infrared spectrum of the ligand shows v(C=N) peak at 1616 cm⁻¹ and absence of C=O peak at around 1656 cm^{-1} in the azo aldehyde indicates Schiff base formation [20]. A downward shift ($v = 4-5 \text{ cm}^{-1}$) in v(C=N) (azomethine) is observed with coordination, indicating that the azomethine group nitrogen is involved in coordination. It is expected that coordination of nitrogen to the metal atom would reduce the electron density in the azomethine absorption [39]. In the FT-IR spectra, the ligand and its complexes exhibit bands at 3049–3058 cm⁻¹ that are assignable to vibrations of aromatic C-H stretching. The synthesized compounds show a band in the region 1480 cm⁻¹ to 1472 cm⁻¹ which may be assigned to v(-N=N-) chromophore groups in the structure [40]. New bands, which are not present in the ligand appeared around 556-549 cm⁻¹, corresponding to M–O and 510–513 cm⁻¹ to M–N vibrations support the involvement of N and O atoms in coordination with metal center



Scheme 1. Preparation of 4-[(*E*)-phenyldiazenyl]-2-[(*E*)-((4-[(*E*)-phenyldiazenyl]phenyl]imino)methyl]phenol and its possible tautomers (*i*):NaNO₂-HCl, 0 °C, (*ii*): 2-hydroxybenzaldehyde, (*iii*): MeOH-CHCl₃mixture(1:1), reflux.

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Fig. 1. The proposed structure of metal(II) complexes; (2b) and (2c).

[18]. A less intense band at ~1476 cm⁻¹ in the spectrum of the ligand may be assigned to v(-N=N-).

3.4. Electronic spectra

Electronic spectra of the synthesized compounds were studied in spectrophotometric grade solvents of different polarities. The data of the azo compounds **1a**, **2a**, **2b** and **2c** are summarized in Table 1. The molar absorptivity coefficient values of the studied compounds increased as the polarity of the solvent increases. This increase in molar absorptivity coefficient values of the compounds indicated that the absorption capacities of these are getting much better as the polarity of the solvent increases.

UV–Vis spectra of the azo salicylaldehyde compound (**1a**) in various solvents are shown in Fig. S4. Maximum absorptions were observed in

Table 1				
UV-Vis data of	the synthesized	dye and	its metal	chelates.

Compound	Solvent	$\lambda_{max} \left(nm \right)$	Absorbance	$\epsilon~(L~mol^{-1}~cm^{-1})\times 10^4$
(1a)	DMF	340	2.804	14.02
	EtOH	339	2.532	12.66
	MeOH	338	2.233	11.17
	CHCl ₃	335	2.046	10.23
	CH ₂ Cl ₂	334	1.903	9.52
	Toluene	333	1.733	8.67
	CCl ₄	330	1.587	7.94
	Hexane	325	1.425	7.13
(2a)	DMF	400	2.862	14.31
	EtOH	362	2.751	13.76
	MeOH	361	2.553	12.77
	CHCl ₃	360	2.234	11.17
	CH_2Cl_2	359	2.001	10.01
	Toluene	351	1.786	8.93
	CCl ₄	350	1.638	8.19
	Hexane	345	1.431	7.16
(2b)	DMF	385	2.885	14.43
	EtOH	375	2.652	13.26
	MeOH	370	2.419	12.10
	CHCl ₃	365	2.114	10.57
	CH_2Cl_2	360	1.897	9.49
	Toluene	355	1.693	8.47
	CCl ₄	350	1.501	7.51
	Hexane	345	1.332	6.66
(2 c)	DMF	390	2.919	14.60
	EtOH	370	2.779	13.90
	MeOH	365	2.393	11.97
	CHCl ₃	360	2.081	10.41
	CH_2Cl_2	355	1.903	9.52
	Toluene	352	1.739	8.70
	CCl ₄	350	1.595	7.98
	Hexane	345	1.449	7.25

 λ_{max} : maximum absorption wavelength; Abs: maximum absorption intensity; ϵ : molar absorptivity coefficient; sample concentration was 2.0×10^{-5} mol L⁻¹.

the range of 325–340 nm depending on the polarity of the solvents. These absorptions were assigned to $\pi \rightarrow \pi^*$ transitions due to chromophore groups in the structure. Absorption intensity in hexane which is an apolar and aprotic solvent has the lowest value. However, in DMF (polarity index of 6.1), absorption intensity and wavelength have the highest value. Solvents used in UV–Vis measurement have polarity index decreasing with order of DMF, EtOH, MeOH, CHCl₃, CH₂Cl₂, C₆H₅CH₃, CCl₄ and *n*-C₆H₁₂. Once the polarity of the solvent increases, there is a slight increase in λ_{max} and ε (L mol⁻¹ cm⁻¹) values. In DMF, an additional absorption maximum was observed at 455 nm. This absorption was attributed to the existence of tautomeric form in highly polar solvent. In DMF and EtOH, there is an absorption shoulder at around 355 nm attributed to the n $\rightarrow \pi^*$ transitions.

Maximum absorbance wavelengths (λ_{max}) of the azo-azomethine ligand (**2***a*) were observed in the 345–400 nm range in various solvents (Fig. 2). Absorption spectra of (**2***a*) in EtOH, MeOH, CHCl₃, CH₂Cl₂, toluene, CCl₄ and hexane were almost identical. However, in DMF, both absorption intensities and maximum absorption wavelengths increased. The maximum absorption band at 455 nm observed for azo-salicylaldehyde (**1***a*) has completely disappeared in the case of the azo-azomethine compound (**2***a*).

UV–Vis spectra of the metal complexes (2b) and (2c) in various solvents are shown in Figs. 3 and 4, respectively. Absorption spectra of the complexes in various solvents are similar. The maximum absorbance values are observed at 385, 375, 370, 365, 360, 355, 350 and 345 nm. In DMF, maximum absorption wavelengths shifted to longer values and the highest absorption values were observed. No d–d transition due to the presence of metal ion was observed in the concentration studied.



Fig. 2. UV-Vis spectra of (2a) azo azomethine dye in various solvents.

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Fig. 3. UV-Vis spectra of the Co(II) complex (2c) in various solvents.

3.5. Computational studies

3.5.1. Stretching frequencies and optimized structures

Tautomers were optimized at HF/3-21G, HF/LANL2DZ, B3LYP/3-21G and B3LYP/LANL2DZ levels. Infrared spectra of the tautomer (**1**) and its metal complexes with copper(II) and cobalt(II) ions were calculated. The optimal level was determined by correlation with the experimental and theoretical stretching frequencies. The correlation coefficients are given in Table 2.

As can be seen in Table 2, the best level for vibrational frequencies was found as HF/3-21G. IR spectra of tautomer (1) and its complexes with Cu(II) and Co(II) ions at this level are represented in Fig. S5.

The calculated and experimental frequencies for tautomer (1) and Cu(II) and Co(II) complexes are given in Table 3.

Optimized structures of the tautomers (**1–3**) are presented in Fig. 5. The determination of tautomer interacting with a metal cation is important for optimized structures of the synthesized metal complexes. Tautomer gives four electrons from HOMO and HOMO-1 when it coordinates with metal cations. Therefore, orbital character of HOMO and HOMO-1 is important to determine the coordinating tautomer.

Characters of oxygen and nitrogen atoms at HOMO and HOMO-1 were calculated with Eq. (1) [49].



Table 2

Correlation coefficients between experimental and calculated stretching frequencies of the tautomer (1) and its Co(II) and Cu(II) complexes.

Level	Tautomer (1)	(2b)	(2 c)
HF/3-21G	0.9974	0.9981	0.9974
HF/LANL2DZ	0.9907	0.9970	0.9936
B3LYP/3-21G	0.9925	0.9981	0.9876
B3LYP/LANL2DZ	0.9975	0.9968	0.9970

where *n* is the atomic orbital coefficient and $\sum n^2$ is the sum of the squares of all atomic orbital coefficients in a specific molecular orbital. The atomic orbital coefficients (greater than 0.1) were used in calculating the orbital characters. The contour diagrams and oxygen and nitrogen character of HOMO and HOMO-1 of all tautomers are given in Fig. 6.

According to Fig. 6, total donor atom characters of HOMO and HOMO-1 for tautomer (1) are higher than tautomers (2) and (3). Therefore, tautomer (1) interacts with metal cation. Optimized structures of copper(II) and cobalt(II) complexes with tautomer (1) and atomic labels are presented in Figs. 7 and S6, respectively. Some geometric parameters are listed in Table 4.

Molecular geometries of (2b) and (2c) complexes were found as distorted tetrahedral and octahedral, respectively. The bond length between oxygen atoms (numbered with 22 and 70) and central metal is shorter than between nitrogen atoms (numbered with 24 and 72) and metal. The angle (24N-97(Cu/Co)-72N) of the copper(II) complex is wider than cobalt complexes. The most important difference between (2b) and (2c) structures is that two water molecules coordinated to cobalt(II) ion in (2c) complex.

3.5.2. UV–Vis spectra of the Co(II) and Cu(II) complexes

The UV–Vis spectra of the Co(II) and Cu(II) complexes were calculated at TD-HF/3-21G level. The solvent effect was investigated for electronic absorption spectrum. All calculations were made in vacuum, water and chloroform with CPCM method. Wavelengths of bands and shoulder in UV–Vis spectra are given in Table S1. The calculated UV–Vis spectra of the synthesized metal complexes in vacuum and two solvents are presented in Fig. S7.

Two bands and a shoulder were calculated at UV–Vis spectrum of the (2b) complex in vacuum, whereas two bands were calculated in water and three bands were obtained in chloroform. One absorption band was calculated for (2c) complex in vacuum, water and chloroform.

3.6. X-ray powder diffraction

In the absence of single crystal, X-ray powder diffraction data are useful for structure determination, especially for deducing accurate cell parameters [50–52]. Structure determination by X-ray powder diffraction data has gone through a recent surge since it has become important to get to the structural information of materials, which do not yield good quality single crystals [22]. The X-ray powder diffraction measurements of the two ligands (**1a** and **2a**) and their complexes (**2b**) and (**2c**) were recorded using Cu-K α source in the range of 20°–50° 2 θ and the

Table 3

Calculated and experimental stretching frequencies of tautomer (1) and its complexes.

Frequency	Tautomer (1)		(2b)	(2b)		
	Theo.	Exp.	Theo.	Exp.	Theo.	Exp.
v_{O-H}	3514	3450	-	-	3422	3320
$v_{C-H(aromatic)}$	3043	3049	3038	3049	3053	3058
$v_{C-H(aliphatic)}$	2884	2930	2975	2925	2968	2930
$v_{c=0/c=N}$	1683	1616	1585	1611	1527	1612
$v_{C=C}$	1578	1567	1509	1575	1501	1557
$v_{N=N}$	1461	1480	1364	1472	1377	1480
v_{M-O}	-	-	545	556	552	549
ν_{M-N}	-	-	492	513	508	510

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Fig. 5. Optimized structures of the tautomers (1-3) of (2a) dye at HF/3-21G level.

diffraction patterns are shown in Fig. 8. The diffractograms and associated data depict the 20 value for each peak, relative intensity and interplanar spacing (d-values). The X-ray diffraction patterns of compounds with respect to major peaks of relative intensity greater than 10% were indexed using DICVOL91 program included in the X'PertHigh-Score Plus software; the indexing method also gives Miller indices (*hkl*), unit cell parameters and unit cell volume. The corresponding parameters are summarized in Table S2. The results indicated that the ligands and complexes have monoclinic crystal system. Moreover, with help of the diffraction data, the crystallite sizes were estimated according to the highest value of intensity compared with the other peaks. The crystallite size calculations were performed using Debye–Scherrer equation [53] and the obtained values indicated that the particles were nano-sized. Similar results were also reported in the literature [39,54,55].

3.7. Photoluminescence studies

Absorption and photoluminescence spectra were collected by excitation at 338 nm. The ligands having (1a) and (2a) azo chromophore group showed a strong blue light. Ligand photoluminescence spectra are given in Fig. 9. The wavelength of 446 nm was the maximum luminescent intensity and 119 nm the full width at half maximum for (1a), having a quantum yield of 35% and an excited-state lifetime of 3.26 ns. The wavelength of 479 nm was the maximum luminescent intensity and 129 nm the full width at half maximum for (2a), having a quantum yield of 41% and an excited-state lifetime of 3.86 ns.

It was noted that photoluminescence intensity and quantum yield of (**2***a*) increased compared to its precursor (**1***a*) as a result of the coupling reaction. A possible explanation may be the extensive π -electron delocalization being able to form a large conjugated system (**2***a*).

Fig. 9 depicts a comparison of excitation and emission spectra of ligands and complexes. Metal complex photoluminescence intensity and quantum yield decreased compared to that of their ligand (2a). Ligand (2a) had a 348 nm excitation maximum wavelength that shifted to 346 nm upon transition metal ion binding, though decreases in excitation intensity for (2a) were dependent on the nature of transition metal ion. Upon excitation at 338 nm, the ligand had a 479 nm emission maximum which shifted to 429 nm upon transition metal ion binding. A possible reason for emission intensity reductions may be coordination complex formation of the O and N-atom on (2a) with the metal ions. Thus the energy transfer from the excited state of the ligand (2a) to metal ions may be possible, hence non-radiated transition of the ligand excited state increases and therefore decreases the fluorescence emission. The extent of fluorescence quenching increased with metal ion



Fig. 6. Contour diagrams and orbital characters of HOMO and HOMO-1.

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Fig. 7. Optimized structure of (2b) at HF/3-21G level and atomic labels.

complex formation as a result of having a lower d-orbital electron number. Emission maxima was in the order of Cu(II) < Co(II) for the complexes. Thus this allows for an interaction between the metal and the ligand (*2a*). Fluorescence enhancement through complexation allows for the advancement of photochemical technologies. Fig. 9 shows a decrease in photoluminescence intensity and quantum yield upon metal complexation of ligand (*2a*). Further, maximum photoluminescence peak for ligand (*2a*), shifted from 479 to 429 nm, while the other peaks

Table 4 Selected bond lengths (Å) and angles (deg.) of Cu(II) and Co(II) complexes at HF/3-21G level in vacuum.

	(2b)	(2 c)
Bond length (Å)		
12N-13N	1.352	1.353
220-97(Cu/Co)	1.866	1.842
23C-24N	1.866	1.452
24N-97(Cu/Co)	2.005	2.025
34N-35N	1.395	1.352
60N-61N	1.354	1.354
700-97(Cu/Co)	1.854	1.955
71C-72N	1.312	1.387
72N-97(Cu/Co)	2.036	1.981
82N-83N	1.356	1.355
Bond angle (°)		
220-97(Cu/Co)-24N	92.7	88.3
220-97(Cu/Co)-700	132.3	170.4
220-97(Cu/Co)-72N	108.3	97.1
24N-97(Cu/Co)-700	106.5	88.5
24N-97(Cu/Co)-72N	128.1	173.2
700-97(Cu/Co)-72N	93.5	86.9



Fig. 8. X-ray powder diffraction patterns of 1a, 2a, 2b, and 2c.

become more intense and distinct. Table 5 gives photoluminescence data for the ligand and its complexes.

3.8. Thermal properties

Thermal study (TG/DTG/DTA) of the synthesized compounds was investigated in the temperature range of 25–1000 °C with a heating rate of 20 °C min⁻¹ under dry air using α -Al₂O₃ as reference. The TG, DTG and DTA curves of the compounds are shown in Figs. S8 and 10.

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Fig. 9. Photoluminescence spectra of the dye and its metal chelates in DMF; samples were excited at 338 nm.

The mass loss against temperature steps for the ligand and its metal complexes is summarized in Table 6. The experimental mass losses were in good agreement with the calculated mass loss values.

It was observed that the (**1a**) azo aldehyde decomposed in one stage, while the (**2a**) ligand decomposed in two stages. For (**1a**) compound, the first stage appeared at 85–260 °C with a mass loss of 81.6% ($C_{12}H_9N_2$), accompanied by two weak endothermic peaks with $T_{max} = 128$ and 233 °C on the DTA curve, which may be attributed to decomposition of azo-benzene group except the aldehyde and hydroxyl groups.

In the (**2a**) ligand, the first decomposition stage was observed in the range of 190–424 °C with weight loss of 51.9% corresponding to $C_{13}H_{10}N_3$. The endothermic peak at 187 °C, and the exothermic peak at 371 °C in DTA curve correspond to the weight loss. The rest of the organic moiety decomposed in the second decomposition step in the range of 424–724 °C with $T_{max} = 519$ °C and 560 °C in DTA curve.

The TG curve of Cu(II) shows two decomposition stages. The molecular backbone of the complex is thermally stable up to about 325 °C. The first decomposition stage appeared at 250–374 °C for Cu(II) complex, with a mass loss of 21.5%, accompanied by an exothermic peak with $T_{max} = 331$ °C on the DTA curve, which may be attributed to the removal of one of the azo-benzene groups (C₁₂H₉N₂). In the second decomposition stage the rest of the other organic moiety of the complex decomposed within the temperature range of 374–647 °C with an exothermic peak in this region ($T_{max} = 461$ °C), leaving CuO as the final residue.

The TG curve of the Co(II) complex shows four decomposition stages. The first step shows a sudden weight loss in the temperature range of 26 to 91 °C with a mass loss of 21.2% indicating the removal



Fig. 10. TG, DTG and DTA curves of (i) Cu(II) and (ii) Co(II) metal complexes.

of methanol and water solvates. An exothermic peak in this region with $T_{max} = 68$ °C on the DTA curve. The second decomposition stage occurs within the temperature range of 91–205 °C with a weight loss of about 3.5% (Cl + H₂O), corresponding to the loss of coordinated water molecule and chloride ion. The third stage of decomposition proceeds within the temperature range of 205–401 °C with an estimated mass loss of 16.5% (C₁₂H₉N₂); an exothermic peak may be attributed to the loss of one of the azo-benzene groups. Also, in this region the DTA curve shows an endothermic peak at $T_{max} = 267$ °C. The final step of the thermal decomposition was observed in the temperature range of 401–832 °C with a mass loss of 51.8% accompanied by an exothermic peak at $T_{max} = 569$ °C in DTA. In this step all organic residues were removed from the structure leaving metal oxide as the final product (CoO). When the metal complexes were heated to higher temperatures, they decomposed to give oxides of the MO type.

Table 5

8

Photoluminescence da	ata for	the prep	ared com	pounds
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Entity	$\lambda_{max}Ex (nm)$	InEx	$\lambda_{max}Em(nm)$	InEm	φ _f (%)	$\tau_{f}(ns)$
(1a)	346 (312;324;364)	582	446 (393;414;471;501)	572	35	3.26
(2a)	348 (325;369;392)	718	479 (408;438;521)	704	41	3.86
(2b)	347 (326;367;386)	477	433 (407;468;506)	469	30	2.76
(2c)	346 (325;367;385)	385	429 (412;468;508)	378	25	2.29

 $\lambda_{max}Ex$: maximum excitation wavelength; InEx: maximum excitation intensity; $\lambda_{max}Em$: maximum emission wavelength; InEm: maximum emission intensity; ϕ_{f} : quantum yield; τ_{f} : excited-state life time.

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Table 6

Thermal data of the compounds.

Compound	Decomp. stage	DTA peak temp. (°C) (endo. \downarrow , exo. \uparrow)	TG range (°C)	DTG _{max} (°C)	Mass loss obs. %	Decomposed assignment
(1 <i>a</i>)	Ι	128 ↓, 233 ↓	85-260	217	81.6	C ₁₂ H ₉ N ₂
	Residue				18.4	-
(2a)	Ι	187 ↓, 371 ↑	190-424	357	51.9	$C_{13}H_{10}N_3$
	II	519 ↑, 560 ↑	424-724	560	48.1	$C_{12}H_9N_2O$
	Residue				-	-
(2b)	Ι	331 ↑	250-374	327	21.5	$C_{12}H_9N_2$
	II	461 ↑	374-647	463	75.7	Rest of the organic moiety
	Residue				2.8	CuO
(2 <i>c</i>)	I	68 ↑	26-91	55	21.2	$H_2O + MeOH$
	II	130 ↑, 195 ↑	91-205	130	3.5	3H ₂ O
	III	267 ↓	205-401	274	16.5	$C_{12}H_9N_2$
	IV	569 ↑	401-832	572	51.8	Rest of the organic moiety
	Residue	·			7	CoO

3.9. Kinetic studies

The kinetics and thermodynamic parameters for non-isothermal decomposition of the ligands and their metal complexes were determined by the Coats–Redfern (CR) [56] and Horowitz–Metzger (HM) [57] methods.

i. Coats-Redfern method

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT}\operatorname{for}(n\neq 1)$$
(1)

$$\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \text{ for}(n=1)$$
(2)

where, α is the fraction of material decomposed, *n* is the order of the decomposition reaction, *R* is the gas constant (8.314 J mol⁻¹ K⁻¹), β is the heating rate and *T* is the temperature corresponding to weight loss.

ii. Horowitz-Metzger (HM) method

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{1-n}\right] = \ln\frac{ART_s^2}{\beta E} - \frac{E}{RT_s} + \frac{E\theta}{RT_s^2} \operatorname{for}(n \neq 1)$$
(3)

$$\ln\left[-\ln\left(1-\alpha\right)\right] = \ln\frac{ART_s^2}{\beta E} - \frac{E}{RT_s} + \frac{E\theta}{RT_s^2} \operatorname{for}(n=1)$$
(4)

where, $\theta = T - T_s$, T_s is the temperature at the DTG peak.

The plot of the left-hand side of Eqs. (1) and (2) against 1 / T and against θ for Eqs. (3) and (4) gives a slope from which activation energy, *E* was calculated and pre-exponential factor, *A* was determined from the intercept.

The thermodynamic parameters of entropy (ΔS^*), enthalpy (ΔH^*) and Gibbs free energy changes (ΔG^*) were calculated from the following equations:

$$\Delta S^* = R \ln \left(\frac{Ah}{kT_s}\right) \tag{5}$$

 $\Delta H^* = E - RT_{\rm s} \tag{6}$

 $\Delta G^* = \Delta H^* - T_s \Delta S^* \tag{7}$

where, *h* is the Planck's constant 6.626×10^{-34} J s and *k* is the Boltzmann constant 1.38×10^{-23} J K⁻¹.

The calculated results are given in Table 7. The kinetics and thermodynamic data obtained by the two methods are comparable. The correlation coefficients (r) of the Arrhenius plots of the thermal decomposition steps were found to lie in the range of 0.98203–0.99975, showing a good fit with linear function. The kinetics data obtained from the TG curves, showed that the activation energies of decomposition were in the range of 48.97–434.80 kJ mol⁻¹. High activation energies reveal thermal stability of the complexes. The entropy of the activation (ΔS^*) gave negative values in all compounds, except the Cu(II) complex. The negative ΔS^* value indicates that complexes are formed spontaneously, and a more ordered activated state as a result of decomposition of other products. Further, positive ΔS^* values indicate dissociation character of degradation [58]. The enthalpy (ΔH^*) and Gibbs free energy change (ΔG^*) values have positive values in the ranges of 45.62–429.81 kJ mol⁻¹ and 57.66–250.44 kJ mol⁻¹, respectively, representing endothermic pathway at all thermal steps. The positive value of ΔG^* , shows that the final residue free energy is greater than that of the precursor compound, thus all the decomposition stages proceed as non-spontaneous processes [59].

4. Conclusions

In this study, a novel azo-azomethine ligand of 2-hydroxy-5-[(E)-phenyldiazenyl]benzaldehyde with *p*-aminoazobenzene and its two metal chelates were synthesized and characterized by analytical and spectral techniques. Compound (**2a**) acts as a bidentate ligand and formed stable complexes with Co(II), and Cu(II) ions. Examination of the infrared spectra shows that the azo-azomethine ligand is bidentate and coordinates through the phenolic oxygen and azomethine nitrogen atoms. The azo-salicylaldehyde and azo-azomethine compounds gave photoluminescence at 446 and 479 nm, where the maximum luminescence intensities and quantum efficiencies of metal complexes were greatly affected. The luminescence peak shifted from 479 to 429 nm upon complexation.

An X-ray powder diffraction study suggested the monoclinic crystal system for the ligands and metal complexes. Also, the thermal study revealed thermal stability of the synthesized metal complexes and indicated that all the decomposition steps were non-spontaneous processes.

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Table 7

Kinetic and thermodynamic parameters of thermal decomposition of the synthesized dye and its metal chelates.

Compound	Step	п	Method	$E kJ mol^{-1}$	$A(s^{-1})$	$\Delta S^*(J \ K^{-1} \ mol^{-1})$	$\Delta H^*(kJ mol^{-1})$	$\Delta G^*(kJ mol^{-1})$	r
(1a)	Ι	0	CR	68.25	1.1×10^5	- 152.53	64.18	139	0.99974
			HM	85.57	$1.9 imes 10^7$	-109.74	81.50	135.27	0.99944
(2a)	Ι	0.25	CR	80	$1.75 imes 10^4$	-170	74.76	181.86	0.99607
			HM	114.77	$3.8 imes 10^7$	-106.02	109.53	176.32	0.99964
	II	0.75	CR	120	1.62×10^5	-153.72	113	241	0.99975
			HM	145.2	1.07×10^7	-118.88	138.27	237.3	0.99802
(2b)	Ι	2	CR	403.33	4.19×10^{33}	393	398.34	162.54	0.9915
			HM	434.80	3.46×10^{36}	448.77	429.81	160.55	0.99273
	II	1.75	CR	189.40	$3.4 imes 10^{11}$	-31.67	183.28	206.59	0.99911
			HM	189.83	4.17×10^{11}	-29.97	183.71	205.77	0.99616
(2 c)	Ι	0.75	CR	50.24	$1.55 imes 10^6$	-127.2	47.51	89.23	0.99762
			HM	59.60	6.89×10^{7}	- 95.65	56.87	57.66	0.99368
	II	2	CR	51.63	$4.3 imes 10^4$	-158.71	48.3	112.26	0.99029
			HM	48.97	$2.69 imes 10^4$	-162.61	45.62	111.15	0.99291
	III	2	CR	115.22	5.92×10^8	- 82.02	110.67	197.48	0.98203
			HM	113.56	$1.06 imes 10^9$	-77.18	109.01	151.23	0.98577
	IV	1.25	CR	95.21	1.65×10^3	-192	88.20	250.44	0.99453
			HM	104.24	$1.63 imes 10^4$	-173	97.21	243.40	0.99379

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.molliq.2014.10.012.

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