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Studies on phenol-keto tautomerism, metal ion binding, and free radical scavenging properties of newly synthesized naphthalene-based tetraimine Schiff base

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Abstract

*In this study, a new tetraimine Schiff base (**T_1**) was obtained by the synthesis of diimine Schiff base (**D_1**), the reduction of nitro group of this Schiff base to amino group and the reacting of amino group with 2-hydroxy-1-naphthaldehyde, respectively. It was characterized by various spectroscopic techniques. The phenol-keto tautomerism of Schiff base (**T_1**) was investigated by UV–vis spectra in different solvents and media. The binding interaction between **T_1** and metal ions, i.e., Cr^{3+}, Fe^{3+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}, Pb^{2+}, Ag^{+} and Ba^{2+} was confirmed in DMF-HEPES buffer (v/v, 1:1) by UV–vis spectroscopy. It showed the favorable coordination toward Cu^{2+}, Co^{2+} and Fe^{3+} ions. In the presence of Cu^{2+}, Co^{2+} and Fe^{3+} ions, yellow color of **T_1** solution changed to colorless. The 1:1 binding stoichiometry between **T_1** and Cu^{2+}, Co^{2+}, Fe^{3+} ions was established using Job's plot. The binding constants (Ka) were calculated to be 1.22×10^4 M^{-1}, 1.62×10^4 M^{-1} and 5.79×10^4 M^{-1} for Cu^{2+}, Co^{2+} and Fe^{3+} ions, respectively, by Benesi–Hildebrand equation. In addition, **T_1** was also found to be potent scavenger of DPPH radicals with half-maximal scavenging concentration (SC_{50}) value less high than that of the standard, ascorbic acid.*

***Keywords:** Schiff bases, tautomerism, colorimetric sensors, free radical scavenging activity.*

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Yeni sentezlenmiş naftaldimin-temelli tetraimin Schiff bazında fenol-keto tautomerliğinin, metal iyon bağlama ve serbest radikal süpürme özelliklerinin çalışılması

Özet

*Bu çalışmada, sırasıyla **D_1** diimin Schiff bazının sentezlenmesi, bu Schiff bazının nitro grubunun amino grubuna indirgenmesi ve amino grubunun 2-hidroksi-1-naftaldehit ile etkileştirilmesi ile yeni dört imin grubu bulunan Schiff bazı (**T_1**) sentezlendi. Bileşik çeşitli spektroskopik teknikler ile karakterize edildi. Schiff bazındaki (**T_1**) fenol-keto tautomerliği farklı çözücü ve ortamlarda UV-GB spektrumları ile incelendi. **T_1** ile bazı metal iyonları Cr^{3+}, Fe^{3+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}, Pb^{2+}, Ag^{+} and Ba^{2+} arasındaki bağlanma etkileşimi DMF-HEPES tampon karışımında (v/v, 1:1) UV–GB spektrofotometrisi ile belirlendi. Sonuçlar tercih edilen bağlanmanın Cu^{2+}, Co^{2+} ve Fe^{3+} iyonları ile olduğunu gösterdi. Cu^{2+}, Co^{2+} and Fe^{3+} iyonu varlığında, **T_1** çözeltisinin rengi sarıdan renksiz olacak şekilde değişti. **T_1** ile Cu^{2+}, Co^{2+} ve Fe^{3+} iyonları arasında 1:1 bağlanma olduğu Job's eğrisi yönteminden belirlendi. Bağlanma sabitleri (K_a) Cu^{2+}, Co^{2+} ve Fe^{3+} iyonları için sırasıyla Benesi–Hildebrand eşitliğinden 1.22×10^4 M^{-1}, 1.62×10^4 M^{-1} ve 5.79×10^4 M^{-1} olarak hesaplandı. Ayrıca, **T_1**'in DPPH radikallerine karşı potansiyel bir süpürücü olduğu, yüzde 50 süpürme konsantrasyon değerinin standard askorbik asitten çok az büyük olduğu belirlendi.*

***Anahtar kelimeler**: Schiff bazları, tautomerlik, kolorimetrik sensörler, serbest radikal süpürme aktivitesi.*

1. Introduction

In coordination chemistry, Schiff bases are well known as mono-, bi- and polydentate ligands. Schiff bases containing symmetrical structure (R-N=*CH*-Ar-*CH*=N-R or R-CH=*N*-Ar-*N*=CH-R) have been extensively synthesized [1-3] and used in coordination chemistry because of forming stable complexes with most transition metal ions easily [4-5]. Schiff bases and their metal complexes have been reported to show antifungal and antibacterial [6], antiproliferative [7], antitubercular [8], analgesic [9], antiviral [10], antipyretic [11], enzim inhibitory [12], antidiabetic [13], anticonvulsant [14], herbicidal [15], anticorrosion [16], and anti-HIV [17] activities. Besides, they are of great importance for photodynamic therapy as radiotracers [18] and DNA cleavage reagents [19]. They can be utilized as catalysts [20], polymer stabilizers [21] and dyes [22].

There are some analytical techniques like as atomic absorption spectroscopy (AAS), atomic emission spectroscopy (AES), inductively coupled plasma-mass spectroscopy (ICP-MS), voltammetry and high performance liquid chromatography for detection of metal ions [23]. But, most of them require expensive instruments. Schiff bases are known to be the most attractive chelators and they can bind with a metal ion selectively and reversibly. Many Schiff bases have colorimetric and optical (absorbance or fluorescent) properties [24] and they are used in chemosensor chemistry for determination of metal cations [25] and inorganic anions [26] simply and inexpensively. Therefore, the ionochromic behavior of Schiff bases have been well reported [27-28].

Schiff bases obtained from 2-hydroxy-aromatic aldehydes are connected with a possibility of formation of an intramolecular hydrogen bond with the imine nitrogen and hydroxyl oxygen atoms [29]. These Schiff bases can occur two types of intramolecular hydrogen bond (O-H…N or O…H-N) and they can exist phenol-imine, keto-amine and zwitterionic forms both in solution and in the crystalline state. The type of the dominant tautomer strongly belongs to aldehydes and amines used for condensation [30]. Furthermore, this tautomeric equilibrium is influenced by solvent polarity, temperature and light [31]. In the literature, tautomerism between phenol-imine and keto-amine forms has been extensively investigated by UV-vis [32], X-ray [33], and theoretical calculation [34]. These Schiff bases exhibited the proton transfer processes that can operate in molecular electronics [35]. Moreover, hydroxyl-substituted Schiff bases possess antioxidant activities [36].

In our previous works, we reported the synthesis of asymmetric-Schiff bases of the type R-N=*CH*-Ar-*N*=CH-R and investigation of their tautomeric properties [37], potentiometric and antimicrobial activities [38], chemosensor properties [39], and intramolecular hydrogen bonding in tetraimine Schiff bases [40].

Based on these considerations, an asymmetric tetraimine Schiff base (**T_1**) was newly synthesized. Its structure was determined by a variety of spectroscopic techniques. The solvent, acid and base effects on the phenol-keto tautomeric equilibrium in compound was determined by UV–vis spectroscopy. The cation sensing ability of **T_1** towards Cr^{3+}, Fe^{3+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}, Pb^{2+}, Ag^{+} and Ba^{2+} ions was investigated with colorimetric and absorption spectroscopic studies. From Job's plot data, the stiochiometry between **T_1** and Cu^{2+}, Co^{2+} and Fe^{3+} ions was determined to be 1:1 [M_2:L_2] recommending that it is bonded to the metal ions as tetradentate ligand with ON(spacer)NO donors. Nitrogen atoms bounded methylene groups in spacer moiety could not act as donor atoms and not coordinate to metal ions. In addition, DPPH free radical scavenging activity of **T_1** was evaluated in vitro.

2. Experimental

2.1. Materials and instrumentation

Ethylenediamine, 4-nitro-benzaldehyde, 2-hydroxy-1-naphthaldehyde, sodium dithionite ($Na_2S_2O_4$), 2-[4-(2-hydroxyethyl)piperazin-1-yl]ethanesulfonic acid (HEPES), 2,2-diphenyl-1-picrylhydrazyl (DPPH) and ascorbic acid were supplied from Merck, Aldrich and Carlo Erba. The metal ion solutions were prepared from nitrate salts of Cr^{3+}, Fe^{3+}, Ni^{2+}, Zn^{2+},Cu^{2+},Co^{2+}, Pb^{2+}, Ag^{+} and Ba^{2+}. The organic solvents were of spectroscopic grade.

Melting points performed on Barnstead Electrothermal BI 9200 were uncorrected. An Elementar Analysensysteme GmbH varioMICRO CHNS analyzer was used to record elemental analysis of the samples. Infrared spectra were determined on a Mattson 1000 FTIR spectrometer using KBr pellets. ^{1}H NMR spectra were operated in DMSO-*d6* on a Bruker Avance DPX FT-NMR spectrometer at 400 MHz by using tetramethylsilane (TMS) as an internal standard. The mass spectra were obtained using an Agilent 1100 MSD spectrometer using the positive ion electrospray ionization mode (ESI^+) at 100 eV. UV–vis spectra were recorded in various solvents (10 µM concentration) within 270–600 nm at room temperature on an Analytik Jena Specord 200 spectrophotometer.

Also, adding 0.2 mL of trifluoroacetic acid and triethylamine to 4 mL of the sample solution supplied acidic and basic media, respectively.

2.2. Synthesis

2.2.1. Synthesis of diimine Schiff base (D_1)

The diimine Schiff base was synthesized by reacting 4-nitro-benzaldehyde with ethylenediamine in EtOH, according to a literature method [41, 42]. It was formed as a light yellow solid, yield: 92 % (g), m.p. 201-202 ^oC.

2.2.2. Synthesis of tetraimine Schiff base (T_1)

Small portions of solid $Na_2S_2O_4$ (10 mmol, 1.742 g) was added to ethanol-water solution (1:1) of $\mathbf{D_1}$ (1 mmol, 0.326 g). It was stirred at 50 ^oC as about one hour to give a clear yellow solution. When the reducing process finished, the ethanolic solution of 2-hydroxy-1-naphthaldehyde (1 mmol, 0.172 g) was mixed with the amino derivative of $\mathbf{D_1}$, and stirred at 55-60 ^oC for 2-3 h. Dark yellow solid($\mathbf{T_1}$)was formed after keeping the solution at room temperature for a week.It was washed with warm water (2x25 mL) and EtOH (2x25 mL) and filtered twice; and recrystallized from EtOH.Yield: 54 % (0.309 g), dec.p. 270 ^oC. IR (KBr, cm^{-1}): 3443 (broad) (OH stretching), 3051 (C-H benzene), 2924/2852 (C-H), 1644/1616 (C=N), 1541 (C=C benzene), 1249 (C-O phenol). ^1H NMR (DMSO-*d6*, 400 MHz): δ 4.01 (s, 4H), 6.73-6.75 (d, 2H, *J* = 9.24), 7.18-7.21 (t, 2H, *J* = 7.21), 7.39-7.43 (t, 2H, *J* = 7.04), 7.62-7.64 (d, 2H, *J* = 7.85), 7.71-7.74 (d, 2H, *J* = 9.43), 8.02-8.04 (d, 1H, *J* = 8.66, CH=N), 9.15-9.17 (d, 1H, *J* = 8.43, CH=N), 14.15 (s, 1H, OH). LC-MS (ESI-negative): m/z (%): 574 (M) (0.4), 571 (2), 323 (100), 284 (25), 230 (47.9), 150 (21.6), 83 (30.6), 60 (31.8). Found for $C_{38}H_{30}N_4O_2$: C, 79.16; H, 5.86; N, 9.49 %. Calculated: C, 79.44; H, 5.23; N, 9.76 %.

2.3. Colorimetric chemosensor activity

2.3.1. Measurement of metal ion sensing

Stock solutions of metal cations (4 mM) was prepared in HEPES buffer (pH = 7.4). The stock solution of $\mathbf{T_1}$ (0.4 mM) was prepared in dimethylformamide (DMF). These solutions were diluted to 40 µM with buffer and DMF, respectively. Each samples were prepared to contain 2 mL of $\mathbf{T_1}$ solution (40 µM) and 2 mL of metal ion solution (40 µM).

2.3.2. UV–vis titration

Increasing volumes (1-10 mL) and concentrations of metal ion solution (40 µM, HEPES) were added to 1 mL of $\mathbf{T_1}$ solution (40 µM, DMF).

2.3.3. Job's plot

Job's plot method is that changing the molar ratio of ligand ($X_L = [L]/\{[L] + [M]\}$) from 0 to 1.0 and keeping total concentration and total volume of $\mathbf{T_1}$ and metal ion at 40 µM and 10 mL.

2.4. Radical scavenging activity

1 mL of DPPH (0.1 mM, DMF) was inserted to different volumes of the sample solutions of $\mathbf{T_1}$(4 µM, DMF). The decrease in absorbance of DPPH solution was recorded at 517 nm after waiting in dark for 30 min. DMF, DPPH solution and ascorbic acid were evaluated as blank, control and standard, respectively. The values were given as percent of scavenging activity. Each experiments were repeated on three parallel measurements [43].

3. Results and discussion

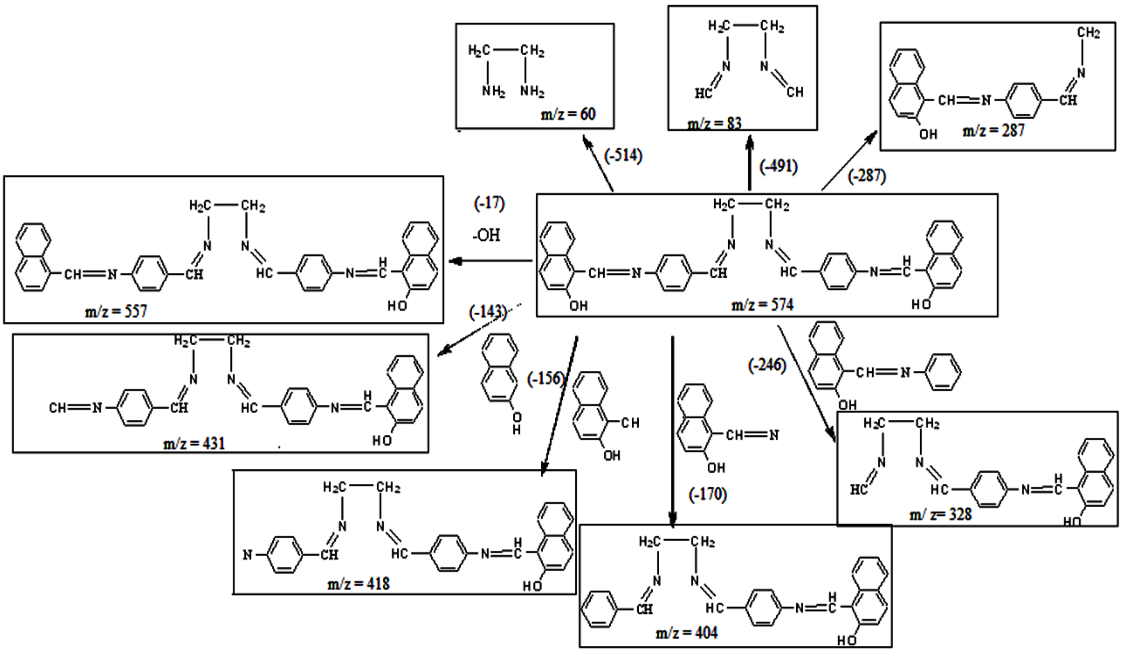
3.1. Chemistry

The structure of a new tetraimine Schiff base (**T_1**) was determined by elemental analysis, and UV–vis, FT-IR, ^{1}H NMR and ESI-mass spectrometries.

The important infrared spectral bands and their tentative assignments for Schiff base (**T_1**) are summarized in the experimental part. The FT-IR spectrum of **T_1** exhibited a broad band within the range 3443 cm^{-1} corresponding to intramolecular hydrogen bonded OH stretchings. The absorptions at 1644 and 1616 cm^{-1} were ascribed to the vibration of (CH=N) [44]. The stretching of aromatic rings was observed at 3051 and 1541 cm^{-1}. The bands at 2924–2852 cm^{-1} were assigned to the vibration of (C-H) and another band around 1249 cm^{-1} was due to the stretching of (C-O).

^{1}H NMR spectral data of Schiff base (**T_1**) are given in the experimental part. However, ^{13}C NMR data have not been recorded because of the solubility problem in DMSO-*d6*. The following signals was showed in ^{1}H NMR spectrum of **T_1**: a broad singlet for O–H group at δ 14.15 ppm [45], and two doublets for azomethine hydrogens (HC=N) at δ 9.15-9.17 ppm (J = 8.43) and δ 8.02-8.04 ppm (J = 8.66) [46]. In addition to this, the multiplet signals in the region 6.73–7.74 ppm (m, 10H) were due to aromatic protons. The singlet at 4.01 ppm was attributed to the CH_2 groups.

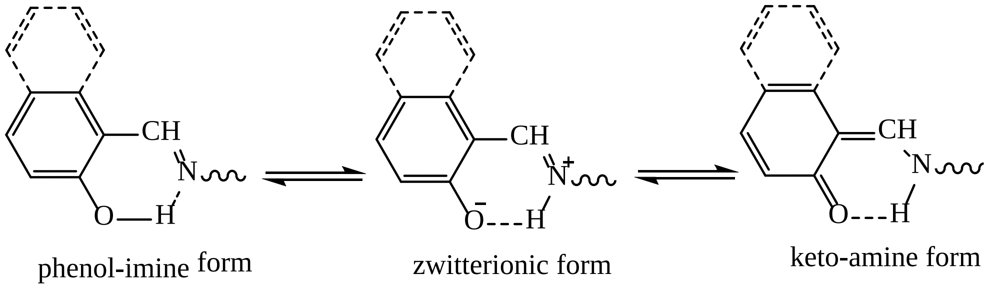
The mass spectrum of Schiff base (**T_1**) was obtained using the chemical ionization technique (API-ES/positive) (100 eV). The spectrum showed the fragment ions at *m/z* = 574, 571, 323, 230, 150, 83 and 60. As can be seen in Scheme 1, the loss of ($C_{34}H_{23}N_2O_2$) and ($C_{36}H_{22}N_2O_2$) fragments gave the peaks at m/z 83 and 60, respectively.



Scheme 1. Fragmentation patterns of the tetraimine Schiff base (**T_1**).

3.2. UV-vis spectroscopic studies of phenol-keto tautomerism

Schiff bases obtained from 2-hydroxy-aromatic aldehydes have showed the phenol-keto tautomerism (Scheme 2). This prototropic equilibrium and forming phenol-keto tautomers were interested in solvent polarity, acidity and alkalinity of media. So, the absorption spectra of $\mathbf{T_1}$ were studied in different solvents, and in acidic and basic media. UV-vis data are presented in Table 1. $\mathbf{T_1}$ had relatively intense absorption bands centered at λ_{max} = 308-310 nm in DMSO and MeOH, and λ_{max} = 313-362 nm in $CHCl_3$ and toluene (Fig. 1a).These bands belonged to π-π* and n-π* transition of imine group of phenol-imine form [40]. The bands due to n-π* transition of (C=O) group of keto form appeared in the region 400-428 nm. Increment of the percentage of keto form was in sequence: toluen (15%) < $CHCl_3$ (37%) < DMSO (59%) < MeOH (65%).



Scheme 2. The phenol-keto tautomerism in Schiff bases.

The added acid showed measurable change in the electronic spectra of $\mathbf{T_1}$. The bands at ca. 308 nm shifted to 340-348 nm in DMSO and MeOH (Fig. 1b). $\mathbf{T_1}$ exhibited in phenol-imine tautomer fully in DMSO and this tautomer was favored in other solutions. After addition of base, the bands did not show any change (Fig. 1c). The equilibrium between phenol-imine and keto-amine tautomers shifted towards keto-amine tautomer, except toluene. Increment of the percentage of this tautomer was in order in acidic media: toluene (30%) ~ $CHCl_3$ (31%) < MeOH (45%), and in basic media: toluene (45%) < DMSO (55%) = MeOH (55%) < $CHCl_3$ (58%).

Table 1. UV-vis data of $\mathbf{T_1}$.

Media	λ_{max} (logε)			
	Solvent			
	DMSO	MeOH	$CHCl_3$	Toluen
Pure	310 (5.24)	308 (4.20)	313 (5.16)	313 (4.51)
	405 (5.10)	400 (4.12)	344 (4.92)	333 (4.33)
	428 (5.12)	423 (4.10)	362(4.90)	362 (4.29)
		469(sh)[a] (3.68)	407 (4.97)	426(sh) (4.13)
			426 (4.97)	
Acidic	340 (5.12)	348 (4.17)	362 (5.23)	365 (4.91)
	384 (5.11)	404 (4.09)	386(sh) (5.19)	387(sh) (4.89)
			412(sh) (5.18)	411 (4.85)
Basic	309 (5.27)	302 (4.40)	312 (5.06)	367(sh) (4.43)
	405 (5.06)	402 (4.19)	408 (4.90)	431(sh) (4.35)
	427 (5.06)	423 (4.19)	426 (4.91)	

[a] shoulder

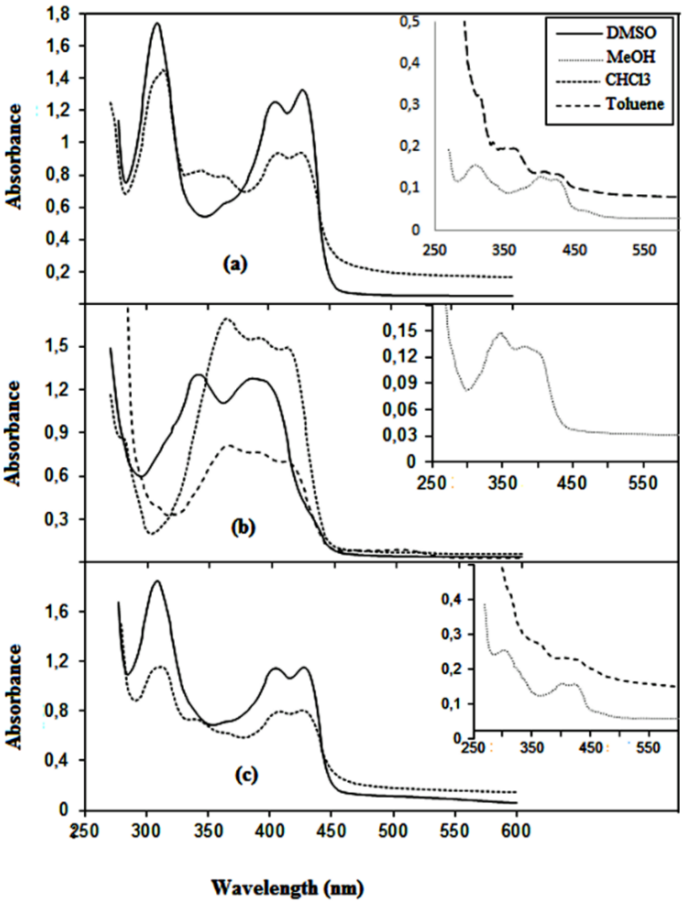


Figure 1. UV-vis spectra of $\mathbf{T_1}$ in various solvents (a), acidic (b) and basic (c) media.

3.3. Sensing properties of T_1

The colorimetric analysis of $\mathbf{T_1}$ was investigated towards various metal ions (as nitrate salts): Cr^{3+}, Fe^{3+}, Ni^{2+}, Zn^{2+},Cu^{2+},Co^{2+}, Pb^{2+}, Ag^{+} and Ba^{2+}.Upon adding of 2 mL (1 equivalent) of Co^{2+}, Cu^{2+}, and Fe^{3+} ions to 2 mL of $\mathbf{T_1}$ solution (1 equivalent), the colorless solution was clearly detectable by the naked eye (Fig. 2). In the presence of Pb^{2+}, Ag^{+} and Ba^{2+} ions, yellow color changed to light yellow. These results demonstrated a high selectivity for Cu^{2+}, Co^{2+} and Fe^{3+} ions, and a weaker interaction for Pb^{2+}, Ag^{+} and Ba^{2+} ions.

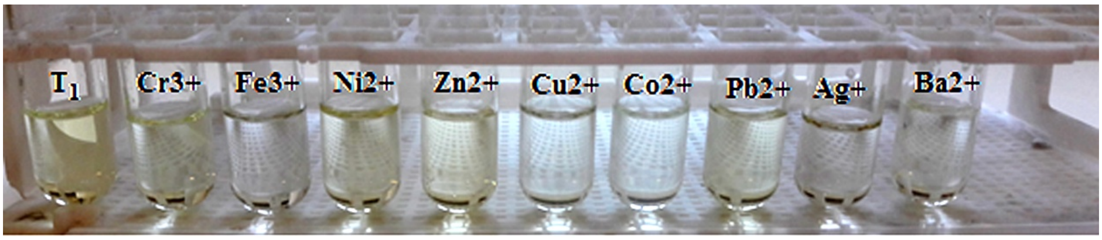


Figure 2. Color changes of $\mathbf{T_1}$ (40 µM, DMF) with various metal cations (40 µM, HEPES buffer).

The interaction between $\mathbf{T_1}$ and cations was specified by UV–vis. The changes in the absorbance properties of $\mathbf{T_1}$ (1 equivalent) was measured as a result of the adding of various cations (1 equivalent). In spectra, $\mathbf{T_1}$ showed five bands at 305, 338 (shoulder), 362 (shoulder), 403 and 426 nm in DMF, and four bands at 303, 334 (shoulder), 401 and 427 nm in DMF-HEPES (1:1). The absorption maxima below 400 nm were assigned to π-π*/n-π* charge transition of (C=N) and benzene ring, and the maxima above 400 nm belonged to n-π* transition of (C=O). On adding of Co^{2+}, Cu^{2+} and Fe^{3+} ions to $\mathbf{T_1}$, the bands at 303 and 334 nm red shifted 17 nm and 38-42 nm, respectively, and the band at 427 nm was disappeared (Fig. 3). These pronounced shifts of the maximum absorption wavelength could be ascribed to the coordination of ions with imine nitrogens of molecule [47]. In contrast, after adding of other cations, no selective response exhibited in absorption spectra of $\mathbf{T_1}$.

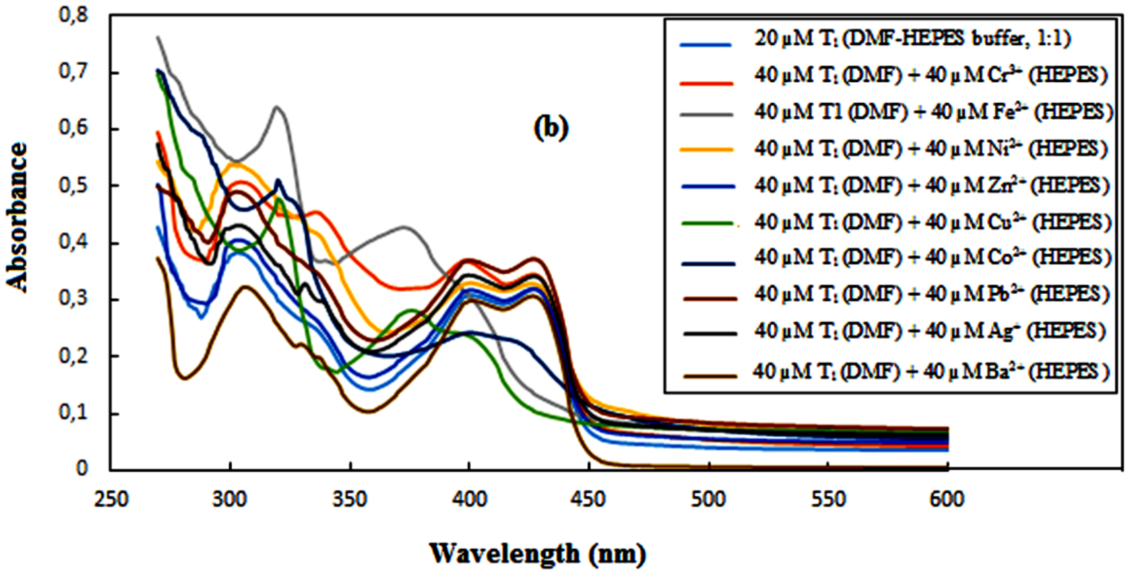


Figure 3. UV-vis spectra of $\mathbf{T_1}$ (40 µM, DMF) with various metal cations (40 µM, HEPES buffer) in 1:1 ratio.

The binding properties of $\mathbf{T_1}$ with Cu^{2+}, Co^{2+} and Fe^{3+} cations were investigated by UV–vis titration (Fig. 4a-c). After adding of 0-10 equivalent volumes of ions to $\mathbf{T_1}$ solution, the bands of Schiff base clearly shifted to red and the absorption intensity was decreased with the increasing metal ion volumes. For $Cu^{2+}$and Fe^{3+}ions volume larger than 1 equivalent, the intensity was decreased suddenly. Isosbestic point was not appeared during the titration.

Based on UV–vis titration, the binding constants (K) of$\mathbf{T_1}$ have been calculated by using Benesi–Hildebrand equation [48] as 1.22×10^4 M^{-1}, 1.62×10^4 M^{-1}, 5.79×10^4 M^{-1} with, Cu^{2+}, Co^{2+} and Fe^{3+} cations, respectively. These values are in the range (10^3–10^5) for with, Cu^{2+} [39], Co^{2+} [49] and Fe^{3+} [50] ions, which have been reported for Schiff base receptors.

Job's plot method was also used to understand the binding the stoichiometry of $\mathbf{T_1}$ and Cu^{2+}, Co^{2+} and Fe^{3+}cations. As can be seen in Fig. 5, the ligand–metal solution (40 µM) exhibited a maximum absorbance at 394, 320 and 397 nm when the molecular fraction of ions and $\mathbf{T_1}$ was close to 1:1. It indicated a 1:1 complex between $\mathbf{T_1}$ and metal ions. Scheme 3 showed that $\mathbf{T_1}$ is tetradentate ligand with ON(spacer)NO donors derived from hydroxyl oxygens and imine nitrogens, and it forms $[M_2L_2]$ dimeric metal complexes with disrupted square planar or octahedral geometries.

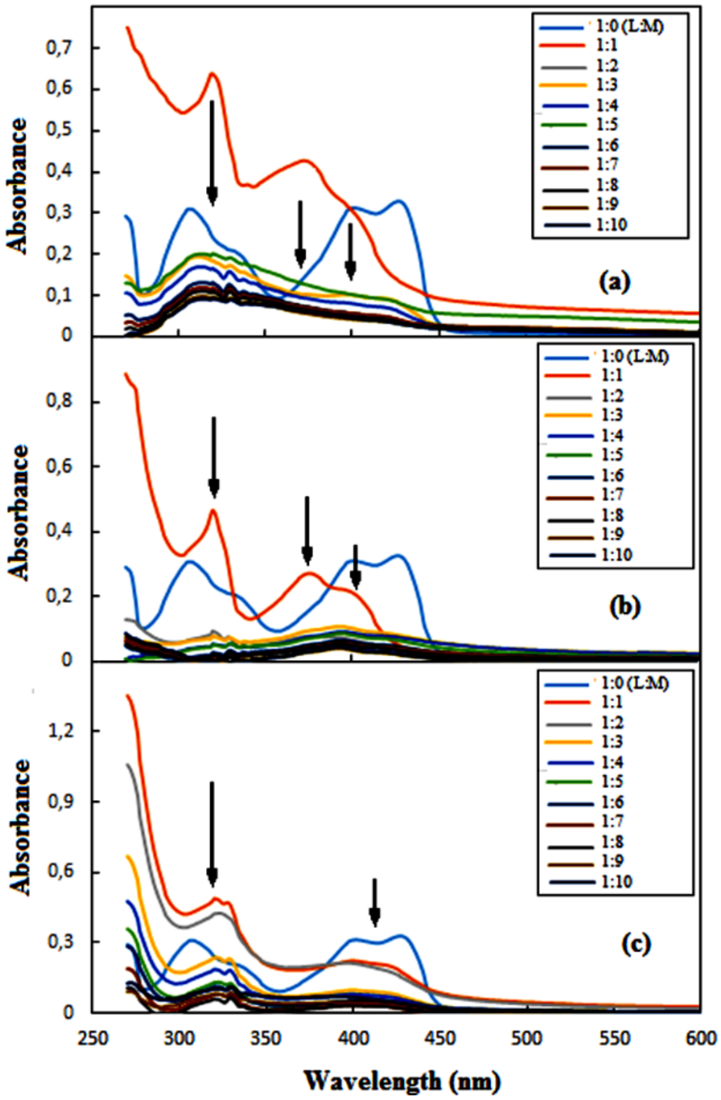


Figure 4. UV-vis titration of $\mathbf{T_1}$ (40 µM, DMF) with various volumes(0-10) of Fe^{3+} (a), Cu^{2+} (b), Co^{2+}(c) ions (40 µM, HEPES).

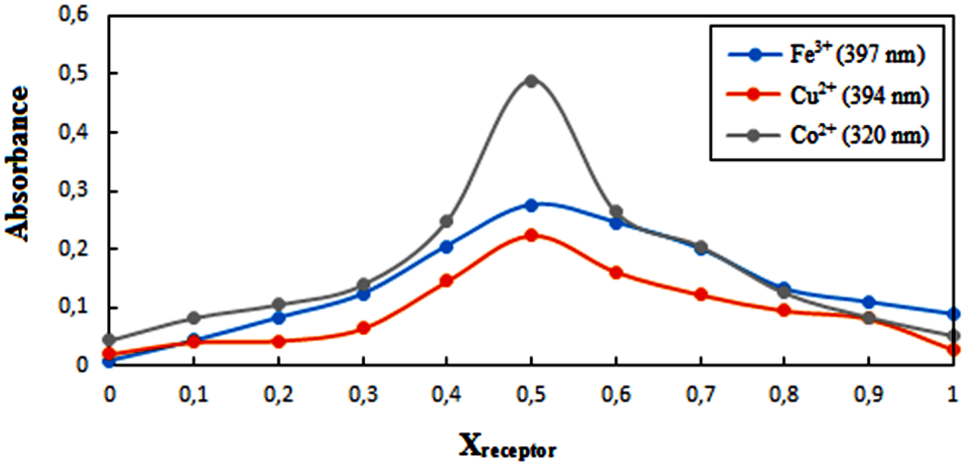
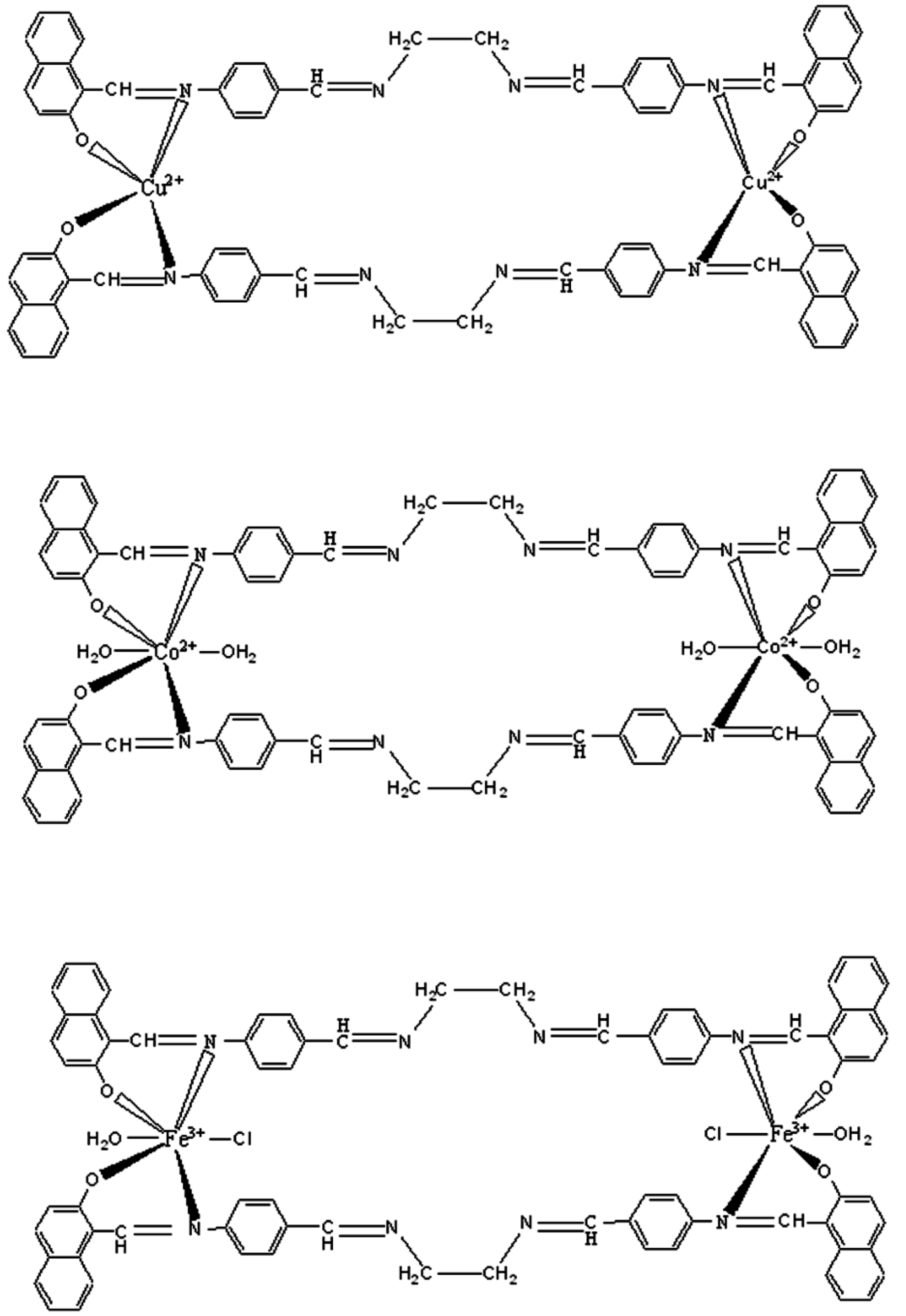


Figure 5. Job's plots of $\mathbf{T_1}$ with Cu^{2+}, $Co^{2+}$and Fe^{3+}ions.



Scheme 3.The proposed interaction of **T**$_1$ with metal ions.

3.4. DPPH scavenging activity

DPPH method is based on the fact that hydrogen atom donors cause the color change of free DPPH radical from purple to yellow [51] and a decrease in the initial concentration of radical in solution. It can be quantified by the reduction of absorbance of DPPH radical at 517 nm. The scavenging activity of compounds on DPPH radical is given in Fig. 6. SC_{50} value the concentration of the samples that inhibites 50% DPPH radical was found as 2.11 µM and 3.17 µM for an ascorbic acid and **T**$_1$, respectively.

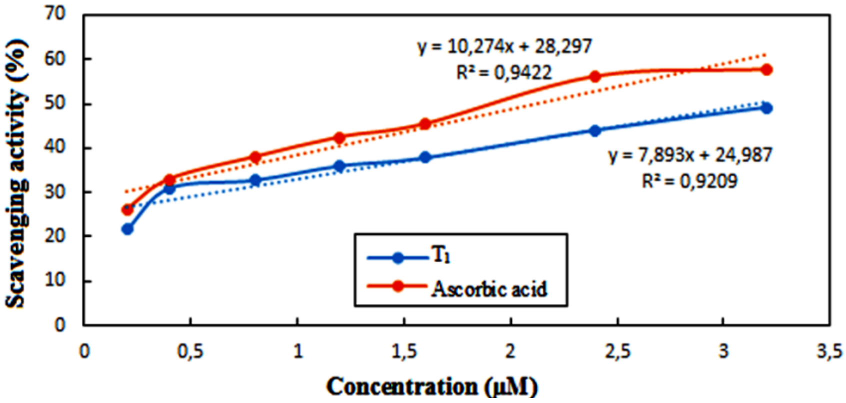


Figure 6. The inhibition of DPPH radicals by**T₁** and ascorbic acid at various concentrations.

5. Conclusion

In this paper, a new tetraimine Schiff base (**T₁**) was synthesized and its structure was defined by elemental analysis and IR, UV–vis, NMR, and mass spectroscopies. The phenol-keto tautomeric property of Schiff base was studied in different media by UV–vis. The results showed that it is found to be the tautomeric mixture in all media, except acidic DMSO. The cation binding behavior of **T₁** toward various metal cations, like Ag^+, Zn^{2+}, Cu^{2+}, Co^{2+}, Pb^{2+}, Ba^{2+}, Ni^{2+}, Cr^{3+}, and Fe^{3+} was examined in 40 µM DMF-HEPES buffer (1:1, *v/v*) by the using electronic absorption spectroscopy. This supported that **T₁** exhibites an high sensitivity and good selectivity for Cu^{2+}, $Co^{2+}$and Fe^{3+}ions. Job's plot analyses confirmed 1:1 ligand-metal stoichiometry for these ions. And, the binding constants were determined by Benesi–Hildebrand relation. As well, yellow color of **T₁** solution changed to colorless upon complexation with Cu^{2+}, Co^{2+} and Fe^{3+} ions and it served such as a'naked eye' receptor for these ions. In addition, **T₁** had almost the same radical-scavenging activitiy with ascorbic acid in DMF solution in the DPPH radical assay.

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