Journal of Molecular Structure 1050 (2013) 192–196

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Synthesis of new tridentate 5-(arylazo) salicylaldimine ligands and their Cu (II) complexes

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HIGHLIGHTS

- Synthesis of 5-(arylazo)salicylaldehydes as preligands.
- New tridentate Schiff base ligands were synthesized via condensation of preligand and 2-aminophenol or 2-aminothiophenol.
- The new ligands were subjected to react with $CuCl_2$.
- The structures of the ligands and metals complexes were established.

ARTICLE INFO

Article history:
Received 31 May 2013
Received in revised form 8 July 2013
Accepted 19 July 2013
Available online 26 July 2013

Keywords:
Salicylaldimine
Schiff's base
Tridentate ligand
Copper (II) complexes

ABSTRACT

New tridentate Schiff base ligands (H_2L) were synthesized *via* condensation of 5-(arylazo)salicylaldehydes and 2-aminophenol or 2-aminothiophenol. When the new salicylaldimines were subjected to react with $CuCl_2$ in the presence of $N(Et)_3$ yield the new complexes. The structure of the metal complexes was established by microanalyses, IR, UV spectra and thermal analyses. The results suggest that the ligands were coordinated to the copper ion in tridentate manner with ONO (or ONS) donor sites of the deprotonated phenolic-OH, azomethine-N, and deprotonated phenolic-OH (or deprotonated thiophenolic-SH). Furthermore, one water molecule was coordinated to the central metal atom. The composition of complexes can be represented as $CuL{\cdot}H_2O$.

1. Introduction

In the recent years, there has been considerable interest in the chemistry of transition metal complexes of Schiff's bases [1,2]. They have played a key role in the development of coordination chemistry, resulting in an enormous number of publications, ranging from pure synthetic work to modern physicochemical and biochemically relevant studies of metal complexes [3]. This is due to the fact that Schiff's bases offer opportunities for inducing substrate chirality, tuning the metal centered electronic factor, enhancing the solubility and stability of either homogeneous or heterogeneous catalysts [4–9], light emitting diode [10], corrosion inhibitor [11], potentiometric sensor [12,13], intermediates to obtain of some heterocyclic compounds [14], to synthesize of conjugate polymers containing azomethine bond [15] and their wide spectrum biological activities [16,17]. Salicylaldimine-based ligands have found applications in preparation of metallo-mesogens, optical metal ion detection and enantioselective catalysis [18,19]. In addition, Schiff bases containing nitrogen, oxygen and sulfur chelating groups in their structures have received much attention and for further studies during the past few years because of their specific properties e.g. electrochemically active compounds [20] catalytically active materials in asymmetric catalysis [21], photo-chromism [22], complexing towards heavy metals [23], determining of some cations [24], intermediates for heterocyclic compounds containing sulfur and nitrogen atoms [25] and antimicrobial activities [26].

Moreover much attention has been paid to photonic materials based on light-induced phase transitions because these types of materials are very useful in new information processing technology. Azo moiety is suitable for this research field because these materials are able to change molecular shape *via* reversible *cis–trans* isomerization upon photo-irradiation. These compounds have potential applications in optical switching, high-density optical data storage and optical computing [27,28]. Due to the clean photochemistry of azobenzene, and substantial change in material properties during light irradiation, it has been investigated as an active component for a variety of applications, such as lithography, non-linear optical devices and optical switches [29]. From a basic point of view, azo dyes belong to the simplest physical systems in which light illumination induces *cis–trans* isomerization and a

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http://dx.doi.org/10.1016/j.molstruc.2013.07.033

local change in the structure of the liquid crystalline phases. These changes can be responsible for the variation of the different electro-optical applications.

Copper (II) complexes of Schiff base derivatives are an important class of bioactive compounds as they exhibit good antibacterial and anti-malarial activities [30]. Recently, copper (II) complexes were employed as catalysts in the aerobic oxidation of benzylic alcohols and the corresponding ligand structures in solution and solid state [31].

So far, there are several metal complexes with differently substituted salicylaldimine ligands. However, metal complexes having azo moiety in the salicylaldimines are still rare. Based on the aforementioned properties of Schiff's bases and azo compounds, the search for new and effective derivatives is of paramount importance. Therefore, the present work described the preparation and characterization of a new type of 5-(arylazo) salicylaldimines as tridentate ligands and their copper (II) complexes with uncomplexed azo moiety.

2. Results and discussion

5-(Arylazo) salicylaldehyde derivatives **A1–4** as pre-ligands were prepared *via* coupling salicyladehyde with the appropriate substituted benzene diazonium chloride (obtained *in situ* by diazotization of the desired aromatic amines using a mixture of sodium nitrite and HCl) in presence of sodium hydroxide. Structural elucidation of A**1–4** derivatives was accomplished by their correct elemental analysis and carful inspection of their spectral data. In the IR spectra, the carbonyl group was observed at 1669–1649 cm^{-1} because the intramolecular hydrogen bonding between OH and the formyl group in structure **A1–4** leads to a decrease of the stretching frequency of C=O, and the hydroxyl group was observed at 3446–3423 cm^{-1}. Their ^{1}H NMR spectra displayed signal about $\delta = 10.32$ ppm characteristic for CH of aldehydic group and signal about $\delta = 11.73$ ppm indicating the presence of OH group; which disappeared in D_2O solution. Moreover, mass spectrum of **A3** (as a representative example): showed a molecular ion peaks at: $m/z = 310$.

Schiff's base ligands $\mathbf{H_2L^{1-8}}$ were synthesized *via* condensation of salicylaldehyde derivatives **A1–4** with 2-aminophenol and 2-aminothiophenol. The imines prepared in this way are formed in nearly quantitative yields and being of high purity. Structure of these Schiff's bases was elucidated by their IR, NMR and mass spectra. IR spectra of $\mathbf{HL^{1-8}}$ showed disappearance of bands for carbonyl group and the presence bands in 1618–1614 cm^{-1} region for CH=N group. Also, showed bands in 3447–3410 cm^{-1} region for OH grouping. According to the ^{1}H NMR spectra, the Ar-OH proton of these ligands displayed as a singlet at: 12.85 ppm due to effect of phenolic OH and hydrogen bonding (D_2O-exchangeable). The azomethine proton of $\mathbf{H_2L^{1-8}}$ appeared as a singlet at 8.60 ppm. Additional structural information can be deduced from mass spectroscopy (C.F Experimental Part).

Due to the successful preparation of Schiff's bases $\mathbf{H_2L^{1-8}}$ the attention was directed, in the present work, to investigate their chemical behavior towards metal cation. Therefore, it was encouraged to synthesize some new copper complexes starting from the Schiff's bases $\mathbf{H_2L^{1-8}}$. Thus, when a solution of the divalent $CuCl_2$ (0.01 mol) was added to a stirred hot solution of $\mathbf{H_2L^{1-8}}$ (0.01 mol) in ethanol in presence of triethylamine, at reflux temperature, the corresponding complexes $\mathbf{CuL^{1-8}{\cdot}H_2O}$ were formed (Scheme 1). All the synthesized copper (II) complexes are air-stable at room temperature and non-hygroscopic, colored solids, insoluble in water, partially soluble in ethanol and methanol, and soluble in DMSO and DMF. Decomposition occurs with conc. nitric acids, and the resultant solution was used after suitable dilution for metal analysis. The elemental analyses for these new compounds gave satisfactory results. Also, indicated the absence of chlorine atoms in the metal complexes and were in perfect agreement with a 1:1 ratio metal/ligand. Elemental analyses of these isolated complexes indicated that they can be represented as $\mathbf{CuL^{1-8}{\cdot}H_2O}$.

The IR spectra of the ligands were compared with those of the metal complexes in order to confirm the binding mode of the Schiff base ligands to the corresponding metal ion in the complexes. The free Schiff base ligands $\mathbf{H_2L^{1-8}}$ showed a strong bands in the region 1618–1614 cm^{-1}, which are the characteristic frequency of the azomethine ν C=N group. The ν C=N band is shifted to lower frequency in all the complexes and displayed at 1606–1600 cm^{-1} region, indicating coordination of the Schiff bases through the azomethine nitrogen atom. In all of these complexes a medium and/or weak band was observed at the 550–415 cm^{-1} range which can be attributed to the ν (Cu—N) and ν (Cu—O) modes. IR spectra showed that $\mathbf{H_2L^{1-8}}$ was coordinated to the metal ions in tridentate manner with ONS donor sites of the azomethine-N, deprotonated phenolic-OH and thiophenolic-SH. The main infrared bands of the ligands and their metal complexes are showed in Table 1.

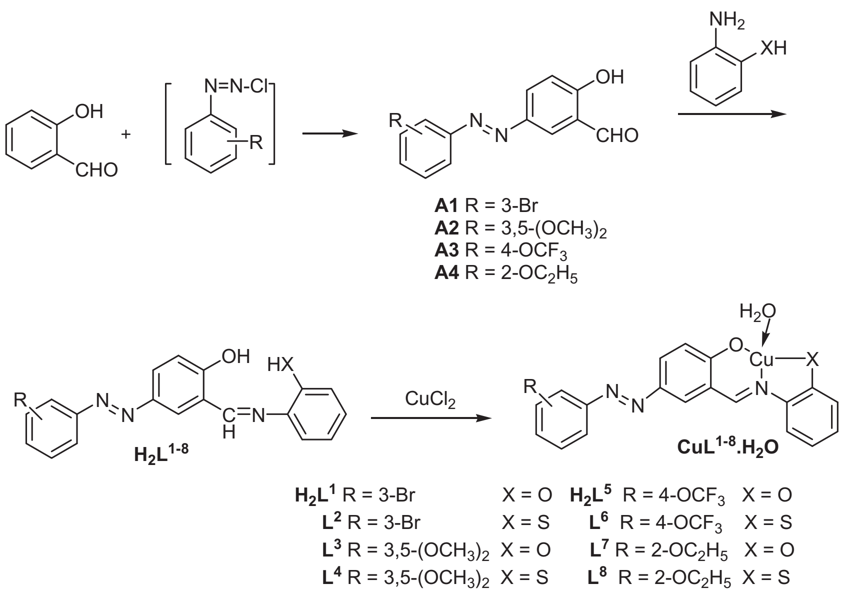
The electronic spectra data of the Schiff bases $\mathbf{H_2L^{1-8}}$ and their complexes $\mathbf{Cu(L^{1-8}){\cdot}H_2O}$ are summarized in Table 1. The spectra of the Schiff base $\mathbf{H_2L^{1-8}}$ exhibit two main peaks: around 350 and 490 nm. This bands corresponding to intraligand transition. The spectra of the complexes $\mathbf{CuL^{1,3,5,7}{\cdot}H_2O}$ show intense bands in the high-energy region about 433 nm which can be assigned to charge transfer L → Cu bands. The spectra of the complexes $\mathbf{CuL^{2,4,6,8}{\cdot}H_2O}$ show intense bands about 392, 482 nm.

TGA: In order to fully characterize the metal complexes in terms of thermal stability, their thermal behaviors were studied. To understand the thermal decomposition process, the copper $\mathbf{CuL^{3}{\cdot}H_2O}$ (as a representative example) was examined. Thermo gravimetric (TGA) and differential thermo gravimetric (DTG) analyses for this metal complex were carried out within the temperature range from ambient temperature up to 1000 °C. It is seen three thermal reactions from thermograms for all complexes (Fig. 1).

The first decomposition step of estimated mass loss 3.7% (calculated mass loss 3.9%) is due to the elimination of one water molecule in the temperature ranges 200–250 °C. The DTG curve gives an exothermic peak at 230 °C (the maximum peak temperature). The second step occurs within the temperature range 250–290 °C with the estimated mass loss 13.3% (calculated mass loss 13.5%) may is due to the elimination of two moieties of methoxy group. The DTG curve gives an exothermic peak at 276 °C (the maximum peak temperature). The third step of the thermal decomposition was in the temperature range 280–749 °C with the estimated mass loss 65.3% (calculated mass loss 65.0%) which is due to the complete decomposition of the organic ligand and loss of the remaining organic moiety as molecule of ligand. The DTG curve gives an exothermic peak at DTG 660 °C (the maximum peak temperature). The remaining weight of 17.1% corresponds to the percentage of the one CuO component.

3. Conclusion

The present study deals with the synthesis of novel 5-(arylazo) salicylaldimine derivatives as ligands to investigate their complexing behavior with Cu ion. The elemental analyses indicated the absence of chlorine atoms in the metal complexes. Also, elemental analyses are in perfect agreement with a 1:1 ratio metal/ligand. IR spectra showed that the ligands were coordinated to the copper ion in tridentate manner with ONO (or ONS) donor sites of the deprotonated phenolic-OH, azomethine-N, and deprotonated phenolic-OH (or deprotonated thiophenolic-SH). The TGA of the synthesized complexes indicated the presence of one molecule of water coordinated with metal ion. Based on spectroscopic data



Scheme 1. Proposed structures of the tridentate ligands and their metal complexes.

Table 1
IR and UV of synthesized compounds.

Compd. no.	Stretching vibration in cm^{-1}			Wave length λ_{max} (nm)
	$\nu_{CH=N}$	ν_{M-O}	ν_{M-N}	
H_2L^1	1618	–	–	356, 487
H_2L^2	1614	–	–	351, 494
H_2L^3	1617	–	–	354, 483
H_2L^4	1615	–	–	355, 497
H_2L^5	1618	–	–	350, 485
H_2L^6	1614	–	–	358, 492
H_2L^7	1616	–	–	353, 487
H_2L^8	1618	–	–	351, 490
$CuL^1 \cdot H_2O$	1605	490	421	436
$CuL^2 \cdot H_2O$	1604	500	421	396, 487
$CuL^3 \cdot H_2O$	1604	515	435	434
$CuL^4 \cdot H_2O$	1603	550	435	398, 484
$CuL^5 \cdot H_2O$	1601	522	435	433
$CuL^6 \cdot H_2O$	1604	531	435	391, 482
$CuL^7 \cdot H_2O$	1600	512	416	437
$CuL^8 \cdot H_2O$	1605	512	406	393, 480

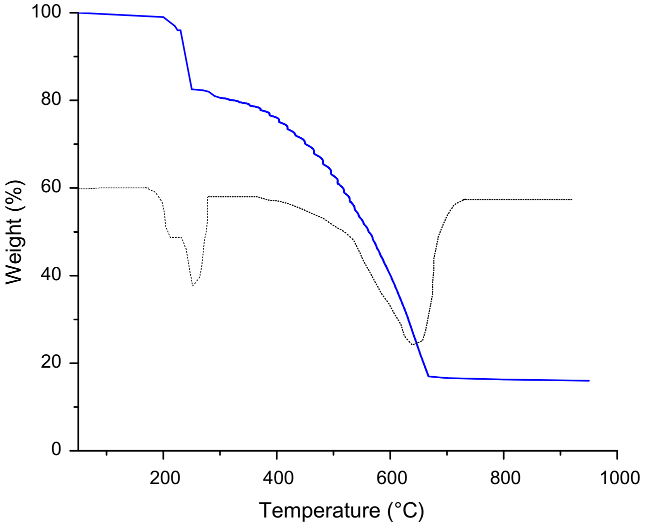


Fig. 1. TGA of **$CuL^3 \cdot H_2O$**.

and the elemental analyses results, it was conclude that the ligands were coordinated to the copper ion in tridentate manner with ONO (or ONS) donor sites. Furthermore, one water molecule was coordinated to the central metal atom. The composition of complexes can be represented as $CuL \cdot H_2O$.

4. Experimental

Melting points were determined on a digital Gallen-Kamp MFB-595 instrument and are uncorrected. Infrared spectra (KBr-disc) were recorded using a FTIR 5300 spectrometer (ν, cm^{-1}). NMR spectra were recorded on a Bruker instrument at 500 MHz with DMSO as solvent. Mass spectra were recorded on GC/MS finnigan SSQ 7000 spectrophotometer & GC Ms-QP 1000 EX mass spectrometer at 70 eV. UV spectra were recorded on UV-2401PC, UV–Vis Recording spectrophotometer. TGA–DTA curves were obtained using a Schimatzu DTG-60H instrument. Platinum pans were used for thermograms obtained between room temperature and 1000 °C. The heating rate was 10 °C/min. Microanalyses were carried out by the Microanalytical Laboratory, National Research Centre, Cairo, Egypt and the Microanalytical Research Center, Faculty of Science, Cairo University.

*4.1. Synthesis of 5-(arylazo)salicylaldehyde derivatives **A1–4***

The appropriate aniline derivative (3-bromoaniline, 3,5-dimethoxyaniline, 4-trifluoromethylaniline or 2-ethoxyaniline) (54 mmol) was dissolved in a mixture of concentrated hydrochloric acid (16 ml) and water (50 ml) and cooled to 0–5 °C. Sodium nitrite (58 mmol) was dissolved in water (16 ml) and cooled. The cold sodium nitrite solution was added in small volumes to the cold aniline hydrochloride solution, and the mixture was well shaken (solution A). The temperature was not allowed to rise above 10 °C. A solution of the salicylaldehyde (54 mmol) in 5% NaOH (90 ml) was cooled to 5 °C (solution B). Solution A was added very slowly to solution B; a dark-red solution was produced. When all the diazonium salt solution had been added, the mixture was allowed to stand in an ice bath for 30 min with occasional stirring. The dark-red precipitate was filtered off, washed well with water, dried and crystallized from ethanol to give **A1–4**.

*4.1.1. 5-((3-Bromophenyl)diazenyl)-2-hydroxybenzaldehyde (**A1**)*

Yield 85%; mp 146–145 °C; IR: ν/cm^{-1}: 3446 (OH), 1649 (C=O); ^{1}H NMR: δ/ppm = 7.14 (d, 1H, *J* = 9.24 Hz, Ar-H), 7.50 (m, 1H, Ar-H), 7.67 (d, 1H, *J* = 6.9 Hz, Ar-H), 7.83 (d, 1H, *J* = 6.9 Hz, Ar-H), 7.90 (s, 1H, Ar-H), 8.05 (d, 1H, *J* = 9.24 Hz, Ar-H), 8.14 (s, 1H, Ar-H), 10.32 (s, 1H, CHO), 11.73 (br, 1H, OH); Anal Calcd for $C_{13}H_9BrN_2O_2$ (305): C, 51.17; H, 2.97; N, 9.18; Found: C, 51.17; H, 2.97; N, 9.18%.

*4.1.2. 5-((3,5-Dimethoxyphenyl)diazenyl)-2-hydroxybenzaldehyde (**A2**)*

Yield 89%; mp 118–119 °C; IR: ν/cm^{-1}: 3321(OH), 1679 (C=O); ^{1}H NMR: δ/ppm = 3.79 (s, 6H, 2OCH$_3$), 6.63 (s, 1H, Ar-H), 7.00 (s, 2H, Ar-H), 7.15 (d, 1H, *J* = 8.4 Hz, Ar-H), 8.04 (d, 1H, *J* = 8.5 Hz, Ar-H), 8.14 (s, 1H, Ar-H), 10.33 (s, 1H, CHO), 11.48 (br, 1H, OH); ^{13}C NMR: 55.8 (2OCH$_3$), 100.9 (2C), 103.6, 118.7, 122.9, 124.7, 130.0, 145.1, 154.1, 161.3 (2C), 163.8, 191.3 (CHO); Anal Calcd for $C_{15}H_{14}N_2O_4$ (286.28): C, 62.93; H, 4.93; N, 9.79; Found: C, 62.80; H, 4.80; N, 9.90%.

*4.1.3. 2-Hydroxy-5-((4-(trifluoromethoxy)phenyl)diazenyl)benzaldehyde (**A3**)*

Yellow crystals; yield 85%; mp 132–133 °C; IR: ν/cm^{-1}: 3423 (OH), 1669 (C=O); ^{1}H NMR: δ/ppm = 6.96 (d, 1H, *J* = 9.25 Hz, Ar-H), 7.51 (d, 2H, *J* = 8.4, AB system), 7.88 (d, 2H, *J* = 8.4, AB system), 7.99 (d, 1H, *J* = 9.25 Hz, Ar-H), 8.08 (s, 1H, Ar-H), 10.29 (s, 1H, CHO), 11.75 (br, 1H, OH); MS, m/z (%): 310 (M$^+$; 15.19), 311 (M + 1; 15.2), 161 ($C_6H_4OCF_3$; 68.4), 153 (24.1), 149 (M-$C_6H_4OCF_3$; 54.5) 120 (19), 95 (100), 94.4 (19), 93 (54.5), 92 (29); Anal Calcd for $C_{14}H_9F_3N_2O_3$ (310): C, 54.20; H, 2.92; N, 9.03; Found: C, 54.20; H, 2.92; N, 9.03%.

*4.1.4. 5-((2-Ethoxyphenyl)diazenyl)-2-hydroxybenzaldehyde (**A4**)*

Yield 93%; mp 146–145 °C; IR: ν/cm^{-1}: 3321(OH), 1679 (C=O); ^{1}H NMR: δ/ppm = 1.37 (t, 3H, *J* = 6.85 Hz, CH$_3$), 4.19 (q, 2H, *J* = 6.85 Hz, CH$_2$), 6.96–7.20 (m, 3H, Ar-H), 7.40–7.45 (m, 2H, Ar-H), 7.68 (d, 1H, *J* = 8.4 Hz, Ar-H), 8.14 (s, 1H, Ar-H), 10.32 (s, 1H, CHO), 11.73 (br, 1H, OH); ^{13}C NMR: 15.3 (CH$_3$), 65.0 (CH$_2$), 115.0, 117.4, 117.3, 121.1, 121.6, 122.6, 125.4, 132.6, 138.7, 142.3, 146.3, 156.4, 163.5, 191.1 (CHO); Anal Calcd for $C_{15}H_{14}N_2O_3$ (270.28):: C, 66.66; H, 5.22; N, 10.36; Found: C, 66.80; H, 5.10; N, 10.50%.

*4.2. Synthesis of tridentate ligands **H_2L^{1-8}***

Equimolar amounts of 5-(arylazo) salicylaldehyde **A1–4** (0.01 mol) and the proper amine (2-aminophenol or 2-aminothiophenol) in ethanol (20 ml) was heated under reflux for 1 h and the reaction mixture was left to cool. The resulting solid product obtained was filtered off and recrystallized from ethanol to give the Schiff base ligands **H_2L^{1-8}**.

*4.2.1. 4-((3-Bromophenyl)diazenyl)-2-((2-hydroxyphenylimino)methyl)phenol (**H_2L^1**)*

Yield 80%; m.p. 229–231 °C; ^{1}H NMR: δ/ppm = 6.89 (t, 1H, *J* = 6.9, Ar-H), 6.95–7.07 (m, 2H, Ar-H), 7.15 (t, 1H, *J* = 8.4, Ar-H), 7.51 (m, 2H, Ar-H), 7.67 (d, 1H, *J* = 7.6, Ar-H), 7.83 (d, 1H, *J* = 7.65, Ar-H), 7.91 (s, 1H, Ar-H), 7.97 (d, 1H, *J* = 9.14, Ar-H), 8.23 (s, 1H, Ar-H), 9.18 (s, 1H, CH=N), 10.10 (br, 1H, OH), 15.06 (br, 1H, OH); ^{13}C NMR: 119.6, 122.3 (2C), 123.9, 127.2, 128.2, 130.0 (2C), 131.9, 133.7, 144.9, 149.5, 152.0, 153.6, 157.6, 161.6 (2C), 163.4, 165.0; Anal Calcd for $C_{19}H_{14}BrN_3O_2$ (396.24): C, 57.59; H, 3.56; N, 10.60; Found: C, 57.70; H, 3.40; N, 10.70%.

*4.2.2. 4-((3-Bromophenyl)diazenyl)-2-((2-mercaptophenylimino)methyl)phenol (**H_2L^2**)*

Yield 89%; m.p. 199–201 °C; ^{1}H NMR: δ/ppm = 6.91–7.83 (m, 8H, Ar-H), 7.91 (s, 1H, Ar-H), 7.97 (d, 1H, *J* = 9.14, Ar-H), 8.23 (s, 1H, Ar-H), 9.23 (s, 1H, CH=N), 11.78 (br, 1H, SH), 14.02 (br, 1H, OH); ^{13}C NMR: 119.4, 122.4 (2C), 123.8, 127.3, 128.3, 130.2 (2C), 130.5, 131.9, 133.7, 144.9, 149.5, 152.4, 153.4, 161.3 (2C), 163.0, 165.1; Anal Calcd for $C_{19}H_{14}BrN_3OS$ (412.30): C, 55.35; H, 3.42; N, 10.19; Found: C, 55.30; H, 3.30; N, 10.20%.

*4.2.3. 4-((3,5-Dimethoxyphenyl)diazenyl)-2-((2-hydroxyphenylimino)methyl)phenol (**H_2L^3**)*

Yield 91%; m.p. 227–229 °C; ^{1}H NMR: δ/ppm = 3.83 (s, 6H, 2OCH$_3$), 6.61 (s, 1H, Ar-H), 6.89 (t, 1H, *J* = 8.4 Hz, Ar-H), 6.95–7.09 (m, 4H, Ar-H), 7.14 (t, 1H, *J* = 8.4 Hz, Ar-H), 7.47 (d, 1H, *J* = 6.9 Hz, Ar-H), 7.92 (d, 1H, *J* = 9.2 Hz, Ar-H), 8.20 (s, 1H, Ar-H), 9.15 (s, 1H, CH=N), 10.05 (br, 1H, OH), 14.95 (br, 1H, OH); ^{13}C NMR: 56.0 (2OCH$_3$), 100.8 (2C), 103.3, 117.1, 119.1, 119.6, 119.8, 120.3, 127.2, 129.1, 130.1, 133.1, 144.1, 151.4, 154.4, 160.7, 161.4 (2C), 167.7; Anal Calcd for $C_{21}H_{19}N_3O_4$ (377.39): C, 66.83; H, 5.07; N, 11.13; Found: C, 66.90; H, 5.00; N, 11.30%.

*4.2.4. 4-((3,5-Dimethoxyphenyl)diazenyl)-2-((2-mercaptophenylimino)methyl)phenol (**H_2L^4**)*

Yield 83%; m.p. 150–152 °C; ^{1}H NMR: δ/ppm = 3.84 (s, 6H, 2OCH$_3$), 6.62 (s, 1H, Ar-H), 6.87 (t, 1H, *J* = 8.4 Hz, Ar-H), 6.95–7.09 (m, 4H, Ar-H), 7.13 (t, 1H, *J* = 8.4 Hz, Ar-H), 7.43 (d, 1H, *J* = 6.9 Hz, Ar-H), 7.95 (d, 1H, *J* = 9.2 Hz, Ar-H), 8.21 (s, 1H, Ar-H), 9.15 (s, 1H, CH=N), 11.78 (br, 1H, SH), 14.95 (br, 1H, OH); ^{13}CNMR: 56.1 (2OCH$_3$), 100.7 (2C), 103.2, 117.3, 119.2, 119.4, 119.8, 120.3, 127.2, 129.1, 130.1, 130.3, 133.1, 144.2, 151.4, 160.7, 161.4 (2C), 167.8; Anal Calcd for $C_{21}H_{19}N_3O_3S$ (393.46): C, 64.10; H, 4.87; N, 10.68; Found: C, 64.30; H, 4.70; N, 10.80%.

*4.2.5. 2-((2-Hydroxyphenylimino)methyl)-4-((4-(trifluoromethoxy)phenyl)diazenyl)phenol (**H_2L^5**)*

Yield 79%; m.p. 224–226 °C; ^{1}H NMR: δ/ppm = 6.85–7.02 (m, 3H, Ar-H), 7.15 (d, 1H, Ar-H), 7.45–7.56 (m, 3H, Ar-H), 7.85–7.97 (m, 3H, Ar-H), 8.22 (s, 1H, Ar-H), 9.19 (s, 1H, CH=N), 10.08 (br, 1H, OH), 15.04 (br, 1H, OH); Anal Calcd for $C_{20}H_{14}F_3N_3O_3$ (401.34): C, 59.85; H, 3.52; N, 10.47; Found: C, 59.90; H, 3.60; N, 10.30%.

*4.2.6. 2-((2-Mercaptophenylimino)methyl)-4-((4-(trifluoromethoxy)phenyl)diazenyl)phenol (**H_2L^6**)*

Yield 85%; m.p. 254–256 °C; ^{1}H NMR: δ/ppm = 7.10–8.14 (m, 10H, Ar-H), 8.33 (s, 1H, Ar-H), 9.23 (s, 1H, CH=N), 11.78 (br, 1H, SH), 14.02 (br, 1H, OH); Anal Calcd for $C_{20}H_{14}F_3N_3O_2S$ (417.40): C, 57.55; H, 3.38; N, 10.07; Found: C, 57.40; H, 3.50; N, 10.20%.

*4.2.7. 4-((2-Ethoxyphenyl)diazenyl)-2-((2-hydroxyphenylimino)methyl)phenol (**H_2L^7**)*

Yield 90%; m.p. 146–145 °C; ^{1}H NMR: δ/ppm = 1.37 (t, 3H, *J* = 6.85 Hz, CH$_3$), 4.23 (q, 2H, *J* = 6.85 Hz, CH$_2$), 6.90–8.10 (m, 10H, Ar-H), 8.19 (s, 1H, Ar-H), 9.18 (s, 1H, CH=N), 10.02 (br, 1H, OH), 13.92 (br, 1H, OH); Anal Calcd for $C_{21}H_{19}N_3O_3$ (361.39): C, 69.79; H, 5.30; N, 11.63; Found: C, 69.60; H, 5.20; N, 11.50%.

*4.2.8. 4-((2-Ethoxyphenyl)diazenyl)-2-((2-mercaptophenylimino)methyl)phenol (**H_2L^8**)*

Yield 88%; m.p. 162–164 °C; ^{1}H NMR: δ/ppm = 1.38 (t, 3H, *J* = 6.85 Hz, CH$_3$), 4.21 (q, 2H, *J* = 6.85 Hz, CH$_2$), 6.94–8.12 (m, 10H, Ar-H), 8.28 (s, 1H, Ar-H), 9.17 (s, 1H, CH=N), 10.32 (br, 1H, SH), 13.92 (br, 1H, OH); ^{13}C NMR: 15.3 (CH$_3$), 65.0 (CH$_2$), 115.2, 117.0, 118.3, 119.7, 121.1, 122.5, 122.8, 125.7, 126.0, 126.8, 127.0, 128.6, 132.7, 142.3, 145.9, 151.9, 156.2, 161.6, 164.5; Anal

Calcd for $C_{21}H_{19}N_3O_2S$ (377.46): C, 66.82; H, 5.07; N, 11.13; Found: C, 66.90; H, 5.20; N, 11.30%.

4.3. *Preparation of the complexes* $\mathbf{CuL^{1-8}\cdot H_2O}$

To a hot solution of $\mathbf{H_2L^{1-8}}$ (0.01 mol) in ethanol (50 ml), a solution of $CuCl_2\cdot 2H_2O$ (0.01 mol) in 3 ml ethanol (70%) was added then a catalytic amount of triethylamine was added. The reaction mixture was heated under reflux while stirring for 3 h then. The solid product that formed while hot was separated by filtration, washed with ethanol and dried to give $\mathbf{CuL^{1-8}\cdot H_2O}$ as colored greenish crystals.

4.3.1. $\mathbf{CuL^1\cdot H_2O}$

Yield 74%; Anal Calcd for $C_{19}H_{14}BrCuN_3O_3$ (473.95): C, 47.96; H, 2.97; Cu, 13.36; N, 8.83; Found: C, 47.96; H, 2.97; Cu, 13.36; N, 8.83%;

4.3.2. $\mathbf{CuL^2\cdot H_2O}$

Yield 78%; Anal Calcd for $C_{19}H_{14}BrCuN_3O_2S$ (489.93): C, 46.40; H, 2.87; Cu, 12.92; N, 8.54; Found: C, 46.40; H, 2.87; Cu, 12.92; N, 8.54%;

4.3.3. $\mathbf{CuL^3\cdot H_2O}$

Yield 81%; Anal Calcd for $C_{21}H_{19}CuN_3O_5$ (456.06): C, 55.20; H, 4.19; Cu, 13.91; N, 9.20; Found: C, 55.20; H, 4.19; Cu, 13.91; N, 9.20%;

4.3.4. $\mathbf{CuL^4\cdot H_2O}$

Yield 78%; Anal Calcd for $C_{21}H_{19}CuN_3O_4S$ (472.04): C, 53.32; H, 4.05; Cu, 13.43; N, 8.88; Found: C, 53.32; H, 4.05; Cu, 13.43; N, 8.88%;

4.3.5. $\mathbf{CuL^5\cdot H_2O}$

Yield 77%; Anal Calcd for: $C_{20}H_{14}CuF_3N_3O_4$ (480.02): C, 49.95; H, 2.93; Cu, 13.21; N, 8.74; Found: C, 49.95; H, 2.93; Cu, 13.21; N, 8.74%;

4.3.6. $\mathbf{CuL^6\cdot H_2O}$

Yield 68%; Anal Calcd for $C_{20}H_{14}CuF_3N_3O_3S$ (496.00): C, 48.34; H, 2.84; Cu, 12.79; N, 8.46; Found: C, 48.34; H, 2.84; Cu, 12.79; N, 8.46%;

4.3.7. $\mathbf{CuL^7\cdot H_2O}$

Yield 75%; Anal Calcd for $C_{21}H_{19}CuN_3O_4$ (440.07): C, 57.20; H, 4.34; Cu, 14.41; N, 9.53; Found: C, 57.20; H, 4.34; Cu, 14.41; N, 9.53%;

4.3.8. $\mathbf{CuL^8\cdot H_2O}$

Yield 77%; Anal Calcd for $C_{21}H_{19}CuN_3O_3S$ (456.04): C, 55.19; H, 4.19; Cu, 13.90; N, 9.19; Found: C, 55.19; H, 4.19; Cu, 13.90; N, 9.19%;

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2013.07.033.

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