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New acyclic 1,2,4-triazole-based Schiff base hydrazone; Synthesis, characterization, spectrophotometric and computational studies

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Abstract

A new 1,2,4-triazole-based Schiff base hydrazone with N, O, S donor set of atoms, H₄L, reaction of has been prepared by condensation N,N'-bis(3-formyl-5methylsalicylidene)ethane-1,2-diamine, H₂L, with 4-amino-3-(4-pyridyl)-5-mercapto-1,2,4triazole. The structure of H_4L was characterized by using FT-IR, UV-Vis and ¹H NMR spectroscopic methods as well as elemental analysis data. The formation constants of copper(II), cadmium(II), mercury(II) and silver(I) complexes of H_4L in DMSO were calculated using a hard model chemometrics method applying the spectrophotometric data. The protonation constants of H_4L were also measured in DMSO-water (1:10) mixture. Furthermore, ¹H chemical shifts of H_4L were studied by the gauge independent atomic orbital (GIAO) and continuous set of gauge transformations (CSGT) methods at the level of density functional theory using B3LYP/6-311++G* basis sets in gas phase. The computed chemical shifts are in reasonably good agreement with the experimental data.

Keywords: Schiff base, Chemometrics method, Hydrazone, 1,2,4-Triazole, stability constant, GIAO.

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1. Introduction

Recently, there is a renewed interest in synthesis and spectrophotometric properties of mixed multi-donor Schiff base hydrazones including heterocyclic moieties such as triazole, tetrazole, oxadiazole, pyridazine and so on [1-6]. Among them, Schiff base hydrazones bearing triazole moiety have attracted considerable attention due to their impressive, chemical and physical properties [7-10] biological activities [11-14], photochromic properties [15,16] and also their analytical applications [17]. On the other hand, 1,2,4-triazole-based hydrazones have long been involved in investigations of metal ion recognition because of number and nature of their donor atoms, and also their ability to accommodate the preferred coordination geometry of the metal ions [18,19]. Furthermore, several metal complexes of 1,2,4-triazole-based ligands were found to display enhanced physico-chemical properties and also biological activity over the uncomplexed free ligands [17,18]. In view of this, several articles devoted to the study of stability constants of metal complexes of triazole-based ligands in the last decade [20-23]. However, a survey of literature reveals that the study available on formation constants of metal complexes of 1,2,4-triazole-based Schiff base hydrazones is rare [24].

Various methods such as potentiometric titration [25], conductometry [26] and spectrophotometric determination [27] have been used for determination of stability constants of metal complexes. Among of these, spectrophotometric methods are more sensitive than others and are suitable for determination of stability constants of metal complexes in solution under different experimental conditions [27]. However, spectrum's overlapping of various chemical species involved in the equilibria is an important problem. At this condition, determination of stability constants by classical methods is very hard and can cause great uncertainties on the obtained results. This problem can be easily overcome

using chemometrics methods [28,29], where one can analyze whole spectra, thereby utilizing all spectral information.

The present paper is devoted to the design and synthesis of new 1,2,4-triazole-based Schiff base hydrazone, H₄L, (Scheme 1) and also spectrophotometric determination of stability constants of its Cu(II), Cd(II), Hg(II) and Ag(I) complexes. The H₄L has been prepared by condensation reaction of N,N'-bis(3-formyl-5-methylsalicylidene)ethane-1,2-diamine, H₂L, with 4-amino-3-(4-pyridyl)-5-mercapto-1,2,4-triazole [30]. The prepared compound has been characterized by spectroscopic methods (¹H NMR, UV-Vis and IR) as well as elemental analysis data. Also, we have tried to develop (i) the electronic properties of 1,2,4triazole-based ligands, and (ii) the calculation of stability constants of metal complexes for different mole ratio of ligand: metal. Furthermore, in order to compare experimental and theoretical NMR data, which may be helpful for correct assignments and understanding the relationship between chemical shielding and molecular structure, complete analyses of the ¹H NMR spectra of H_4L is reported. For this reason, the ¹H NMR isotropic chemical shieldings of H₄L were systematically studied by the GIAO/DFT (Gauge Independent Atomic Orbitals/ Density Functional Theory) [31,32] and CSGT/DFT (Continuous Set of Gauge Transformations/ Density Functional Theory) [33,34] methods with 6-311++G* basis set in gas phase.

2. Experimental

2.1. Materials

All chemicals and solvents were of reagent grade and purchased commercially. All solutions were prepared fresh daily. 2,6-diformyl-4-methylphenol [35], N,N'-bis(3-formyl-5-methylsalicylidene)ethane-1,2-diamine (H_2L) [36] and 4-amino-5-(4-pyridyl)-3-mercapto-1,2,4-triazole [30] were prepared as described previously.

2.2. Instrumentation

¹H NMR spectra were obtained with a Bruker Avance 300 MHz spectrometer. Absorption spectra were obtained with a Perkin-Elmer Lambda spectrophotometer in the range 300-600 nm, using 1cm path quartz cells. The measurements were performed at 25 (\pm 0.5) °C. The pH measurements were made using a Metrohm 691 pH meter equipped with a glass calomel combined electrode. Elemental analyses were performed on an Elementar Vario EL III elemental analyzer. Infrared spectra were recorded as pressed KBr discs, using a Unicom Galaxy Series FT-IR 5000 spectrophotometer (4000-400 cm⁻¹). All calculations were performed in MATLAB 7.8 (R2009a) and Microsoft Excel 2007.

2.3. Theoretical calculations

The structure data and ¹H chemical shifts of H_4L in gas phase were calculated using Gaussian-03 [37] series of programs. A starting molecular mechanics structure for the DFT calculations was obtained using the Hyper Chem 5.02 program [38]. The geometry of the prepared compound was fully optimized at the B3LYP/6-31G* level. Vibrational frequency analyzes, calculated at the same level of theory, indicate that the optimized structure is at the stationary points corresponding to global minima without any imaginary frequency. The calculations of the computed magnetic isotropic shielding tensors were performed using GIAO/DFT [31,32] and CSGT/DFT [33,34] methods at the B3LYP/6-311++G* basis set.

2.4. Preparation of H_4L

To a suspension of 4-Amino-5-(4-pyridyl)-3-mercapto-1,2,4-triazole (1 mmol) in DMF (5 mL), was added a solution of *N*,*N'*-bis(3-formyl-5-methylsalicylidene)ethane-1,2-diamine, H₂L, (0.5 mmol) in DMF (5 mL). The mixture was refluxed for 3 h and then filtered whilst hot. The crude orange product was collected and washed with ethanol and dried in air. Yield 50%, m.p. >300 °C, IR (KBr, cm⁻¹); 2920, 2856, 1637 (C=N), 1606, 1582 ((C=N)py), 1471 (C=C), 1255 (N-N), 1271 (C-O), 1217, 1091, 831 (C=S), 592. ¹H NMR (DMSO-d₆, ppm); $\delta_{\rm H} 2.28$ (s, 6H), 4.01 (s, 4H), 7.50 (s, 2H), 7.85 (br,s, 6H), 8.66 (s, 2H), 8.75 (br,s, 4H), 9.98

(s, 2H), 14.58 (br, 4H). Anal. Calc. for C₃₄H₃₀N₁₂O₂S₂: C, 58.10; H, 4.30; N, 23.92; S, 9.12 %. Found: C, 57.90; H, 4.60; N, 23.70; S, 9.10 %.

2.5. Thermodynamic calculations

The pH of the solution (DMSO/water, 1/10 V/V) containing H_4L (25 mL of 5.0×10^{-5} M) was gradually adjusted in the range of 1.5 to 10 using hydrochloric acid and potassium hydroxide solutions. Then the absorbance spectra of the solution were recorded in wavelength range of 300-600 nm. All experiments were carried out at the temperature (25±0.5) °C. Also, the effect of the addition of metal ions to the DMSO solution of H_4L was studied. The concentration of H_4L in DMSO was kept constant, and the metal ions were progressively added to the solution. After each addition, UV-Vis spectra of the solution were recorded.

3. Result and discussion

3.1. Characterization

The IR spectrum of H_4L containing vibrational bands at 1637, 1606, 1582 and 1255 cm⁻¹ which are assigned for v_8 and v_{as} of the azomethine, pyridine C=N and N–N bands, respectively [6,39]. The band at 831 cm⁻¹ can be assigned to the C=S stretching modes of mercapto substitute [6]. ¹H NMR spectrum of H_4L contains slightly broad signals in the region 14.58 ppm assigned to NH/SH and OH protons, as were confirmed by deuterium exchange when D₂O was added to DMSO-d₆ solution. The CH=N imine protons exhibit a singlet resonance in the region 9.98 ppm (See supplementary material).

3.2. Analysis of experimental data

In order to obtain some information about the stoichiometry, stability and selectivity of H_4L toward different two and monovalent metal ions, we investigated the complexation of H_4L with Cu^{2+} , Cd^{2+} , Hg^{2+} and Ag^+ ions spectrophotometrically in DMSO. It was found that the addition of metal ions to the H_4L solution affected on absorption spectrum of the ligand.

The changes in the UV–Vis spectrum of H_4L upon addition of Cu^{2+} , Cd^{2+} , Hg^{2+} and Ag^+ ions are presented in Figures 1-4, respectively.

The maximum wavelength of the ligand was observed at 353 nm. The maximum wavelengths of complexes were observed at 417, 359, 360 and 358 nm for Cu^{2+} , Cd^{2+} , Hg^{2+} and Ag^+ , respectively. Notably, the CT_1 band at *ca*. 353 nm decreased gradually, and the new band at *ca*. 420-435 nm appeared and simultaneously grew with increasing metal ions concentration. Also, the clean isobestic points at *ca*. 380-400 and *ca*. 460 nm appear after addition of metal ions, indicating interaction between metal ions and ligand.

The conditional stability constants were calculated by using hard-modeling analysis of spectrophotometric-mole ratio data. The computational procedure was performed using some Matlab codes written in our laboratory. The same procedure was applied to calculate protonation constants of the ligand by analysis of recorded spectrophotometric-pH metric data. The calculated spectra profile and concentration profiles are shown in supplementary material. The best model of complex equilibrium in solution for each metal ion was selected based on the degree of calculated fitting and experimentally recorded spectra (i.e. total residual sum of squares), the shape of spectra profiles (molar absorptivity) and meaningful concentration profiles (the non-negativity and unimodality restrictions). The stability constants values as well their standard deviation are listed in Table 1. The data show the sequence of the stability constants of complexes vary as Cu(II) > Hg(II) > Ag(I) > Cd(II). This may be due to different geometry tendencies of the metal ions. The high stability constant of ML for copper complex makes it superior as a suitable ligand for developing an analytical method for selective determination of copper ion.

3.3. pH dependence of the electronic absorption spectra of H₄L in DMSO

UV-Vis absorption electronic spectrum of H_4L in DMSO: water (1:10) at different pH values were carried out to understand the role of the phenolic functions in the acid-base

behavior of this ligand. The involvement of the phenol and triazole groups in the protonation steps is well depicted in absorption spectra. At acidic pH, the λ_{max} at 354 nm is observable, while at alkaline pH the spectra exhibit two λ_{max} at 308 and 432 nm, respectively. The different behavior of the chromophore can be attributed to the deprotonation of the phenolic and triazole groups, respectively, which are in agreement with data reported in the literatures [39,40,22]. In other words, the change in λ_{max} is due to the presence of various forms at low and high pH values. By monitoring of the spectra from acidic to basic pH, the band with $\lambda_{max} = 432$ nm starts to appear from pH \approx 5.5 and reaches its maximum absorbance at pH \approx 10, where protonated species are prevalent in solution. This means that the deprotonation of hydroxyl and triazole groups start in pH=5.5-10. We can conclude that the bands centered at 432 and 308 nm are arising from the deprotonated ligand; while the band located at 354 nm is mainly arising from the protonated species, Figure 5. The pKa values and their standard deviation are 3.61 ± 0.01 and 6.81 ± 0.01 for phenol and triazole moieties of H₄L, respectively. The calculated spectra profile and concentration profiles are shown in supplementary file.

3.4. Computational studies

The fully optimized geometries for different configurations of keto-enol and thione-thiol structures of H_4L (totally, for 8 structures) were calculated with the 6-31G* basis set at B3LYP level of theory [41,42]. Theoretical calculations show that the thione form, Figure 6, is stable than others in gas phase (see supplementary material). The validity of stable structure was confirmed by performing a frequency analysis. The selected bond lengths, bond angles and torsion angles of the optimized structure of H_4L are given in Table 2.

Moreover, in order to comparison between experimental and theoretical NMR data, which may be helpful in making correct assignments and understanding the relationship between chemical shielding and molecular structure, complete analyses of the ¹H NMR spectra of

H₄**L** is reported. For this reason, ¹H NMR chemical shifts of **H**₄**L** in gas phase were calculated (Table 3) using Gauge Independent Atomic Orbitals/Density Functional Theory (GIAO/DFT) [31,32] and Continuous Set of Gauge Transformations/ Density Functional Theory (CSGT/DFT) [33,34] methods with B3LYP/6-311++G* basis set. The following conclusions can be straightforwardly derived based on presented data. On an absolute scale, the computed NMR chemical shifts for **H**₄**L** at the DFT level of theory are in acceptable agreement with the experimental data. Differences between the calculated and measured values may be a result of solvent interactions, particularly in the case of hydrogen-bonding atoms (OH groups). The GIAO/DFT computed magnetic isotropic shielding tensors correlate better with the experimental data than the CSGT/DFT ones. The correlation between the experimental ¹H chemical shifts and the computed magnetic isotropic shielding tensors is linear (Figure 7 and Table 3) and it is described by the equation:

 $\delta_{exp} = a + b\sigma$

Parameters a and b for all complexes are:

 δ_{1H} = -0.9534 σ + 31.596 (R^2 = 0.9886) for GIAO method

and

 δ_{1H} = -0.7511 σ + 30.286 (R^2 = 0.9804) for CSGT method

Conclusions

Synthesis, FT-IR, ¹H NMR and UV-Vis data of new acyclic triazole-based Schiff base hydrazone, H_4L , is reported. The ¹H NMR chemical shifts of H_4L in gas phase was also systematically studied by GIAO/DFT and CSGT/DFT methods at B3LYP/6-311++G(d) basis set. The GIAO/DFT computed magnetic isotropic shielding tensors correlate better with the experimental data than the CSGT/DFT ones.

Moreover, the conditional stability constants were calculated by using hard-modeling analysis of spectrophotometric-mole ratio data. The data show the sequence of the stability constants of Cd(II), Cu(II), Hg(II) and Ag(I) complexes of H₄L vary as Cu(II) > Hg(II) > Ag(I) > Cd(II). The complex geometry may be affected on this variation. The high stability constant of ML for copper(II) complex makes H₄L superior as a suitable ligand for developing an analytical method for selective determination of copper(II) ion.

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Supplementary material

Supplementary data associated with this article can be obtained free of charge via http://www.araku.ac.ir/~h_khanmohammadi/SupportingInformation-9.doc

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	Metal / Ligand $logK_{\hat{a}}$			Me	Metal / Ligand $logK_{\hat{a}}$			
	Cu ²⁺	ML M2L M2L2 SSE ^b	6.10±0.01 10.83±0.01 16.70±0.01 0.05	Ag^+	ML M2L M3L SSE	3.98±0.01 9.09±0.01 13.00±0.02 0.01		
	Hg ²⁺	ML M2L SSE	5.39 ± 0.02 10.72 ± 0.01 0.01	Cd ²⁺	ML ML2 SSE	3.20 ± 0.01 8.92 ± 0.01 0.01	_	
^a L, Schiff b	ase; ^b SS	SE, Sum of Sc	quares Errors.				•	
^a L, Schiff base; ^b SSE, Sum of Squares Errors.								
P								

Table 1.	Results	of logK ₃ for	Metal-Ligand	Complexes ^a
	1	01 10 51-4 101	Litter and and	e e

Bond lenghts		Bond lenghts		Bond lenghts	
N(29)-N(30) N(26)-N(24) N(29)-C(28)	1.359 1.395 1.312	N(26)-C(79) N(26)-C(28) N(24)-C(22)	1.396 1.392 1.292	C(79)-S(80) N(30)-C(79)	1.683 1.359
Bond angles		Bond angles		Bond angles	
N(29)-N(30)-C(79) N(24)-N(26)-C(79) N(24)-N(26)-C(28) N(26)-N(24)-C(22)	115.0 125.7 124.6 112.8	N(29)-C(28) -N(26) N(30)-C(79)-N(26) N(26)-C(79)-S(80) N(30)-C(79)-S(80)	110.1 101.6 131.8 126.4	N(30)-N(29)-C(28) C(79)-N(26)-C(28)	104.5 108.5

Table 2. Selected calculated bond lengths (Å) and bond angles (°) for H_4L .



Table 3.Selected hydrogen chemical shifts (δ , ppm) in d₆-DMSO and calculated magnetic isotropic shielding tensors for more stable isomer of **H**₄Lin gas phase

Hydrogen	-	-	Hydrogen	-	Hydrogen	-	Hydrogen	-
a	1 2 3	4.02 27.92 26.96	C	7.50 24.63 25.01	e	7.87 23.39 24.65	g	7.87 23.98 24.79
b	1 2 3	9.98 22.27 22.71	d	2.20 29.48 28.69	f	8.66 23.73 24.60	h	8.75 23.27 22.95

1; Experimental chemical shifts, 2; computed magnetic isotropic shielding tensors at GIAO B3LYP/6-311++G* for all atoms and 3; computed magnetic isotropic shielding tensors at CSGT B3LYP/6-311++G* for all atoms

R

Figure Captions:

Scheme 1. Synthesis of acyclic triazole-based Schiff base hydrazone (H₄L)

Figure 1: Experimental absorption spectra for the Cu^{2+} complex with H₄L. The analytical concentration of H₄L is 5.0×10^{-5} (mol·L⁻¹), The concentrations of Cu^{2+} ion is: (1) 0.0; (2) 2.0×10^{-6} ; (3) 1.0×10^{-6} ; (4) 1.8×10^{-5} ; (5) 2.6×10^{-5} ; (6) 3.4×10^{-5} ; (7) 4.2×10^{-5} ; (8) 5.0×10^{-5} ; (9) 5.8×10^{-5} ; (10) 6.6×10^{-5} ; (11) 7.4×10^{-5} ; (12) 8.2×10^{-5} ; (13) 9.0×10^{-5} ; (14) 9.8×10^{-5} and (15) 1.0×10^{-4} (mol·L⁻¹).

Figure 2: Experimental absorption spectra for the Cd^{2+} complex with **H**₄**L**. The concentration of ligand and Cd^{2+} ion is the same as described in Figure 1.

Figure 3: Experimental absorption spectra for the Hg^{2+} complex with H_4L . The concentration of ligand and Hg^{2+} ion is the same as described in Figure 1.

Figure 4: Experimental absorption spectra for the Ag⁺ complex with H₄L. The analytical concentration of H₄L is 5.0×10^{-5} (mol·L⁻¹), The concentrations of metal is: (1) 0.0; (2) 2.0×10^{-6} ; (3) 1.0×10^{-6} ; (4) 1.8×10^{-5} ; (5) 2.6×10^{-5} ; (6) 3.4×10^{-5} ; (7) 4.2×10^{-5} ; (8) 5.0×10^{-5} ; (9) 5.8×10^{-5} ; (10) 6.6×10^{-5} ; (11) 7.4×10^{-5} ; (12) 8.2×10^{-5} ; (13) 9.0×10^{-5} ; (14) 9.8×10^{-5} ; (15) 1.0×10^{-4} ; (16) 1.1×10^{-4} ; (17) 1.2×10^{-4} ; (18) 1.3×10^{-4} ; (19) 1.4×10^{-4} ; (20) 1.5×10^{-4} (mol·L⁻¹).

Figure 5: The electronic absorption spectra of H_4L in DMSO/water (1:10) solution at pH 1.5–10.0.

Figure 6: B3LYP/6-31G* geometry optimized structure of the H₄L.

Figure 7: Plot of experimental chemical shifts *vs.* magnetic isotropic shielding tensors from (a) the CSGT B3LYP/6-311++G* and (b) GIAO B3LYP/6-311++G* calculations for **H**₄**L**.





Figure 2.



Figure 4.



Figure 6.



Figure 7.

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1,2,4-triazole-based New acyclic Schiff base hydrazone; Synthesis, characterization, spectrophotometric and computational studies

Formation constants of copper(II), cadmium(II), mercury(II) and silver(I) complexes of new bisiminated 1,2,4-triazole-based Schiff base hydrazone in DMSO have been determined by hard model chemometrics method. Furthermore, ¹H chemical shifts of the prepared ligand were studied by the GIAO/DFT and CSGT/DFT methods using B3LYP/6-311++G* basis sets.



Research highlights:

> Synthesis of new acyclic 1,2,4-triazole-based Schiff base hydrazone is reported > Formation constants of metal complexes were determine by hard model chemometrics method > The 1H chemical shielding of ligand was studied by GIAO and CSGT methods at DFT level of theory. Acceleration