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Complexation of manganese(II), cobalt(II), nickel(II) and copper(II) by a ligand derived from 1,2,4-triazole: Potentiometric studies and Density Functional Theory calculations

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ABSTRACT

DFT calculations have been conducted to understand the conformational and tautomeric preference of 4-amino-5-(2-hydroyphenyl)-2,4-dihydro-3*H*-1,2,4-triazole-3-thione ligand. The results suggest that the thione tautomer is found to be the most stable form in the gas phase, which is in very good agreement with the FT-IR and crystallographic data. The protonation constants of the ligand and the stability constants of its complexes with Mn(II), Co(II), Ni(II) and Cu(II) have been determined by potentiometry in water-ethanol (90:10, *v*:*v*) mixture. The absolute pKa values of the ligand have been calculated using DFT method to complement and help the assignment of potentiometric data. DFT calculations have also been carried out for some metallic complexes species formed in solution in order to propose their most probable structures.

1. Introduction

Among organic compounds, which can serve as ligands, 1,2,4-triazole and its derivatives have received much interest because of their many interesting features [1]. The substituted 1,2,4-triazoles attracted more attention than the unsubstituted one, because they also display a broad range of biological activity, finding application as antitumor, antibacterial, antifungal and antiviral agents and exhibit rich coordination modes, leading to new complexes with innovative structures [1-7].

Previously, the substituted 1,2,4-triazole, 4-amino-5-(2-hydroyphenyl)-2,4-dihydro-3*H*-1,2,4-triazole-3-thione, is synthesized but insufficiently characterized [8]. This compound contains the thioamide group, which is capable of undergoing thione-thiol (HN-C=S ↔ N=C-SH) tautomerism as illustrated in Figure 1.

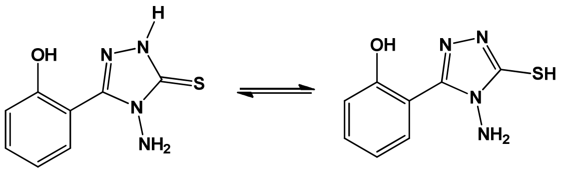

Figure 1. Formula of the ligand and its tautomeric forms.

There is no data concerning the structure of this ligand in solution, but an x-ray diffraction study reported by Dinçer *et al.* indicates that in solid state this compound exists as thionic form [9].

Given the promising properties of this ligand, it is of interest to study its acid-base character. Indeed, it has been generally recognized that the acid-base character is one of the important factors that governs the coordination behavior of ligands. In this study, the acidity constants of 4-amino-5-(2-hydroyphenyl)-2,4-dihydro-3*H*-1,2,4-trazole-3-thione were determined by potentiometric pH titration.

Literature survey reveals that the biological activities of ligands are often enhanced after coordination to a metal [10,11]. Therefore this paper reports some potentiometric studies on the coordination behavior of the ligand towards essential metal (II) such as manganese (II), cobalt (II), nickel (II) and copper (II) ions. The presence of S=C–N–NH_2 (see Figure 1) moiety in 4-amino-5-(2-hydroyphenyl)-2,4-dihydro-3*H*-1,2,4-trazole-3-thione ligand allows a bidentate coordination to a metal ion through the amine and thione substituents providing a stable five-membered ring [12].

Usually, a variety of conformational changes are required to achieve coordination, and this is often greatly influenced by the electronic properties of the metal ion [13]. Thus it is worthwhile to study the conformational preference of the free ligand taken in its two tautomeric forms by quantum mechanics density functional theory (DFT) calculations as extensive literature search shows that no such investigation has been previously reported. Furthermore the pK_a calculations were performed using DFT method to complement and help the analysis of potentiometric data. Indeed, the title compound has several potentially protonatable and deprotonatable sites, then measurement of pK_a value by simple titration do not provide clear information about the site of protonation or deprotonation. In the present study, we have also carried out

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DFT calculations for some metallic complexes species formed in solution, in order to propose their most probable structures.

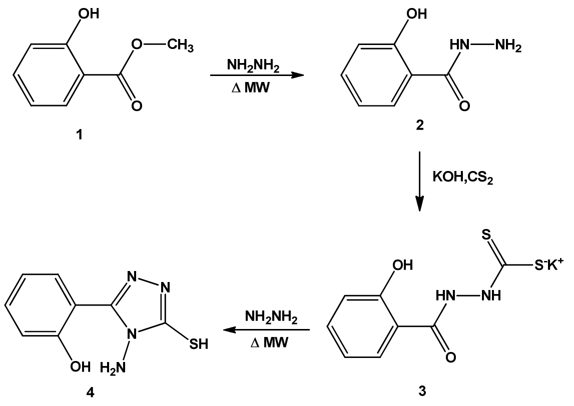
2. Experimental

2.1. Reagents

Starting materials for the synthesis of the ligand were purchased from Fluka or Aldrich and were used without purification. Hexahydrated metal chlorides were obtained from Merck, exact concentrations of metal solutions were determined by titration with EDTA. Carbonate free sodium hydroxide (the titration solution 0.1 M) was prepared and standardized against a standard hydrochloride acid solution (0.1 M).

2.2. Synthesis and characterization of the ligand

Multimode microwave reactor (a modified microwave oven CandyMGA 20M) has a single magnetron (2450 MHz) with maximum delivered power of 800 W. Melting points were determined on a Stuart scientific SPM3 apparatus fitted with a microscope and are uncorrected. IR spectra were recorded on Perkin Elmer (Spectrum one) FT/IR Fourier transform infrared spectrometer, in the range 4000-400 cm^{-1}, using KBr disks. Electronic absorption spectra in ethanol solution were recorded on a UV-Visible JASCO V 560 spectrophotometer using quartz cells (0.5 cm) in the 400-200 nm. ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d6 solutions on a Bruker Avance 300 (300.13 MHz for ^{1}H and 75.47 MHz for ^{13}C) spectrometer. Chemical shifts are reported in ppm (δ) using TMS as internal reference and coupling constants (*J*) are given in Hz. 4-Amino-5-(2-hydroyphenyl)-2,4-dihydro-3*H*-1,2,4-trazole-3-thione was prepared following the reaction sequences depicted in the following Scheme 1.



Scheme 1

The 2-hydroxy benzohydrazide, **2**, have been synthesized by reaction of methyl-2-hydroxybenzoate, **1**, with hydrazine hydrate in methanol. This mixture was heated in the microwave for 20 min, whilst 6 hours were required by conventional procedure. The compound **3** is obtained in excellent yield and its physicochemical features are identical to those commercial product. Treatment of **3** with an excess amount of hydrazine gave only one pure product. The analytical data of this product indicate that the reaction took place with keeping a phenol skeleton. Its mass spectra [molecular ion at *m/z* 209 $(M+H)^{+}$ and 231 $(M+Na)^{+}$] indicate the incorporation of on hydrazine molecule. Elemental analysis indicates a molecular formula $C_8H_8N_4OS$, compatible with the structure of the expected product, 4-amino-5-(2-hydroxy phenyl)-2,4-dihydro-3*H*-1,2,4-triazole-3-thione, **4**. To a solution of potassium 2-(2-hydroxy benzoyl) hydrazinecarbadithionate **3** (10 mmol) and 98% hydrazine (20 mmol) was added water (10 mL). This mixture was heated by micro waves with a fixed power of 300 W for 5 min. After this period, 50 g of ice was added to the reaction mixture and the white solid was precipitated by acidification with concentred hydrochloric acid. The precipitate thus formed was collected by filtration and washed several times with cold water to eliminate acid trace. White solid obtained was recristallized with ethanol.

4-Amino-5-(2-hydroxyphenyl)-2,4-dihydro-3H-1,2,4-triazole-3-thione (**4**): Yield: 65%. M.p.: 205 °C. FT-IR (KBr, ν, cm^{-1}): 3467 (O-H), 3293-3197 (NH_2), 1611 (C=N), 1302 (C=S). UV (Ethanol, ν_{max}, nm (ε)): 340 (1600), 318 (8700), 290 (11600), 252 (23100). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 5.6 (s,2H, NH_2), 6.69-7.43 (m, 4H, Ph), 10.39 (br, 1H, OH), 13.85 (s, 1H, SH). ^{13}C NMR (75.5 MHz, DMSO-d_6, δ, ppm): 113.4 (C-2), 116.6 (C-6), 119.5 (C-4), 131.2 (C-3), 132.6 (C-5), 149.5 (C-5, triazolic ring), 156.4 (C-3, triazolic ring), 165.4 (C-1); DEPT 135 δ (ppm) phenolic ring: 116.6 (C-6), 119.5 (C-4), 131.2 (C-3), 132.6 (C-5). Anal. calcd. for $C_8H_8N_4OS$: C, 46.14; H, 3.87; N, 26.90. Found: C, 46.20; H, 3.82; N, 26.86%.

2.3. Potentiometric measurements

The potentiometric titrations were carried out in water-ethanol (90:10, *v*:*v*) solution at a 0.2 mol/L ionic strength (NaCl) and 0.01 mol/L (HCl) in a thermostated vessel at 25.0±0.1 °C under nitrogen atmosphere. The solutions were titrated with carbonate free NaOH (0.1 mol/L), the pH values were measured with a Schott instruments Titroline easy. The pH meter readings in water-ethanol (90:10, *v*:*v*) mixture differs by an amount of 0.02 from the corrected reading in aqueous medium. Accordingly the presence of 10% of ethanol in the solvent has a minor influence on the protonation or complexes stability constants obtained [14]. The measurements were carried out for the ligand alone at the concentration $C_L = 5.10^{-4}$ mol/L, and for the ligand in the presence of metal cation at the ligand/ metal ratio 1:2. The Sirko program was used to calculate both protonation and stability constants of the ligands and their complexes [15]. Computer-refined values of the constants corresponding to the minimum standard deviation were retained and used for the calculation of species distribution.

2.4. Computational methods

The B3LYP [16,17] density functional method as implemented in the Gaussian 03 package [18] was used throughout the whole study. All structures were fully optimized using the 6-31+G(d,p) basis set. The solvation free energies for the protonated and neutral species were obtained theoretically using a conductor-like polarizable continuum variant (CPCM) [19]. CPCM calculations were performed as single points (without optimization) on the gas-phase geometries.

The pK_a calculations were carried out using the following relationship (discussed in detail in reference [20]:

$$pKa=\left[G_{gas}(B)-G_{gas}\left(BH^{+}\right)+\Delta G_{solv}(B)-\Delta G_{solv}(BH^{+})-269.0)\right]/1.3644 \quad (1)$$

The acidity constant of S-H was calculated using the methodology proposed by Panina [21]. The procedure has been obtained using a training set of ten RSH thiols with known hydroxyl pK_a values. The optimized structures of the complexes were obtained at B3LYP level where the 6-31G(d) basis set has been used for all atoms except the metal ions in which the ECP basis sets downloaded from the EMSL Basis Set Library have been used.

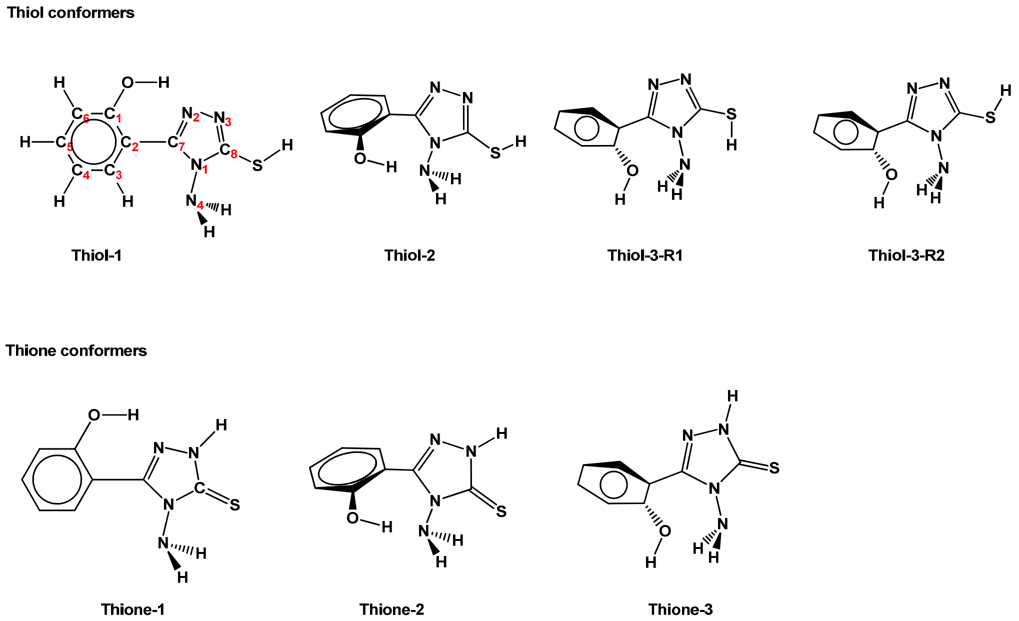


Figure 2. Schematic representation of the different tautomers/rotamers forms of triazol. Standard numbering and adopted nomenclature are presented.

3. Results and discussion

3.1. Experimental characterization of the ligand and its tautomeric forms

Tautomerism has been found to be important in the chemistry of 1,2,4-triazole family in general. In the case of aminosulfanyltriazoles such as our ligand (product **4**), tautomerism may involve the substituent group C=S. It has been reported that the crystal structure of product **4** corresponded to the thione form, but they showed thiol-thione tautomerism in solution. The spectrometric data available for the ligand 4-amino-5-(2-hydroyphenyl)-2,4-dihydro-3*H*-1,2,4-triazole-3-thione are IR spectrum recorded as KBr disk from powder and ^{1}H and ^{13}C NMR spectra recorded in DMSO-d6 solutions. A careful examination of the IR spectra (KBr disk) reveals the presence of only the thionic tautomeric form in solid state by the observation of an intense band at 1302 cm^{-1} attributable to a (C=S) stretching vibration and by the absence of any band in the range of the S-H stretching vibration (2450-2560 cm^{-1}). In the UV spectra in solution (ethanol), the presence of a shoulder with weak intensity at 340 nm characteristic of $n \rightarrow \pi^*$ transition can be attributable also to thione (C=S) form. NMR recorded in DMSO-d_6 reveal the absence of the C=S group of the thione and presence of the S-H group of the thiol form. The O-H and S-H resonances were observed in the ^{1}H NMR spectrum 10.39 and 13.85 ppm, respectively. Its spectrum ^{13}C NMR also confirms the presence of 2-substituted phenolic ring (DEPT 135: 116.6; 119.5; 131.2; and 132.6). The existence of the triazolic ring was confirmed mainly by the resonances C-3 and C-5 (156.4 and 149.5 ppm, respectively). The IR spectra reveals the existence of only the thionic form in solid state in agreement with the X-ray molecular structure determination [9], but the UV and NMR spectrum reveal the presence of one form (thione) in ethanol and the other form (thiol) in DMSO. There is probably equilibrium between the two forms in solution, which is dependent on the nature of the solvent and it is not possible to determine the proportion of each form.

3.2. Tautomerism and conformational stability of the ligand by DFT calculation

The following figure shows the tautomeric forms of the ligand and their conformers for which we performed the calculations, with the numbering scheme and the nomenclature used in this paper.

The two groups of structures correspond to two classes of tautomers:thione (Thione-1, Thione-2, Thione-3) and thiol (Thiol-1, Thiol-2, Thiol-3-(R1 and R2)). The analysis of the conformational species of 4-amino-5-(2-hydroyphenyl)-2,4-dihydro-3*H*-1,2,4-triazole-3-thione must take into consideration the rotation around C_2-C_7 (see Figure 2) leading to various low energy conformers for both tautomers.

The relative energies of both tautomers and their conformers obtained in gas phase, after including the ZPVE corrections, are given in Table 1.

The first conspicuous fact is that the Thione-1 conformer of thione tautomeric form is the global minimum of the potential energy surface in gas phase followed directly by Thione-2 with a difference of energy of 1.61 kcal/mol. This DFT calculation is in good agreement with the X-ray [9] and FTIR spectroscopic data discussed above, indicating that in solid state the parent compound exist in thione tautomer.

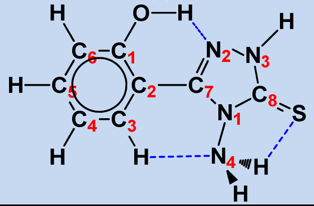
The crystal structure of the ligand reported by Dinçer *et al.* [9] is topologically similar to the global minimum thione-1 obtained by DFT calculation in gas phase. Notice that the energy gap between thione (thione-1) form and the most stable thiol tautomer (Thiol-1) is relatively important, about 12.23 kcal/mol.

Among a number of physical and chemical factors that are responsible for the tautomeric equilibrium, solvation occupies one of the most important roles. The energetic parameters of the tautomeric forms in the aqueous phase (e = 78.5) obtained with CPCM continuum model of solvation at B3LYP/6-31+G(d,p) level are also listed in Table 1. Using solvent effects (CPMC model), the energy difference indicate that the thione tautomer is still more stable than thiol form, this relative energy is too high to allow a significant population of the thiol tautomer at room temperature to be formed.

Table 1. Zero-point corrected total energies E_0+ZPVE (a.u.), relative energies $\Delta E_{(ZPVE)}$ (kcal/mol) in gas aqueous phases and dipole moment μ (Debye). At B3LYP/6-31+G(d,p) level of theory.

Structures	**Gas phase**			**Aqueous phase**			
	E_0+ZPVE	**$\Delta E_{(ZPVE)}$**	**μ**	**E_0**	**ΔE_0**	**ΔGs**	**μ**
Thiol-1	-1001.918054	12.23	5.74	-1002.099294	13.76	-3.85	8.15
Thiol-2	-1001.908315	18.34	4.73	-1002.095605	16.08	-7.36	6.88
Thiol-3-R1	-1001.908453	18.26	8.21	-1002.095614	16.07	-7.26	11.48
Thiol-3-R2	-1001.908973	17.93	6.37	-1002.095379	16.22	-6.31	8.87
Thione-1	-1001.937552	00.00	1.86	-1002.120591	00.40	-2.62	2.77
Thione-2	-1001.934985	01.61	2.56	-1002.121233	00.00	-4.18	3.74
Thione-3	-1001.921485	10.08	8.15	-1002.115207	03.78	-8.76	11.11

Table 2. Important geometric parameters and optimized hydrogen bonds of the thione-1 obtained at B3LYP/6-31+G(d,p). For numbering of the atoms see Figure 2.

Bonds lengths (Å)	**Thione-1**	**Exp.** [a]	**Bond angle (°)**	**Thione-1**	**Exp.** [a]	**Dihedral angle (°)**	**Thione-1**	**Exp.** [a]
$S{=}C_8$	1.667	1.677	$<S-C_8-N_1$	127.4	125.9	$N_2-C_7-C_2-C_1$	0.003	10.9
C_2-C_7	1.463	-	$<N_2-N_3-C_8$	113.7	112.9			
N_1-N_4	1.397	1.399	$<O-H\cdots N_2$	143.4	140.2			
$OH\cdots N_2$	1.766	1.893	$<N_4-H\cdots S$	88.8	108.3			
$N_4H\cdots S$	3.029	2.734	$<C_3-H\cdots N_4$	126.6	125.2			
$C_3H\cdots N_4$	2.265	2.352	$<S-C_8-N_1$	127.4	125.9			

[a] Ref. [9].

It is worth to mention that the presence of a solvent modify the hierarchy only between Thione-1 and Thione-2 conformers, the most stable becomes Thione-2. From this point, we can conclude that the polarity of the water has great effects on the structures of the thione conformers.

The overall succession of the studied structures is the following: Thione-1 ≈ Thione-2 > Thione-3 > Thiol-1 > Thiol-2 > Thiol-3-R1 > Thiol-3-R2. Noteworthy that the relative energy differences between Thione-1 and Thione-2 is very small, then it is very likely that 1,2,4-triazole-3-thione exists mostly in a mixture of these two conformers in the gas and solution phases.

The optimized bond length and angles obtained for Thione-1 at B3LYP/6-31+G(d,p) level are listed in Table 2 along with available experimental data. The thione-1 tautomeric form being topologically similar to the X-ray crystal structure reported by Dincer *et al.* [9].

Overall, the optimized parameters obtained by the B3LYP method is approximately similar than those observed experimentally. The $S{=}C_8$ bond lengths of 1.677 Å for x-ray and 1.667 Å for B3LYP/6-31+G(d,p) are indicative of a significant double-bond character. The title molecule consists of 2 aromatic rings, the hydroxyphenyl ring and 1,2,4-triazole ring. The molecule is almost coplanar and the dihedral angle between the planes is 10.9 ° and 0.003 ° by X-ray and B3LYP/6-31G(d,p), respectively. As can be seen, between the calculated and observed dihedral angle parameter, there is a difference. Given that the experimental result was obtained from molecule in the solid state while the theoretical result belongs to isolated molecule in gaseous phase, this difference is not surprising.

In Thione-1 tautomeric form, the co-planarity of triazole ring and the benzene ring facilitates the formation of three intramolecular interactions, $O-H\cdots N_2$, $C-H\cdots N_4$ and bifurcated $N_4-H\cdots S$ H-bonds. The intramolecular $O-H\cdots N_2$, $C-H\cdots N_4$ and $N_4-H\cdots S$ H-bonds are predicted as 1.893, 2.352 and 2.734 Å by x-ray and 1.766, 2.266 and 3.029 Å by B3LYP/6-31+G(d,p), respectively.

3.3. Potentiometric studies on the protonation constants of the ligand

The titration curve of the ligand presents three inflexion points at pH values 5.4-8.0 and 9.5, respectively. Therefore, three equilibriums corresponding to the protonation can be assumed in these conditions. Regardless of its tautomeric form, the ligand has only two ionization hydrogen atoms (H_2L), but it has several nitrogen atoms potentially protonables.

The overall constant β_{qr} calculated by the Sirko program are defined by the equation:

$$qH^{+} + rL^{2-} \rightarrow [\,H_qL_r]^{q-2} \quad \beta_{qr} \tag{2}$$

The species distribution diagrams as function of pH (Figure 3) shows that the deprotonation of H_3L^+ is achieved at pH 5-6 and leads to the successive formation of H_2L, HL^- and L^{2-} in agreement with the experimental titration curve. The values of overall (log β_{qr}) and successive (log K_i) protonation constants of the ligand are listed in the Table 3.

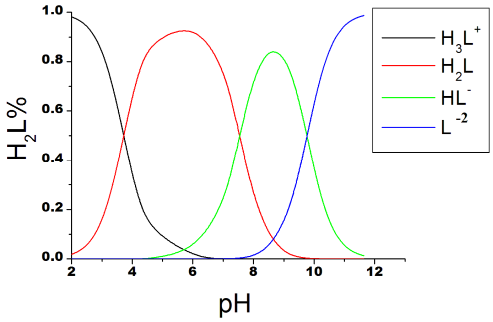


Figure 3. Species distribution diagram of the ligand.

The title compound has several potentially protonatable and deprotonatable sites, then measurement of pK_a value by simple titration do not provide information about the site of protonation or deprotonation. In addition the parent compound exists in two tautomeric forms making the experimental determination of the actual protonation state at a given pH more complicated. The pK_a values determined by potentiometric pH titrations in aqueous solution are the following: Protonation of the neutral ligand pK_a = 3.72, for deprotonation two values have been obtained 7.54 and 9.77. The third acidity constant (pK_a = 9.77) can be attributed without ambiguity to the deprotonation of the phenolic group.

Table 3. Protonation constants of the ligand (Log K_i)*.

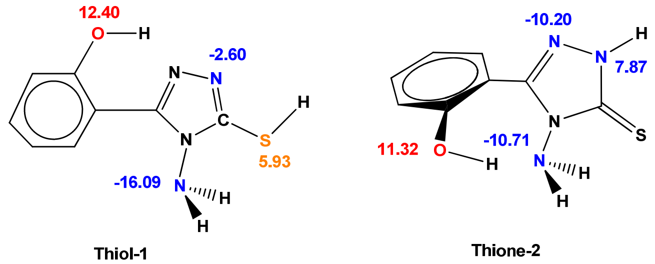
q	r	Log $ß_{qr}$	Equilibrium	Log K_i
1	1	3.72±0.03	H_2L /H_3L^+	3.72
2	1	11.26±0.05	HL^-/H_2L	7.54
3	1	21.03±0.07	L^{2-}/HL^-	9.77

* q = number of protons; r = number of ligands.

Table 4. Stability constants of the complexes*.

M_p	H_q	L_r	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
1	0	1	6.19 ± 0.11	6.78 ± 0.08	6.33 ± 0.10	13.67 ± 0.16
1	1	1	9.38 ± 0.27	10.40 ± 0.17	10.73 ± 0.17	17.80 ± 0.19

* p= number of metals; q = number of protons; r = number of ligands.



Thiol-1

Thione-2

Figure 4. Theoretical results of pK_a values obtained for both tautomers.

The second (7.54) can be attributed to the deprotonation of the thiol group or the NH group of the triazole ring depending of the tautomeric form. However it is difficult to assign a protonation site for the first value (3.72).

In order to confirm the assignment made for the experimental acidity constants of the parent compound in water solution, the calculations of the pK_a values were carried out.

3.4. Theoretical prediction of absolute pK_a values of the ligand

According to our DFT calculation (see Table 1) the Thiol-1 and Thione-2 conformers of thiol-thione tautomers of the ligand are the most stable species in solution. An overview of the theoretical results of pK_a values obtained for both tautomers (Thiol-1 and Thione-2) using procedure described above is given in Figure 4.

The sites of protonation or deprotonation reported in Figure 4 are in the focus of the present study because they are of relevance for metal-ion binding. As can be seen on Figure 4, the calculated pK_a value obtained for the phenolic group of Thione-1 tautomeric form has the small deviation compared to the experimental value (pK_a = 9.77 assigned to the phenol group). The confusion about the acidity constant pK_a = 7.54 is not definitely resolved, indeed the values obtained for thiol (pK_a = 5.93 of SH) and thione (pK_a = 7.87 of NH) forms are close to the experimental value (within 0.33 to 1.61). However, based on thermodynamic stability, one can conclude that the pK_a = 7.33 value should correspond to the deprotonation of the Nitrogen atom N_3 of the triazol ring.

In the case of amino group present in both tautomeric forms our calculations give large negative values of pK_a. This suggests that the basicity of the NH_2 group is too weak to be detected. Our calculation is in very close agreement with the experimental observation obtained for 4-amino-3-methyl-1,2,4-triazoline-5-thione that excludes any protonation on the amine nitrogen atom even with excess of hydrochloric acid, indicating that the amino group it is a very weak base [22].

The smaller experimental value of pK_a = 3.72 is very different from the calculated value pKa = -10.20 obtained for the N_2 site of thione tautomer. However, the pKa value calculated for the N_2 site (pK_a = -2.60) of thiol form is only slightly erroneous. Then it is possible to assign the smaller experimental value of pK_a = 3.72 to the N_3 site (pK_a = -2.60) of thiol tautomeric form.

3.5. Potentiometric Studies on the Stability of the complexes

The coordination behavior of the ligand towards manganese(II), cobalt(II), nickel(II) and copper(II) ions was studied in solution by potentiometry. In the case of metal-ligand system, the overall stability constant β_{pqr} calculated by the Sirko program are defined by the equation:

$$pM^{2+} + qH^{+} + rL^{2-} \rightarrow [M_pH_qL_r]^{(2p+q-2r)} \qquad \beta_{pqr} \qquad (3)$$

The species distribution diagram of the metal(II)-ligand as function of pH are reported in Figure 5.

The titration curves indicate that at least two metallic species was formed. Several models have been tested. The best fit of the titration curve is obtained with considering the formation of only $[MHL]^+$ and [ML] species. The values of overall stability constants (Log β_{pqr}) of the complexes are listed in the Table 4.

The stability sequence observed for the complexes is Cu(II) > Ni(II) > Co(II > Mn(II), in agreement with Irving-Williams series.

3.6. Geometric optimization of the complexes by DFT calculation

To have more insight on the interactions of our triazole ligand with metals, research on the geometry and structures of triazole-metal compounds are of great importance. It is well known that Co(II) and Mn(II) ions are inclined to adopt octahedral coordination geometry with ligands. The ligands act as monoanionic bidentate and coordinate to Cu(II), Ni(II), Co(II) and Mn(II) ions generating complexes of general formula $[MHL]^+$ and [ML]. The more significant specie obtained by potentiometric titrations carried out in water-ethanol (90:10, *v:v*) solution is the complex $[MHL]^+$. The ligand is coordinated in a bidentate way after deprotonation.

Notice that the ligand can exhibit thione-thiol tautomerism (HN-C=S ↔ N=C-SH), then the labile hydrogen atom may be attached to either nitrogen or sulfur atom.

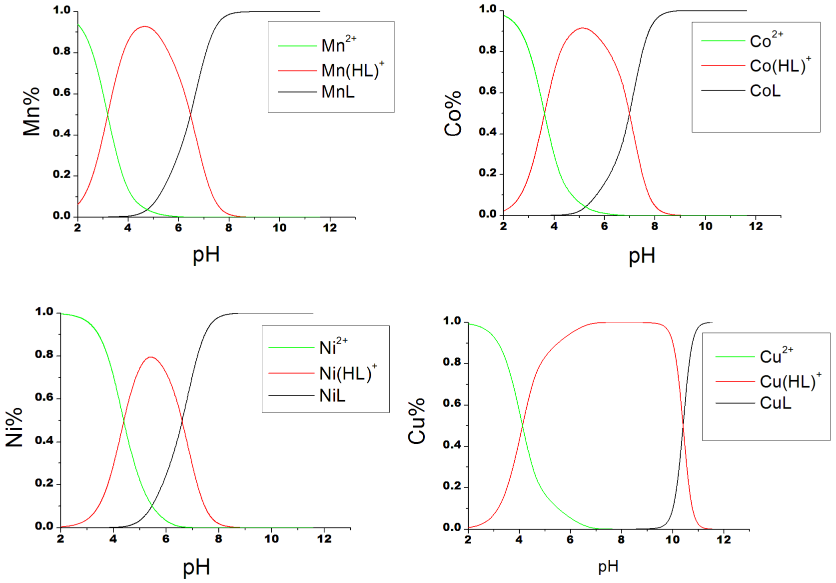


Figure 5. Species distribution diagram of the Mn(II), Co(II), Ni(II) and Cu(II) complexes.

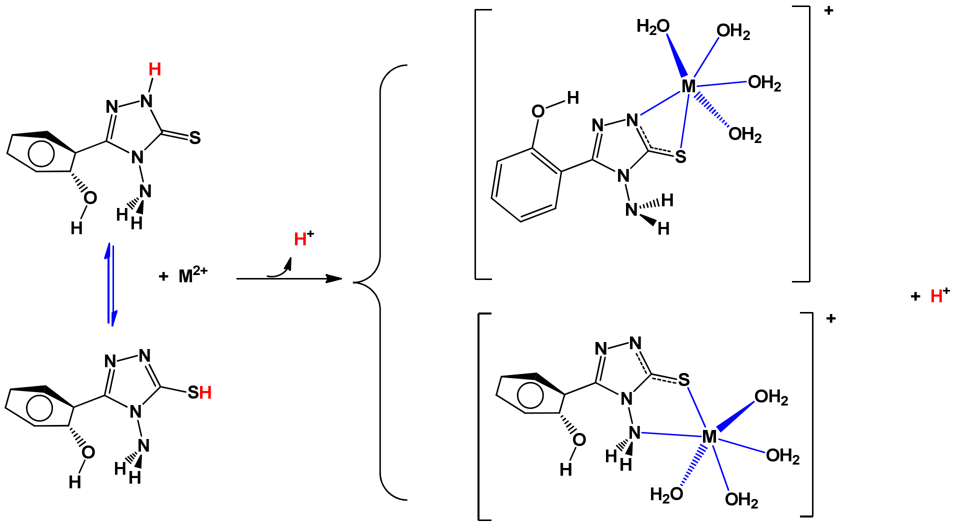


Figure 6. Possible structure of [MHL]$^+$ complexes (M= Co(II) and Mn(II)).

It must be outlined that the resulting protonation constant values obtained in this study for the ligand, leads to the conclusion that the protons of the S-H of the thiol form or N-H of the endocyclic nitrogen atom present in thione tautomeric form are the first deprotonated sites in aqueous solution.

The preferable coordination modes of 4-amino-5-mercapto-1,2,4-triazole to bond with metal ions is usually through S=C-N-N which is a bidentate mode able to form stable five-membered rings with the transition metals. Based on the literatures, the coordination modes adopted in this study for the ligand is presented in Figure 6.

Quantum chemical DFT method was employed to model the geometry of the complexes. Selected structural parameters of [MHL]$^+$ complexes (M = Co(II) and Mn(II)) are listed in Table 5.

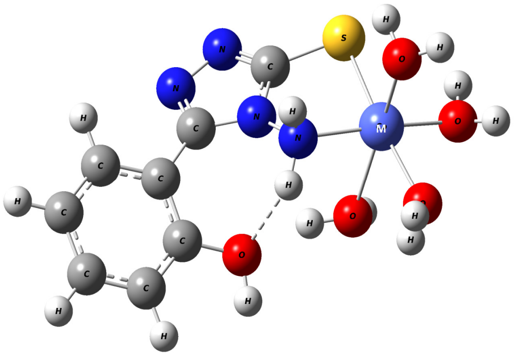
The Mn and Co metal atoms display a distorted octahedral environment (see optimized geometry included in Table 5). In the reported structure, the average Mn–OH$_2$ distance is 2.118 Å and the average Co–OH$_2$ distance is 2.179.

Another relevant structural parameter is the N–M–S angle. In the present investigation, the angle is 86.6 ° for N–Mn–S and 87.0 ° for N–Co–S, these values fit nicely in the range shown by the compounds having the same coordination environment [23].

4. Conclusion

The synthesis of 4-amino-5-(2-hydroyphenyl)-2,4-dihydro-3*H*-1,2,4-triazole-3-thione ligand and its characterization using spectroscopic (IR solid-state, UV/Vis, ^{1}H and ^{13}C solution-state) methods has been reported. DFT calculations have been applied to the study of structures and the acidity constants of the two possible tautomers of the ligand, using the B3LYP/6-31+G(d,p) level of theory.

Table 5. Selected interatomic distances (Å) and angles (°) for complexes obtained at B3LYP level. For numbering of the atoms see Figure 2.



Optimized geometry of complexes (M = Co(II) and Mn(II))

	Mn	Co
Bond length		
M-S	2.351	2.304
$M-N_4$	2.108	2.045
$S-C_8$	1.754	1.752
N_1-N_4	1.417	1.416
$OH\cdots N_4$	1.875	1.929
$M-OH_2$	2.104	2.030
$M-OH_2$	2.136	2.070
$M-OH_2$	2.123	2.269
$M-OH_2$	2.110	2.346
Bond angle		
N_4-M-S	86.6	87.0

Spectroscopic studies and DFT calculations on the ligand show that the thione is the prevalent form in both solution and solid states. According to DFT calculations three strong hydrogen bonds stabilize the thione form.

Potentiometric titration of the ligand in water-ethanol (90:10, *v*:*v*) mixture allows to the determination of its protonation constants 3.7; 7.5 and 9.7. Calculated absolute pK_a values obtained at B3LYP/6-31+G(d,p) level were found to be in agreement with the measured values, confirming high predictive power of the theoretical approach used. The stability constants of the Metal-Ligand complexes of Mn(II), Co(II), Ni(II) and Cu(II) were also determined by potentiometric titration for both species $[M(HL)]^+$ and [ML] formed in the present experimental conditions. The stability order obtained is in agreement with Irving-Williams series. DFT calculations undertaken in the framework of octahedral geometry for the complex suggest that the ligand is coordinated to the metal in a bidentate mode through sulfur and amino nitrogen atoms.

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