

Synthesis, spectroscopic studies and crystal structure determination of a Zn(II) complex of 1-(2-hydroxybenzylidene)thiosemicarbazide

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Abstract: The ligand 1-(2-hydroxybenzylidene)thiosemicarbazide (H_4L) was prepared by reaction of thiosemicarbazide and 2-hydroxybenzaldehyde in a reflux ethanol solution. The complexes are prepared by reaction of the ligand with the appropriate metal salt in methanol solutions. Elemental analysis, IR and UV spectroscopies, conductance measurement, fluorescence and room temperature magnetic susceptibility measurement were used to characterize the compounds. For the zinc complex its structure was determined by single X-ray diffraction technique. The zinc compound crystallizes in the tetragonal space group $I4_1/cd$ with the following unit cell parameters: $a = 14.1357(3) \text{ \AA}$, $b = 24.9289(9) \text{ \AA}$, $V = 4982.2(3) \text{ \AA}^3$, $Z = 16$, $R_1 = 0.033$ and $wR_2 = 0.08$. In the crystal of the mononuclear complex $[Zn_2(H_3L)_2Cl_2] \cdot (CH_3OH)_2$ each Zn(II) center is five coordinated by one nitrogen atom, one thionyl sulfur atom and one phenoxo oxygen atom of the ligand and one chloride atom. For the two ligand molecule the phenoxo oxygen atom acts as bridge between the two Zn(II) ions. For both metal centers the coordination polyhedron is best described as a pentagonal pyramid. The molecules are linked together by multiple hydrogen bond interaction resulting in a three-dimensional network.

Keywords: Schiff base, metal transition, crystal, luminescence, square pyramidal.

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I. Introduction

Thiosemicarbazide and its derivatives are widely used in the preparation of organic ligands and their complexes [1–5]. Many thiosemicarbazide-based compounds are obtained by condensation with a keto precursor [6–8] and by alkylation of different parts of the thiosemicarbazide group [9–11]. The ligands derived from thiosemicarbazide are polydentate with several donor sites such as S, N and O. These different sites, depending on the topology of the ligand, can have several modes of coordination. This ability to generate multiple complexes is well reported in the literature [12–15]. Complexes containing thiosemicarbazide motifs are known for their biological activities [4,16,17]. The biological activity of thiosemicarbazide-based ligands and of the complexes obtained depends on the chemical group attached to the carbon atom of C=S group. They are anticancer [5,18], anti-inflammatory [19], antibacterial [20–22], antifungal [23], antiviral [23–25] or anti-HIV [26,27]. The type of metal used can enhance the biological properties of the complex compared to the free ligand. The zinc atom is an essential trace element present in metallo-enzymes in which it can play a catalytic role [28,29]. For these reasons, synthesis of different thiosemicarbazone ligands and their complexes with the first series of transition metals have received considerable attention. It is in this context that we have tried to

synthesize the ligand 1-(2-hydroxybenzylidene)thiosemicarbazide (H_4L) and its zinc complex which are characterized by spectroscopic and X-ray diffraction techniques.

II. Materials and Method

2.1 Starting materials and Instrumentations

Commercially available 2-hydroxybenzaldehyde, thiosemicarbazide and $ZnCl_2$ were purchased from Aldrich and used without further purification. The analyses for carbon, hydrogen, nitrogen, sulphur and chlorine were carried out using a LECO CHNS-932 instrument. The IR spectra were recorded as KBr discs on a Perkin Elmer Spectrum Two spectrophotometer ($4000-400\text{ cm}^{-1}$). The molar conductance of 10^{-3} M solution of the metal complex in acetonitrile was measured at $25\text{ }^\circ\text{C}$ using a WTW LF-330 conductivity meter with a WTW conductivity cell. Emission spectra were recorded on a Varian Cary Eclipse spectrofluorimeter. Samples in adequate solvent solutions were placed in 1 cm path length quartz cuvettes for room temperature measurements.

2.2 Synthesis of the ligand

2-Hydroxybenzaldehyde (1.2212 g, 10 mmol) and thiosemicarbazide (0.9114 g, 10 mmol) were refluxed during 3 hours in ethanol (20 mL) (Scheme 1). On cooling an orange precipitate appeared and was isolated by filtration. The solid was washed with cold ethanol and dried on P_2O_5 in a desiccator to yield monohydrated 1-(2-hydroxybenzylidene)thiosemicarbazide (H_4L) (Scheme 1). Color: Orange. Yield: 81%. M.p.: $216\text{ }^\circ\text{C}$. IR (KBr, ν , cm^{-1}): 3451 (O-H (phenol)), 3313 (N-H), 1601 (C=N), 1538-1462 (C=C aromatic), 1263 (C-Ophenolic), 1110 (N—N), 748 (C=S). $^1\text{H NMR}$ (250 MHz, DMSO- d_6 , δ , ppm): 7.18-7.40 (m, 4H, Ar-H), 7.9 (s, 2H, $-NH_2$), 8.38 (s, 1H, H-C=N), 9.80 (s, 1H, HN-N), 11.40 (s, 1H, OH). $^{13}\text{C NMR}$ (250 MHz, DMSO- d_6 , δ , ppm): 115.99 (C6), 119.23 (C4), 120.29 (C2), 126.73 (C3), 131.05 (C5), 139.56 (C7), 154.26 (C1), 177.36 (C8). MS (ESI-TOF, m/z): 196.1 $[H_4LH]^+$. Anal. calcd. for $C_8H_9N_3OS$: C, 49.21; H, 4.65; N, 21.52, S, 16.42. Found: C, 49.26; H, 4.61; N, 21.44; S, 16.35.

2.3 Synthesis of the complex

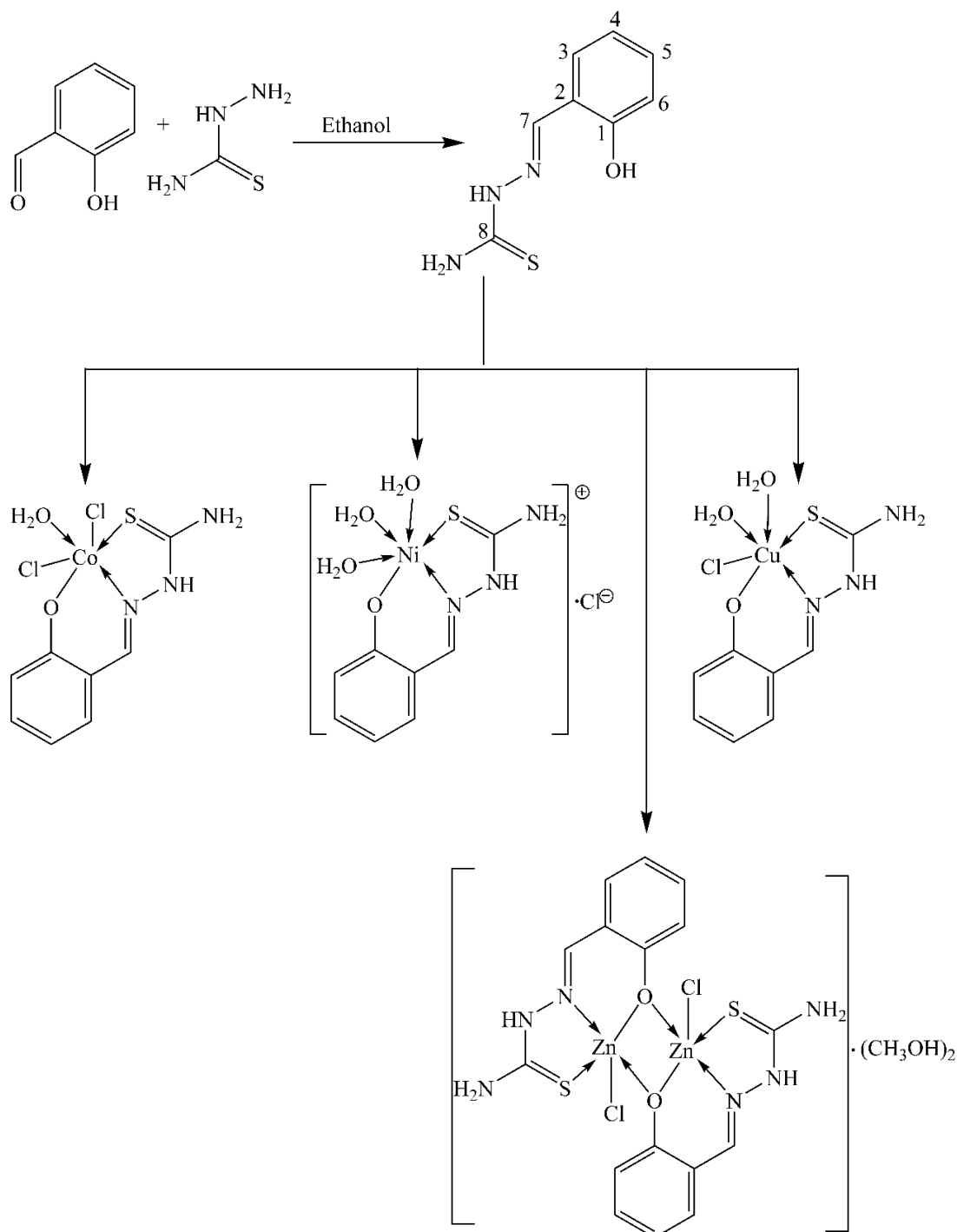
A 10 mL of methanol solution of H_4L (195.1 mg, 1 mmol) was mixed with 10 mL of methanol solution of the appropriate metal hydrated salt (0.5 mmol) ($CoCl_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $ZnCl_2 \cdot 2H_2O$) to give a suspension. The resulting mixture was stirred and refluxed for two hours. On cooling the suspension was filtered and the resulting filtrate was kept at 298 K. After seven days, precipitate was recovered for Co(II), Ni(II) and Cu(II) complexes. For Zn(II) complex, crystals suitable for X-ray analysis were collected.

(1) $[Co(H_3L)(H_2O)(Cl)_2]$. Yield: 55 %. IR (KBr, ν , cm^{-1}): 3385 (O-H); 3237 (N-H), 1599 (C=N), 1550-1470 (C=C aromatic), 1200 (C-Ophenolic), 1126 (N—N), 669 (C=S). Anal. calcd. For $CoC_8H_{10}Cl_2N_3O_2S$: C, 28.09; H, 2.95; N, 12.28; Cl, 20.73; S, 9.37. Found: C, 28.03; H, 2.90; N, 12.25; Cl, 20.77; S, 9.32. Λ ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$): fresh solution: 14; after 15 days: 27. Diamagnetic. $\mu_{\text{eff}} = 0.00\ \mu_B$. UV-visible (λ_{max} (nm), acetonitrile): 583, 485, 387, 345, 313.

(2) $[Ni(H_3L)(H_2O)_3] \cdot (Cl)$. Yield: 58 %. IR (KBr, ν , cm^{-1}): 3279 (O-H), 3175 (N-H), 1600 (C=N), 1554-1472 (C=C aromatic), 1157 (C-Ophenolic), 1122 (N—N), 668 (C=S). Anal. calcd. For $NiC_8H_{14}ClN_3O_4S$: C, 28.06; H, 4.12; N, 12.27; Cl, 10.35; S, 9.36. Found: C, 28.02; H, 4.15; N, 12.30; Cl, 10.32; S, 9.33. Λ ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$): fresh solution: 42; after 15 days: 53. $\mu_{\text{eff}} = 3.41\ \mu_B$. UV-visible (λ_{max} (nm), acetonitrile): 866, 515, 380.

(3) $[Cu(H_3L)(H_2O)_2(Cl)]$. Yield: 62 %. IR (KBr, ν , cm^{-1}): 3283 (O-H), 3187 (N-H), 1599 (C=N), 1560-1470 (C=C aromatic), 1201 (C-Ophenolic), 1123 (N—N), 661 (C=S). Anal. calcd. For $CuC_8H_{12}ClN_3O_3S$: C, 29.18; H, 3.67; N, 12.76; Cl, 10.77; S, 9.74. Found: C, 29.14; H, 3.66; N, 12.80; Cl, 10.81; S, 9.72. Λ ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$): fresh solution: 21; after 15 days: 25. $\mu_{\text{eff}} = 2.04\ \mu_B$. UV-visible (λ_{max} (nm), acetonitrile): 695, 452, 458.

(4) $[Zn_2(H_3L)_2(Cl)_2] \cdot 2(CH_3OH)$. Yield: 49 %. IR (KBr, ν , cm^{-1}): 3387 (O-H), 3188 (N-H), 1598 (C=N), 1544-1474 (C=C aromatic), 1154 (C-Ophenolic), 1119 (N—N), 726 (C=S). Anal. calcd. For $Zn_2C_{18}H_{24}Cl_2N_6O_4S_2$: C, 33.04; H, 3.70; N, 12.85; Cl, 10.84; S, 9.80. Found: C, 33.00; H, 3.66; N, 12.80; Cl, 10.81; S, 9.76. Λ ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$): fresh solution: 12.0; after 15 days: 20.0. Diamagnetic.



Scheme 1: Synthetic scheme for the ligand and M^{II} ($Mn = Co, Ni, Cu, Zn$) complexes preparation.

2.4 X-ray data collection, structure determination and refinement

Details of the X- rays crystal structure solution and refinement are given in Table 1. Diffraction data were collected using an XtaLAB AFC12 (RINC): Kappa single diffractometer with graphite monochromatized $MoK\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). All data were corrected for Lorentz and polarization effects. No absorption correction was applied. Complex scattering factors were taken from the program package *SHELXTL*[30]. Structure, solution and refinement were performed using *SHELXT*[31] and *SHELXL-2014/7*[32]. All hydrogen atoms were added in calculated positions and refined in riding mode on the parent atom. Molecular graphics were generated using *ORTEP-3*[33].

Table-1. Crystallographic data and refinement parameter for the complex.

Empirical formula	C ₁₈ H ₂₄ Cl ₂ N ₆ O ₄ S ₂ Zn ₂
Formula weight (g/mol)	654.19
Temperature (K)	100
Crystal system, space group	Tetragonal, I4 ₁ cd
Crystal size (mm)	0.32 × 0.26 × 0.20
Mo Kα(Å)	0.71073
a (Å)	14.1357(3)
b (Å)	14.1357(3)
c (Å)	24.9286(9)
V (Å ³)	4981.2(3)
Z	8
D _{cal} (g cm ⁻³)	1.745
F(000)	2656
μ (mm ⁻¹)	2.346
θ _{max} (°)	29.138
h, k, l ranges	-19 ≤ h ≤ 15, -17 ≤ k ≤ 18, -33 ≤ l ≤ 30
Measured reflections	15020
Independent reflections	2959
Reflections [I > 2σ(I)]	2850
R _{int}	0.084
R[F ² > 2σ(F ²)]	0.033
wR(F ²)	0.079
Goodness-of-Fit	1.06
Data/parameters/restraints	2952/169/4
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.40, -0.58

III. Results and Discussion

3.1 General study

The 1:1 condensation reaction between thiosemicarbazide and 2-hydroxybenzaldehyde yield the ligand 1-(2-hydroxybenzylidene)thiosemicarbazide abbreviated as H₄L. Mixing a methanolic solutions of MCl₂ and H₄L in molar ratio of 1:1 gives a yellow powder. The elemental analyze and the physicochemical characterization allow to formulate the compounds. The complex **4** was formulated as [Zn₂(H₃L)₂(Cl)₂]·2(CH₃OH) and the formulation was confirmed by X-ray diffraction study. In the infrared spectrum of the ligand a strong band pointed at 1601 cm⁻¹ attributed to the C=N bond is the evidence that the condensation occurred. The strong band which appears at 748 cm⁻¹ was attributed the C=S. The bands at 3451 cm⁻¹ and 1263 cm⁻¹ were assigned respectively to the phenolic H—O— and the C—O_{phenolic}. The ¹H NMR spectrum of the ligand recorded in DMSO-d₆ reveals a broad band signal at 11.40 ppm attributed to the phenolic —OH group. The signals at 9.80 ppm and 7.9 ppm are assigned respectively to the HN— and the —NH₂ of the semicarbazide moiety. The proton of the imine group H—C=N is revealed at 8.38 ppm. The ¹³C NMR spectrum reveals a band at 177.36 ppm (—C=S) assigned to the carbon atom carrying the thione function of the thiosemicarbazide. The carbon atom of the azomethine group (H—C=N) is pointed 139.56 ppm. Upon coordination to the M(II) ions the main bands of the free ligand are shifted to low frequencies. The band attributed to phenolic O—H disappeared upon coordination indicating the deprotonation of the ligand. The ν_{C—O} vibration at 1263 cm⁻¹ in the spectrum of the free ligand shifts to low frequencies for all the complexes. This fact is indicative of the involvement of the phenoxo oxygen atom in coordination in all of the complexes. The

infrared spectra of the complexes show bands at ca. 1598 cm^{-1} , bands in the ranges 3237-3175 cm^{-1} and 726-661 cm^{-1} which are respectively attributed to the imine function ($\nu_{\text{C=N}}$), to the $\nu_{\text{N-H}}$ stretching and to the thione moiety ($\nu_{\text{C=S}}$). These facts are indicative of the coordination of the ligand to Mn(II) ion through the nitrogen azomethine atom, the phenoxo oxygen atom and the thione sulfur atom. In the ligand spectrum, the band at 1110 cm^{-1} assigned to $\nu_{\text{N-N}}$ is shifted to the high frequencies (1122-1126 cm^{-1}) after coordination with the metal centers. This observation is consistent with the increase in the N-N bond strength, confirming the coordination of the azomethine nitrogen atom to zinc ion. For complexes **1-3**, bands of coordinated water are pointed in the region 3283-3236 cm^{-1} which are confirmed by the bands near 840 cm^{-1} [34]. In the spectrum of complex **4**, a broad band at 3385 cm^{-1} is attributed to the lattice methanol [35]. The molar conductivity for a freshly prepared acetonitrile solution of the complexes was measured. After standing for two weeks the conductivity measurement was repeated. The Co(II); Cu(II) and Zn(II) show values in the between 12 and 27 $\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ which are characteristic of a neutral electrolyte [36]. The Ni(II) complex is a 1/1 electrolyte owing to, the measured values of 42 $\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ for freshly acetonitrile solution and 53 $\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ after standing for two weeks [36]. All the complexes are stable in acetonitrile solution. The cobalt complex is diamagnetic, indicating the oxidation of Co(II) in Co(III). The electronic spectrum of the cobalt complex shows a three bands centered at ca. 583 nm, 485 nm and 387 nm which are attributed to $^1\text{A}_{1g} \rightarrow ^3\text{T}_{2g}$, $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ and $^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$ transitions respectively indicating a distorted octahedral environment around the metal center [37]. Bands appearing at 345 nm and 313 nm are due to LMCT charge transfer [38]. The room temperature magnetic susceptibility measurement shows for Ni(II) complex a value of 3.41 μ_B which is slightly higher than the spin only value of 2.82 μ_B for Ni^{2+} . This value agrees with value reported for Ni^{2+} in octahedral environment [39,40]. The electronic spectra of the nickel(II) complex gives three main bands at 866 nm, 515 nm and 380 nm indicating an octahedral environment around the metal center. These bands are respectively assigned to transitions $^3\text{A}_{2g} \rightarrow ^3\text{T}_{2g}$, $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}$ (F) and $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}$ (P) [41,42]. The Cu(II) complex shows value of 2.04 μ_B which is higher than reported for Cu^{2+} (1.73 μ_B). The value of 2.04 μ_B lies in the range corresponding to mononuclear copper complex with one unpaired electron and is consistent with an octahedral or a square pyramidal geometry [43]. The electronic spectrum of the copper complex shows a strong broad d→d band centered at ca. 695 nm which is indicative of a distorted octahedral environment around the Cu center [44,45]. Additional bands at 452 nm and 458 nm are due the LMCT charge transfer.

3.2 X-ray structure of $[\text{Zn}_2(\text{H}_3\text{L})_2(\text{Cl})_2]\cdot 2(\text{CH}_3\text{OH})$

Yellow crystals suitable for X-ray diffraction of complex **4** were grown by slow evaporation of the compound from methanol solution. The complex crystallizes in the tetragonal system with space group of $I4_1/cd$. Crystal data, collection and refinement parameters are listed in Table 1. An ORTEP diagram of the complex **4** with the atomic numbering is presented in Fig. 1. The packing diagram is displayed if Fig. 2. Selected bond distances and angles are listed in Table 2. Hydrogen-bonding data are listed in Table 3. The asymmetric unit contains two zinc atoms, two deprotonated ligand molecules, two chloride atoms and two lattice methanol molecules solvent. Each of the ligand acts in tridentate fashion through one imino nitrogen, one thione sulfur atom and one phenoxo oxygen atom which acts as bridge between two zinc(II) centers. The chelation results in the formation of a five-membered ring ZnSCNN and a six-membered ring NCCCOZn. Each of the Zn(II) center resides in a distorted square pyramidal environment according to the Addison parameter $\tau = 0.0962$ ($\tau = (\alpha - \beta)/60$ where α and β are the largest angles subtended by Zn atom) [46]. The basal plan is occupied by three atoms (N, O, S) of the same ligand molecule and one phenoxo oxygen atom of the second ligand molecule. The apical position is occupied by a chloride atom. The sum of the angles in the basal plane which is 339.62° deviates severely from ideal value of 360° and the angles formed by the chloride atom in the apical position with the atoms in the basal plan are higher than 90° [$\text{Cl1—Zn1—O1} = 101.37(10)^\circ$, $\text{Cl1—Zn1—N3}^i = 106.24(9)^\circ$, $\text{Cl1—Zn1—S1}^i = 110.53(4)^\circ$, $\text{Cl1—Zn1—O1}^i = 109.85(11)^\circ$] (Table 2) indicating a severe distortion of the geometry around the zinc center. The Zn1—O1—Zn1^i and O1—Zn1—O1^i are respectively 102.72(11)° and 77.18(11)° (Table 2). The distance Zn—Cl which is 2.3066(10) Å is higher than the value reported for a square pyramidal zinc complex [47]. The bonds distances values for Zn1—O1 and Zn1—O1i are slightly different with respectively 2.033(2) Å and 2.038(3) Å. These values are comparable to those reported for the complex $[\text{Zn}_2(\text{Ssal})_2]\cdot 2\text{CH}_2\text{Cl}_2$ (SsalH₂ is bis(N-salicylidene)-4,4'-diaminodiphenyl)thioether) [48]. The interatomic distance Zn1—S1 of 2.380(1) Å is longer than the mean value of 2.2529(6) Å found for a semicarbazide derivatives complexes [49,50]. The distances C2—N3 and C1—S1 values of 1.280(5) Å and 1.705(4) Å are indicative of a double bond character for these bonds upon coordination to Zn(II) ion [1], while the bond distance C1—N2 [1.342(5)] Å is simple in character. These facts show clearly that no thioiminolisation occurs during the reaction.

Intramolecular hydrogen bond type of N—H...OMe is observed. The dinuclearZn(II) molecules are assembled together by intermolecular hydrogen bonding interactions of type N—H...Cl and MeO—H...Cl leading to the formation of a 3D supramolecular structure (Table 3).

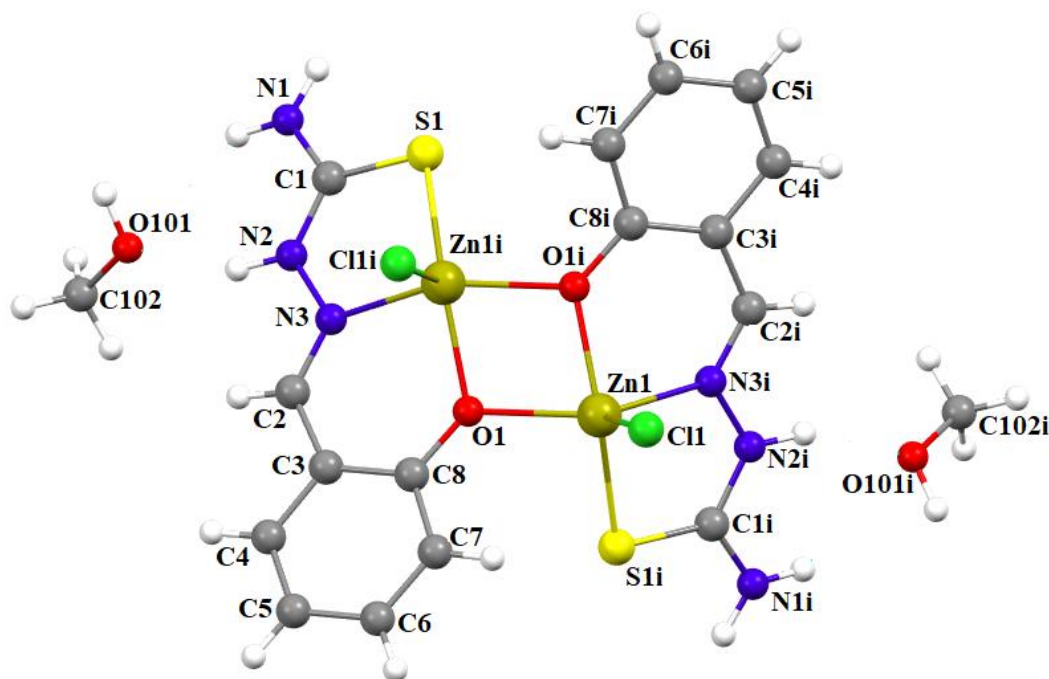


Figure 2: Ball-and-stick representation of the molecular structure of the complex, $[Zn_2(H_3L)_2(Cl_2)] \cdot 2(MeOH)$ (1), showing the atom-labelling scheme.

Table-2. Selected bond distances [\AA] and angles [deg] for the Zn^{II} complex.

C1—N1	1.331 (5)	O1—Zn1	2.038 (3)
C1—N2	1.342 (5)	Zn1—N3 ⁱ	2.142 (3)
C1—S1	1.701 (4)	Zn1—S1 ⁱ	2.3795 (10)
Cl1—Zn1	2.3066 (10)	N2—N3	1.374 (5)
O1—C8	1.325 (4)	C2—N3	1.279 (5)
O1—Zn1 ⁱ	2.034 (2)	Zn1—Zn1 ⁱ	3.1804(6)
C8—O1—Zn1 ⁱ	126.9 (2)	O1—Zn1—Cl1	109.87 (11)
Zn1 ⁱ —O1—Zn1	102.73 (11)	N3 ⁱ —Zn1—Cl1	106.24 (9)
O1 ⁱ —Zn1—O1	77.17 (11)	O1 ⁱ —Zn1—S1 ⁱ	147.44 (11)
O1 ⁱ —Zn1—N3 ⁱ	83.62 (12)	O1—Zn1—S1 ⁱ	97.25 (8)
O1—Zn1—N3 ⁱ	141.68 (13)	N3 ⁱ —Zn1—S1 ⁱ	81.57 (9)
O1 ⁱ —Zn1—Cl1	101.39 (10)	Cl1—Zn1—S1 ⁱ	110.53 (4)

Symmetry code: (i) $-x, -y+1, z$.

Table-3. Hydrogen-bond geometry (\AA , $^\circ$)

$D-H \cdots A$	D—H	H $\cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1N1 \cdots Cl1 ⁱ	0.91(4)	2.72(5)	3.443(4)	137(4)
N1—H1N1 \cdots O101	0.91(4)	2.45(5)	3.193(5)	139(4)
N1—H1N2 \cdots Cl1 ⁱⁱ	0.93(4)	2.46(5)	3.339(4)	160(6)
N2—H2N \cdots O101	0.92(4)	1.92(5)	2.786(5)	156(6)

C2—H2A...S1 ⁱⁱⁱ	0.95	2.92	3.740(4)	145.7
C7—H7...S1 ^{iv}	0.95	2.94	3.396(4)	110.8
O101—H101...Cl1 ⁱ	0.93(7)	2.52(7)	3.233(4)	134(5)
C102—H10C...S1 ⁱⁱ	0.98	3.01	3.965(5)	166.3

Symmetry codes: (i) $-y+1/2, -x+1, z+1/4$; (ii) $y-1/2, x+1, z+1/4$; (iii) $x+1/2, -y+3/2, z$; (iv) $-x, -y+1, z$.

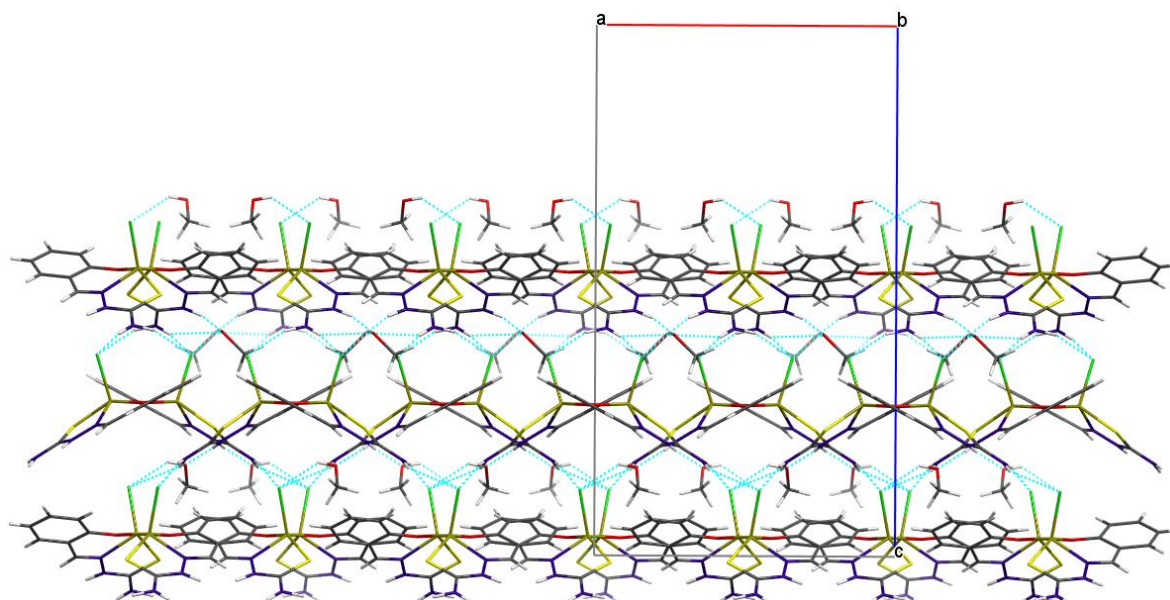


Figure 2. A view of the supramolecular layer in the title compound, in projection in *ab* plane, showing hydrogen-bonded interactions that support the three-dimensional coordination framework. Hydrogen bonds are shown as dashed blue lines.

3.3 Fluorescence properties

In the present work we have studied the emission spectra at room temperature of the Zn (II) complex. As shown in Figures 3, 4, 5 and 6, the emission spectra of complex **4** at different concentrations in methanol, in ultra-pure water, in DMSO and in DMF are quite different in both emission wavelengths and emission intensities. When the spectra of the complex are compared at 4.10^{-5} mol / L, in DMF in ultra-pure water, in methanol and in DMSO, a significant improvement in fluorescence appears, depending on the coordination capacity of the solvent. DMSO is the most coordinating of these solvents and it is observed that the fluorescence is better in this solvent. Then we have methanol and water that follow in terms of coordination capacity. The fluorescence in methanol is higher than that obtained in water. DMF, which is the least coordinating solvent, gives the lowest fluorescence intensities. It is also observed that in DMF the intensity of the fluorescence is almost independent of the concentration (Figure 6). This is probably due to the weak coordination capacity of the DMF. On the other hand, in water, methanol and DMSO there is an increase in the intensity of fluorescence as a function of the concentration (Figure 3). Due to the coordination possibilities of these three solvents, the oxygen atom of DMSO is better coordinated with the zinc atom than the oxygen atom in methanol which is better coordinated than the oxygen atom in water molecule (Figure 4 and Figure 5). This observation is due to the inductive donor effect of the methyl group in DMSO and methanol [51]. For all the solvents studied, no displacement of λ_{em} is observed. Only the intensity of the fluorescence depends on the concentration (Figure 3, Figure 4, and Figure 5).

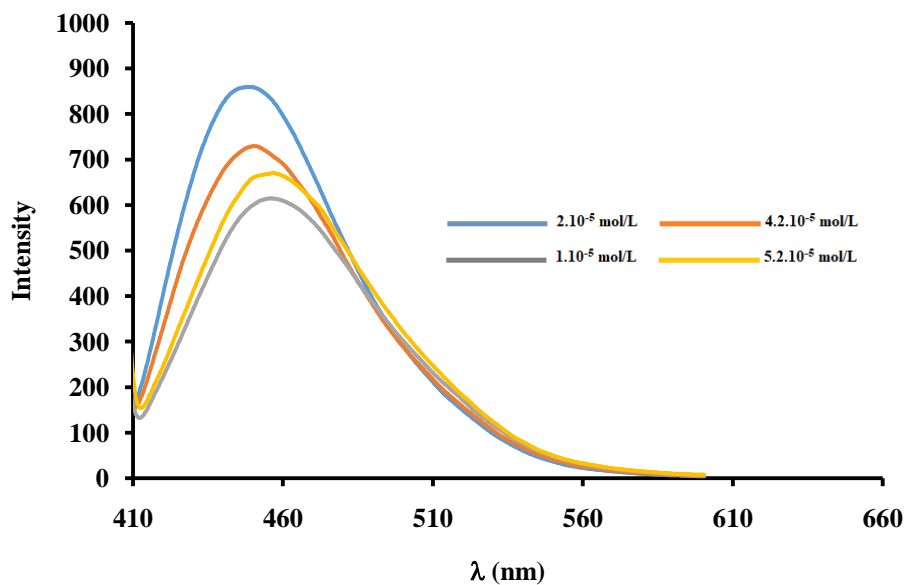


Figure 3: Fluorescence spectra of the complex 4 recorded at room temperature in DMSO at different concentration.

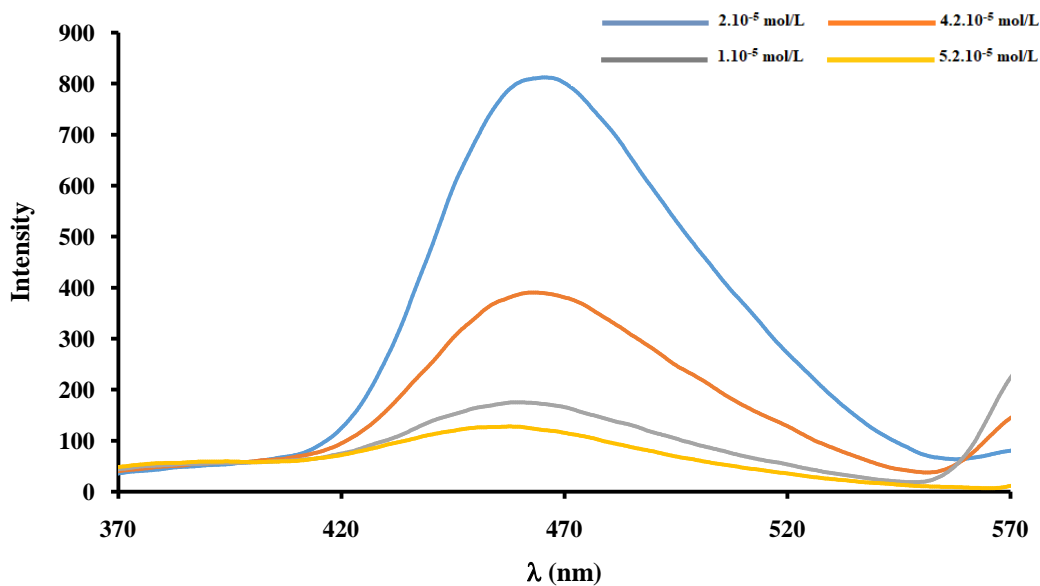


Figure 4: Fluorescence spectra of the complex 4 recorded at room temperature in methanol at different concentration.

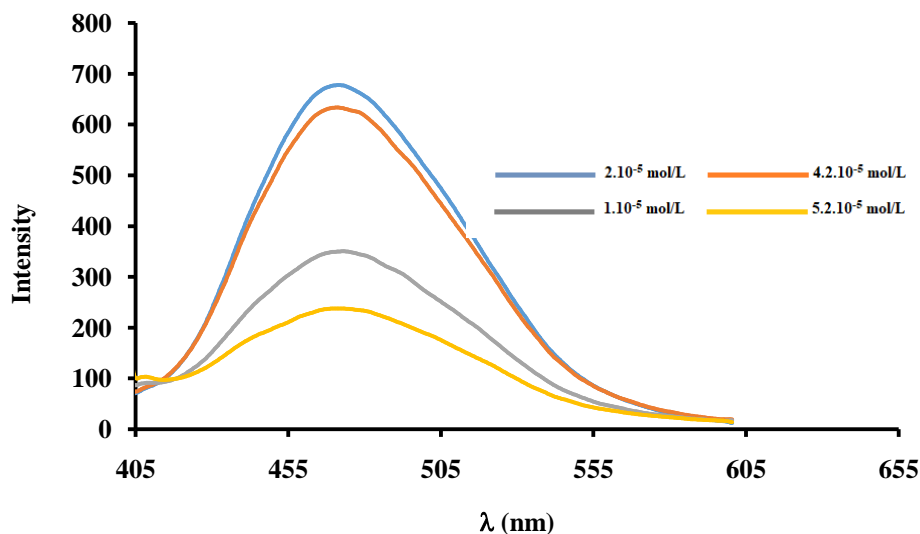


Figure 5: Fluorescence spectra of the complex **4** recorded at room temperature in ultra-pure water at different concentration.

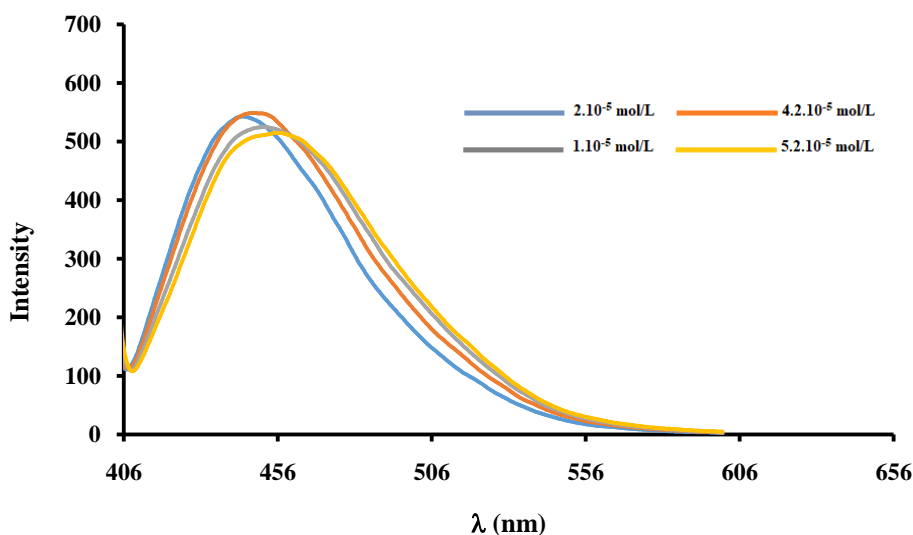


Figure 6: Fluorescence spectra of the complex **4** recorded at room temperature in DMF at different concentration.

IV. Conclusion

The ligand containing the thiosemicarbazide moiety 1-(2-hydroxybenzylidene)thiosemicarbazide was prepared. The complex Co(III), Ni(II), Cu(II) and Zn(II) complexes of the ligand were synthesized and characterized by UV-Vis, FTIR, NMR elemental analyses; conductivity and magnetic susceptibility measurement. The zinc complex is additionally characterized by X-ray diffraction technic. The magnetic moment of the diamagnetic complex Ni(II) and Cu(II) are respectively $3.41 \mu_B$ and $2.04 \mu_B$. For each complex the ligand is mono deprotonated and acts in tridentate fashion through the imino nitrogen atom, the phenoxo oxygen atom and the thione sulfur atom. With the result obtained we suggest the structure for the Co(III), Ni(II) and Cu(II) complexes in which the environment is octahedral. The structure of the zinc(II) complex obtained from X-ray diffraction shows a square pyramidal geometry around the Zn(II) center.

V. Supporting information

CCDC-1996165 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>, or by

emailingdata_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

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