

Synthesis and Crystal Structure of Anickel (II) and Zinc (II) Complex From 1,5-Bis [(2-Thiophenyl) Methylidene] Thiocarbonohydrazide

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Abstract: The title mononuclear nickel and zinc complexes, $Ni(C_{11}H_9N_4S_3)_2$ and $Zn(C_{11}H_9N_4S_3)_2 \cdot 2(C_3H_7NO)$, were prepared by the reaction of Nickel(II) or Zinc(II) acetate with 1,5-bis[(2-thiophenyl)methylidene]thiocarbonohydrazide in a methanol solution. It features mono-deprotonated bis-bidentate ligands, which coordinate to metal (II) ions by hydrazyl N and thiocarbonyl S atoms, yielding a tetracoordinated metal ions complexes. In Ni(II) complex the geometry around the metal ion is described as square planar. In the Zn(II) the metal atom shows severely tetrahedral distortion from an ideal square-planar coordination geometry, as reflected by the dihedral angle between ZnN_2 and ZnS_2 planes of $73.03(13)^\circ$. Two intramolecular hydrogen bonds are observed between the solvate dmf molecules and the coordinated ligands: $N2-H2N \cdots O1^i$ and $N6-H6N \cdots O2^{ii}$ in this complex.

Keywords: Schiff base, Thiocarbonyl, Nickel, Zinc, tetrahedral, Electrochemistry.

I. Introduction

Organic molecules containing thiohydrazone moieties are interest compounds useful to study the bonding of metal ions to synthesize inorganic complexes [1-3] which have found utility in a wide range of applications [4-6]. Schiff bases issued from keto-precursor and hydrazone have been largely investigated owing to their capacity to append various substituents [7, 8]. Because of the capability to provide various modes of coordination, this chemistry is able to generate stable structures [9, 10]. The combination of versatility of the binding modes and the nature of the metal ion is expected to generate new compound. These ligands may design to yield special topological structures. The molecular design can be modulated to link in different manners metal ions resulting in original architectures. In the course of our studies on the chemistry of transition metal compounds, we have prepared and characterized a number of chelates containing N and O donor sites [11-15]. Considerable interest is accorded to the development of multidentate ligands containing different binding sites such as N, O or S [16, 17]. Herein we present a structurally characterized nickel(II) and zinc(II) complexes synthesized from potentially heptadentate Schiff base ligand.

II. Experimental Section

2.1. Material and measurements

Thiocarbonohydrazide, 2-thiophenecarboxaldehyde and metal salts were commercial products of highest chemical grade (Aldrich). Solvents were purified according to standard procedures. Elemental analysis of C, H and N was performed by the analytical laboratory of the Department of Inorganic Chemistry (University of Padua, Italy). FTIR spectra were recorded with a Nicolet 5SXC FT-IR spectrophotometer using KBr pellets. Molar conductance measurement was made using a WTW LF-330 conductivity meter with a WTW conductivity cell on about 1 mmol dm^{-3} dimethylformamide solution at room temperature. Room temperature magnetic susceptibility measurements were made on solid complex using a Johnson-Mathey Gouy balance with $Hg[Co(SCN)_4]$ as the calibrator. Electrochemical measurements were performed with a BAS CV 27 voltammogram and a BAS A-4 XY register using a graphite carbon ($\phi 5 \text{ mm}$) working electrode, a platinum wire as auxiliary and a double junction, with porous ceramic wick, Ag/AgCl reference electrode, standardized for the redox couple ferricinium/ferrocene ($E_{1/2} = 0.400 \text{ V}$, $\Delta E_p = 60 \text{ mV}$). Cyclic voltammetry studies of ligands and complex were carried out on 0.01 M solutions in dimethylformamide containing 0.1 M $[NBu_4][PF_6]$ (tetrabutylammoniumhexafluorophosphate: TBAHFP) as supporting electrolyte. The range of potential studied

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was between +1 and -1.5 V. The solution was purged with nitrogen steam for 5 min before measurement and the working electrode was polished before experiment with diamond paste. The procedure was performed at room temperature and a nitrogen atmosphere was maintained over the solution during the measurements.

2.2. X-ray data collection, structure determination, and refinement

Slow evaporation of dmf solution gave X-ray quality crystals of the compound. The details of the X-ray crystal structures solution and refinement are given in Table I. The details of the X-ray crystal data, structure solution and refinement are given in Table 1. Diffraction data were collected using a CAD4 EXPRESS diffractometer with graphite monochromatized Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). All data were corrected for Lorentz and polarization effects and for absorption by semi empirical methods based on symmetry-equivalent and repeated reflections. Complex scattering factors were taken from the program package *SHELXTL* [18]. The structures were solved by direct methods which revealed the position of all non-hydrogen atoms. All the structures were refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters for all non hydrogen atoms [19]. The hydrogen atoms were located in their calculated positions and refined using a riding model. Molecular graphics were generated using *ORTEP-3* [20].

Table-1. Crystallographic data and refinement parameters for (1) and (2).

| Compound | Ni(HL) ₂ | Zn(HL) ₂ ·2DMF |
|---|--|--|
| Formula of refinement | C ₂₂ H ₁₈ N ₈ S ₆ Ni | C ₂₂ H ₁₈ N ₈ S ₆ Zn·2(C ₃ H ₇ NO) |
| Molecular weight (g/mol) | 645.51 | 798.37 |
| Crystal system | Orthorhombic | Monoclinic |
| Space group | Pbca | P2 ₁ |
| a (Å) | 11.719(1) | 12.1802 (9) |
| b (Å) | 9.040(1) | 9.7488 (7) |
| c (Å) | 25.788(1) | 16.8456 (12) |
| β (°) | 90 | 109.181 (1) |
| V (Å ³) | 2732(2) | 1889.2 (2) |
| D _c (g cm ⁻³) | 1.569 | 1.403 |
| Z | 4 | 2 |
| Crystal size (mm) | 0.30 × 0.30 × 0.06 | 0.35 × 0.15 × 0.10 |
| Crystal colour | yellow | yellow |
| Crystal habit | square plate | prismatic |
| Mo K α (Å) | 0.71073 | 0.71073 |
| μ (mm ⁻¹) | 1.20 | 1.02 |
| T(K) | 293(2) | 293(2) |
| 2 θ _{max} | 25.24 | 25.02 |
| hklrange | -14, 14 ; -10, 10 ; -30, 30 | -14, 14 ; -11, 11 ; -20, 20 |
| Measured reflections | 16273 | 14527 |
| Independent reflections | 2490 | 3541 |
| Reflections with I > 2 σ (I) | 1650 | 2747 |
| Parameters | 172 | 430 |
| Restraints | 1 | 3 |
| R _{int} | 0.045 | 0.048 |
| R ₁ (F) [I > 2 σ (I)] | 0.042 | 0.036 |
| wR ₂ (F ²) | 0.115 | 0.102 |
| Goodness-of-fit | 0.999 | 1.06 |
| $\Delta\rho_{\text{min, max}}$ (Å ⁻³) | -0.37, 0.54 | -0.31, 0.35 |

2.3. Synthesis of ligand (H₂L)

To a 50 mL round bottom flask thiocarbonohydrazide (2.12 g, 0.020 mol) dissolved in methanol (10 mL) and 2-thiophenecarboxaldehyde (4.49 g, 0.040 mol) in methanol (10 mL) were added to yield immediately and quantitatively a white precipitate. The precipitate was separated by filtration, washed with methanol and ether and dried under vacuum. The compound is insoluble in common organic solvent. Yield 4.15 g, 70.5%; m.p. 482 K. IR data (cm⁻¹) 3448, 1592, 1540, 1505, 1259, 1227 and 710. Anal. Calc. for C₁₁H₁₀N₄S₃(%): C, 44.87; H, 3.42; N, 19.03; S, 32.67. Found: C, 44.85; H, 3.40; N, 19.07; S, 32.69. Mass spectrum (m/z, 294).

2.4. Synthesis of [Ni(HL)₂] (1)

Methanolic solution (5mL) of nickel acetate tetrahydrate (0.3111 g, 1.25 mmol) was added to a methanolic suspension (10 mL) of the ligand prepared above (0.6958 g, 2.5 mmol). The resulting mixture was refluxed for two days. The green solution was filtered and then allowed to evaporate slowly. The resulting powder was recrystallized from dimethylformamide solution. After one week, yellow powder was obtained. The powder was separated and dried in air. The resulting powder was recrystallized again from dimethylformamide solution. After one week, yellow crystals suitable for X-ray analysis were obtained (yield: 75%); Anal. Calc. for

C₂₂H₁₈NiN₈S₆ (%): C, 40.93; H, 2.81; N, 17.36; S, 29.80. Found: C, 40.81; H, 2.71; N, 16.85; S, 28.99. Selected IR data (cm⁻¹, in KBr pellet): 1575, 1562, 1512, 1429, 1366 and 1210. μ_{eff} = diamagnetic.

2.5. Synthesis of [Zn(HL)₂] \cdot 2DMF (2)

Methanolic solution (5mL) of zinc acetate dihydrate (0.2744 g, 1.25 mmol) was added to a methanolic suspension (10 mL) of the ligand prepared above (0.6958 g, 2.5 mmol). The resulting mixture was refluxed for one day. The yellow solution was filtered and then allowed to evaporate slowly. The resulting powder was recrystallized from dimethylformamide solution. After one week, yellow crystals suitable for X-ray analysis were obtained. The crystals were separated and dried in air (yield: 65%); Anal. Calc. for C₂₈H₃₂ZnN₁₀O₂S₆ (%): C, 42.12; H, 4.04; N, 17.54; S, 24.10. Found: C, 42.14; H, 4.06; N, 17.50; S, 24.12. Selected IR data (cm⁻¹, in KBr pellet): 3314, 3100, 1575, 1559, 1504 and 1240. Paramagnetic.

III. Results and Discussion

3.1. Spectroscopic studies

The results of the elemental analysis are in good agreement with the calculated values. The mononuclear complexes are stable in air, non-hygroscopic, insoluble in water but are easily soluble in methanol and DMF. The electrolytic nature of the complexes was measured in DMF at 10⁻³ M. The molar conductivities Λ are 4.1 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ for Ni(II) complex and 1.3 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ for Zn(II) confirming that they are non-electrolytic in DMF solutions [21]. In the solid-state IR spectrum of the ligand H₂L, characteristic band of ligand observed at 1575 cm⁻¹ is assigned to the conjugated C=N vibration band. Bands in the region 3300-3100 cm⁻¹ are attributed to the ν (N—H) vibrations of the hydrazide moieties. The band at 1210 cm⁻¹ is assignable to the thione C=S function. Upon coordination, the solid-state IR spectra of the complexes were compared with that of the ligand. It was found that C=N bands vibration in these complexes are 1575 and 1562 cm⁻¹ for Ni(II) complex and 1575 and 1559 cm⁻¹ for Zn(II) complex. The presence of the first band at 1575 cm⁻¹ show that one of the azomethine is not coordinated to the metal center. The presence of the new second bands showing a shift to lower frequencies is indicative of the involvement of one of the nitrogen atom of azomethine (CH=N) groups in Metal-Nitrogen bond formation. The remaining of bands in the region 3300-3100 cm⁻¹ ν (N—H), the absence of a band at 1210 cm⁻¹ ν (C=S) combined to the apparition of a band near 710 cm⁻¹ ν (C—S) indicates evidence for ligand coordination to the metal ions in its monodeprotonated form. The solid state UV–Vis spectrum of the ligand HL shows two absorption bands at 294–296 and 328–334 nm due to $\pi \rightarrow \pi^*$ transitions of the aromatic rings and $n \rightarrow \pi^*$ transitions of the C=N groups. The UV–Vis spectrum was recorded in methanol solution in the range of 260–800 nm for nickel(II) complex. LMCT bands observed at 424 nm and 450 nm can be assigned respectively to N \rightarrow Ni and S \rightarrow Ni charge transfer. The high intensity charge transfer (CT) band S \rightarrow Ni hide some of the three expected transitions corresponding to ¹A_{1g} \rightarrow ¹A_{2g}, ¹A_{1g} \rightarrow ¹B_{1g} and ¹A_{1g} \rightarrow ¹E_g for square planar Ni(II) complex [22]. Only a weak broad band in the 520–600 nm region is attributed to the square planar Nickel(II) d–d transition. These observations coupled to X-ray crystal structure analysis support a square-planar geometry for the nickel(II) complex.

3.2. Electrochemistry study

The electrochemical properties of the Ni(II) complex was examined by cyclic voltammeter using a graphite carbon working electrode and a Pt-wire auxiliary electrode in dry dimethylformamide using 0.1 M [n-Bu₄N]⁺ClO₄⁻ as the supporting electrolyte. The voltammetric parameters were studied in the scan rate interval 100–180 mV s⁻¹. In Figure 1, curve (a) describes the electrochemical behavior of the free ligand in DMF medium. We note one oxidation and one reduction peaks (*Epa*₁, *Epc*₁). The electro activity field is limited by the solvent's walls of oxidation and reduction. Curve (b) shows the electrochemical behavior of the Ni complex. Two new peaks (*Epa*₂, *Epc*₂), which are attributed to oxidation and reduction peaks of Ni complex with the organic ligand are revealed.

The ligand showed one irreversible oxidation at *Epa*₁ = 1.14 V and one irreversible reduction at *Epc*₁ = -1.45 V versus Ag/AgCl in the scan rate of 0.10 Vs⁻¹. The complex [Ni(HL)₂] exhibited one anodic wave at *Epa*₂ = 1.66 V with corresponding one cathodic wave *Epc*₂ = -1.1 V. The anodic wave is assigned to the oxidation of [Ni(HL)₂] complex Ni^{II}/Ni^{III} while the corresponding cathodic peak wave is attributed to the

reduction process of the [Ni(HL)₂] complex $\text{Ni}^{3+} + \text{e}^- \rightarrow \text{Ni}^{2+}$ which appears at different position of *Epc*₁ of the ligand reduction process. A cathodic response recommended for reduction Ni^{III}/Ni^{II} is observed at -1.10 V versus Ag/AgCl (Figure 2). Those facts are indicative that the oxidation and reduction processes of the complex are not based on the ligand. Changes in peak intensities *Epa*₁, *Epa*₂ and *Epc*₂ depending on the potential scan rate (log I_p = f(log V)) are shown in Figure 3. In the range 100-180 mV/s the dependency of *Epa*₁ peak is linear and the slope of the straight line (0.48) is close proximity of 0.5 which is indicative that the electrochemical behavior of the ligand is limited by diffusion. *Epa*₂ and *Epc*₂ are also a linear dependence but the recorded

slopes (0.42 and 0.44 respectively) are not indicative of electrochemical reaction kinetics controlled by diffusion phenomena [23].

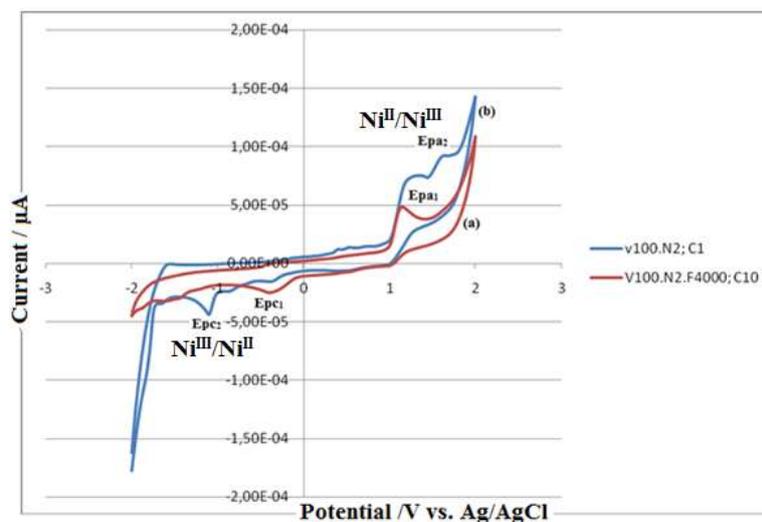


Figure 1: Cyclic Voltammograms of the complex (blue) and the ligand (red) in DMF containing 0.1 M $[NBu_4][PF_6]$. Scan rate: 100 mV. Working electrode: a 5 mm diameter of graphite carbon electrode.

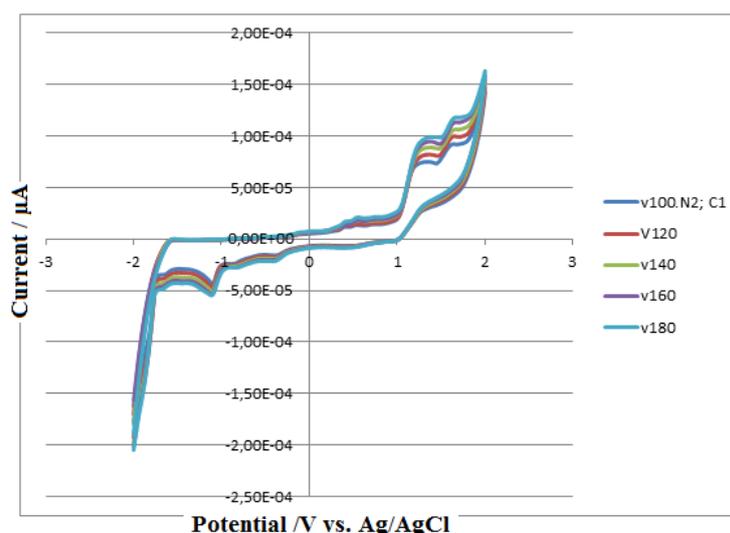


Figure 2: Cyclic Voltammograms of the complex in DMF containing 0.1 M $[NBu_4][PF_6]$. Scan rate: 100, 120, 140 180 and 200 m V. Working electrode: a 5 mm diameter of graphite carbon electrode.

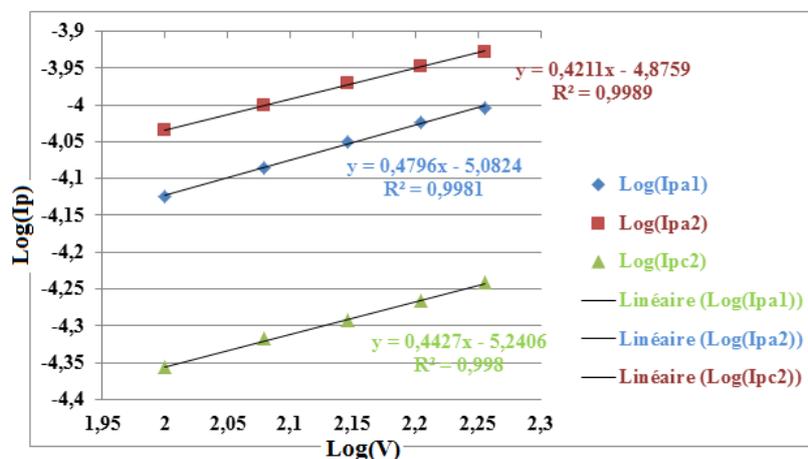


Figure 3: $\text{Log}(I_p) = f(\text{log}V)$

3.3. Crystal structures of complexes

The nickel(II) complex crystallizes in the orthorhombic space group *Pbca*. A perspective view of the complex structure is shown in Figure 4 and main bond lengths and angles are listed in Table 2. The X-ray structure determination reveals that the complex consists of a discrete centrosymmetric mononuclear unit [Ni(HL)₂]. The potential heptadentate ligand H₂L acts like a bidentate monodeprotonated ligand with the thiophenyl groups and one of the thiohydrazonic moieties remaining uncoordinated. The nickel(II) ion is linked to two molecules ligand by one imino nitrogen atom (N1, N1ⁱ) and one sulfur atom, in his thiolato form, (S3, S3ⁱ) per each molecule ligand (i = -x+1; -y; -z+1), resulting in square planar geometry. The square planar coordination geometry is almost regular in the Ni(II) complex. The four bond angles around the metal are all close to 90°. The bite angles corresponding to the formation of the five-membered rings (NiSCNN) slightly contracted with a value of 86.17(8)° while the others are slightly enlarged to 93.83(8)°. This low flatness deviation is attested by the trans angles N1–Ni–N1ⁱ and S3–Ni–S3ⁱ which are 180(1)° [24]. Inspection of the bond lengths indicates that the ligand is coordinated to the Ni(II) ions in his thiolato form. Indeed the bonds length C11–S3 with 1.724(4) Å value is consistence with a simple bond [22]. The values of bond lengths C5–N4 (1.281(5) Å) and (C6–N1 (1.300(4) Å) indicate a double bonds character [25]. The Ni–S and Ni–N bond lengths values [2.1699(8) Å and 1.913(3) Å] are comparable to those found for the corresponding distance [2.1766(7) Å and 1.908(3)] in the tetracoordinated square planar complex [Ni(L)₂ (were HL = benzyl-3-(3-hydroxyphenyl methyl ethylene)hydrazine carbodithioate)] [26].

Table-2. Selected bond distances [Å] and angles [deg] for the Ni^{II} and Zn^{II} complexes.

| | | | |
|-----------|-----------|-----------|------------|
| Ni1—N1 | 1.913(3) | Zn1—N8 | 2.036(4) |
| Ni1—S3 | 2.1699(8) | Zn1—N4 | 2.066(5) |
| C1—S1 | 1.705(6) | Zn1—S5 | 2.2634(19) |
| C4—S1 | 1.714(4) | Zn1—S2 | 2.2815(17) |
| N2—N1 | 1.386(4) | S2—C6 | 1.739(6) |
| N1—C6 | 1.300(4) | S5—C17 | 1.745(6) |
| C2—C1 | 1.335(7) | N1—C5 | 1.263(7) |
| S2—C7 | 1.712(4) | N1—N2 | 1.364(7) |
| S2—C10 | 1.702(4) | N3—N4 | 1.379(6) |
| N2—C11 | 1.299(4) | N4—C7 | 1.291(8) |
| N4—N3 | 1.366(4) | N2—C6 | 1.367(7) |
| N3—C11 | 1.349(5) | N3—C6 | 1.307(7) |
| C11—S3 | 1.724(4) | N8—Zn1—N4 | 121.0(2) |
| C5—N4 | 1.281(5) | N8—Zn1—S5 | 86.76(14) |
| S3—Ni1—S3 | 180.0(1) | N4—Zn1—S5 | 114.42(15) |
| N1—Ni1—N1 | 180.0(1) | N8—Zn1—S2 | 114.26(13) |
| N1—Ni1—S3 | 86.17(8) | N4—Zn1—S2 | 86.05(13) |
| N1—Ni1—S3 | 93.83(8) | S5—Zn1—S2 | 138.44(9) |

Table-3. Hydrogen bonds for the Ni^{II} complex [Å and deg].

| D—H...A | D—H | H...A | D...A | D—H...A |
|---------------|---------|---------|-----------|---------|
| N2—H2N...O1i | 0.91(2) | 2.01(4) | 2.868(8) | 156(7) |
| N6—H6N...O2ii | 0.91(2) | 1.93(3) | 2.819(10) | 165(7) |

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

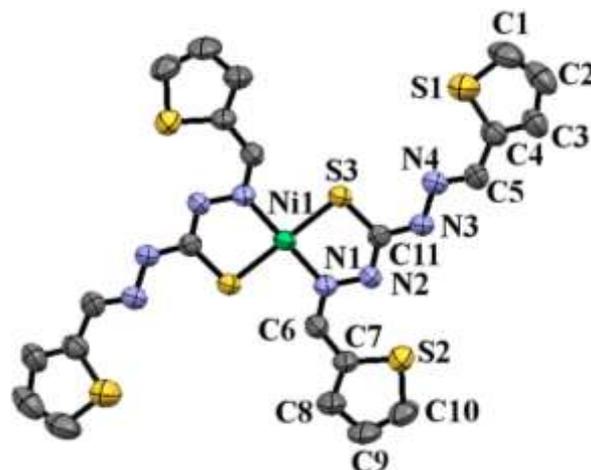


Figure 4: ORTEP plot (30% probability ellipsoids) showing the molecule structure of the Ni^{II} complex.

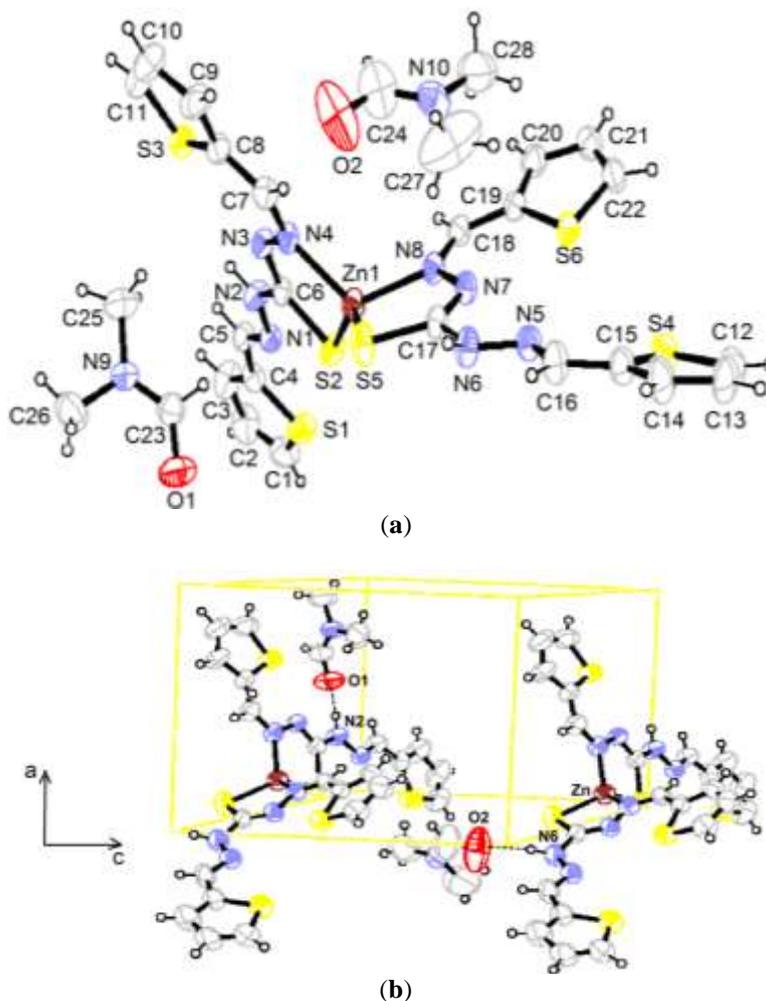


Figure 5:(a) ORTEP plot (30% probability ellipsoids) showing the molecule structure of the Zn^{II} complex. (b)The Crystal packing of the Zn^{II} complex with hydrogen bonds.

The zinc(II) complex crystallizes in the monoclinic space group P_2_1 . The coordination of the thiocarbonohydrazone to Zn^{II} results in the formation of two five membered (ZnSCNN) chelating rings. The following bonds C6–N2, C17–N7 which are simple in character in the uncoordinated ligand molecule are altered in the complex and become double bond character with bond lengths of 1.307(6) Å and 1.292(7) Å respectively. The bond C6–S2 and C17–S5 which were double in character become a simple bond with values length of 1.745(6) Å and 1.739(6) Å respectively. These facts are indicative of deprotonation of the N2–H and N7–H resulting in thio iminisation of the ligand upon coordination. The title compound crystallizes in the monoclinic space group of P_2_1 and Figure 5 depicts its mononuclear structure. The Zn(II) center of the molecule complex is tetracoordinated. Two molecules ligands are coordinated to the Zn^{II} ion. Each molecule ligand provides one nitrogen atom from hydrazone and one S atom from the thiocabono moieties which constitute the severely distorted tetrahedral environment around the Zn^{II} center. The dihedral angle between the ZnN₂ and ZnS₂ planes is 73.03(13)°. The severely distorted tetrahedral geometry can be indicated by the bond angles subtended at Zn: N–Zn–N = 121.0(2)°, S–Zn–S = 138.44(9)° and S–Zn–N in the range of 86.05(13)–114.42(15)°. The Zn–S bond lengths values [2.2634(19) Å and 2.2815(17) Å] are comparable to those found for the corresponding distance [2.3117(6) Å] in the tetracoordinated complex [Zn(5-CF₃pyS)₂(bipy)] [27]. The Zn–N bond distances [2.036(4) Å and 2.066(5) Å] are essentially the same as those found in zinc complexes with hydrazone ligands [2.113(2) Å][28]. The zinc and sulfur atoms as well as the zinc and the nitrogen atoms are rigorously coplanar for the (ZnS₂) and (ZnN₂). In this compound, there is hydrogen bonding involving the NH of the hydrazone moieties of the ligand molecules [N2 and N6] and the oxygen atoms of the uncoordinated dmf molecules [O1 and O2] (Table 2)

IV. Conclusion

Thiocarbohydrazone derivatives, with thiophenyl ring showed variety of modes coordination in the Ni^{II} and Zn^{II} complexes which are prepared and characterized by elemental analysis, magnetic moment, molar conductivity, IR, UV-Vis and X-ray diffraction techniques. It is observed that the Nickel complex is diamagnetic while the zinc complex is paramagnetic. The complexes are non-ionic electrolyte. In both structure the ligand H₂Lacts as bidentate ligand through thiolato S and azomethine N atoms. Considering the magnetic moment, infrared spectra and the electronic spectrum data for Ni(II) complex, square planar geometry is proposed for the Ni(II) complex. The Zn(II) complex shows tetrahedral geometry. These observations are confirmed by X-ray diffraction studies.

V. SupplementalData.

CCDC 1055807 and 1055808 contains the supplementary crystallographic data for the complexes. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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