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# Zinc(II) complexes derived from di-2-pyridyl ketone $N^4$-phenyl-3-semicarbazone: Crystal structures and spectral studies

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ABSTRACT

Six zinc(II) complexes, $Zn(HL)Br_2$ (**1**), $Zn(HL)Cl_2$ (**2**), ZnL(OAc) (**3**), $ZnLN_3$ (**4**), $ZnL_2$ (**5**) and $ZnL_2 \cdot H_2O$ (**6**), have been synthesized and characterized by different physicochemical techniques. Complex **1** is five coordinated and has a distorted square pyramidal geometry. Complexes **5** and **6** are six coordinated and have distorted octahedral geometries. In complexes **1** and **2**, the ligand moieties are coordinated in the neutral form (HL), and in the other complexes they are monoanionic ($L^-$).

## 1. Introduction

Semicarbazones are very versatile ligands in both the neutral and anionic form. These compounds are have the formula $R_2C{=}N{-}NH{-}(CO){-}NH_2$. The coordination possibilities derived from the many potential donor atoms in the semicarbazones are increased if the substituents include additional donor atoms and they can also be modified by placing substituents on the backbone donor atoms. These classes of compounds usually react with metallic cations giving complexes in which the semicarbazones behave as chelating ligands. Research on the coordination chemistry, analytical applications and biological activities of these complexes has increased steadily for many years [1]. It has also been reported that many complexes of semicarbazones have antimicrobial and antitumor activities [2].

Zinc shows a fairly high affinity towards the main coordinating atoms such as sulfur, nitrogen and oxygen. This means high flexibility in the structure, coordination mode and coordination number of the complexes produced [3]. We have recently reported the synthesis, spectral characterization and structural studies of cadmium(II) complexes of the present semicarbazone, with the aim to correlate the structural features and chelating ability [4]. Di-2-pyridyl ketone $N^4$-phenyl-3-semicarbazone tautomerizes into keto and enol forms and as a result a small negative charge resides on the nitrogen atom of the pyridine ring which enhances its biological activity [5–7]. This paper deals with the synthesis, spectral and structural studies of zinc(II) complexes of a potential quadridentate ligand, di-2-pyridyl ketone $N^4$-phenyl-3-semicarbazone (HL).

## 2. Experimental

### 2.1. Materials

Di-2-pyridyl ketone (Aldrich) and $N^4$-phenylsemicarbazide (Aldrich) were used as received. $ZnBr_2$, $ZnCl_2$, $Zn(OAc)_2 \cdot 2H_2O$ and $NaN_3$ were commercial products of higher grade (Aldrich) and solvents were purified according to standard procedures. Elemental analyses were carried out using a Vario EL III CHNS analyzer at SAIF, Kochi, India. Infrared spectra were recorded on a JASCO FT-IR-5300 spectrometer in the range 4000–400 $cm^{-1}$ using KBr pellets. Electronic spectra were recorded on a Cary 5000, version 1.09 UV–Vis–NIR spectrophotometer using solutions in DMF.

### 2.2. Synthesis of di-2-pyridyl ketone-$N^4$-phenyl-3-semicarbazone (HL)

Di-2-pyridyl ketone-$N^4$-phenyl-3-semicarbazone (Fig. 1) was prepared by the earlier reported method [4].

### 2.3. Synthesis of complexes

#### 2.3.1. Synthesis of $Zn(HL)Br_2$ (**1**), $Zn(HL)Cl_2$ (**2**) and ZnL(OAc) (**3**)

A solution of the ligand HL (0.317 g, 1 mmol) in 20 ml of methanol was treated with a methanolic solution of the appropriate zinc(II) salt (1 mmol). The solution was heated under reflux for 4 h. The resulting solution was allowed to stand at room temperature

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and after slow evaporation yellow crystals separated out, which were collected, washed with ether and dried over $P_4O_{10}$ *in vacuo*.

$Zn(HL)Br_2$ (**1**): Yield ~0.35 g; found (calc): C, 40.16 (40.76); H, 2.79 (2.78); N, 12.91 (13.25); IR data ($cm^{-1}$): 3239, 1597, 1661, 1147, 407.

$Zn(HL)Cl_2$ (**2**): Yield ~0.28 g; found (calc): C, 47.66 (47.72); H, 3.33 (3.41); N, 15.44 (15.57); IR data ($cm^{-1}$): 3369, 1597, 1667, 1153, 404.

ZnL(OAc) (**3**): Yield ~0.32 g; found (calc): C, 54.25 (53.73); H, 4.33 (4.30); N, 15.82 (15.71); IR data ($cm^{-1}$): 1597, 1521, 1156, 414, 516.

### 2.3.2. Synthesis of $ZnLN_3$ (**4**)

A solution of the ligand HL (0.317 g, 1 mmol) in methanol was treated with a methanolic solution of $Zn(OAc)_2 \cdot 2H_2O$ (0.219 g,1 mmol). The solution was heated under reflux and sodium azide (0.130 g, 2 mmol) was added in portions to the solution and further refluxed for 4 h. The resulting solution was allowed to stand at room temperature and upon slow evaporation gave yellow crystals. The crystals that separated out were collected, washed with ether and dried over $P_4O_{10}$ *in vacuo*. Yield ~0.25 g; found (calc): C, 54.25 (53.73); H, 3.33 (3.27); N, 26.44 (26.56); IR data ($cm^{-1}$): 1595, 1518, 1148, 404, 502.

### 2.3.3. Synthesis of $ZnL_2$ (**5**)

A solution of the ligand HL (0.317 g, 1 mmol) in 20 ml of methanol was treated with a methanolic solution of $Zn(OAc)_2 \cdot 2H_2O$ (0.109 g, 0.5 mmol). The solution was heated under reflux for 2 h. The resulting solution was allowed to stand at room temperature and after slow evaporation yellow crystals were separated out, which were collected, washed with ether and dried over $P_4O_{10}$ *in vacuo*. Yield ~0.20 g; found (calc): C, 61.53 (61.94); H, 3.96 (4.04); N, 20.01 (20.07); IR data ($cm^{-1}$): 1597, 1515, 1223, 420, 518.

### 2.3.4. Synthesis of $ZnL_2 \cdot H_2O$ (**6**)

A solution of the ligand HL (0.317 g, 1 mmol) in methanol was treated with a methanolic solution of $Zn(OAc)_2 \cdot 2H_2O$ (0.219 g, 1 mmol). The solution was heated under reflux and sodium azide (0.065 g, 1 mmol) was added in portions to the solution and further refluxed for 4 h. The resulting solution was allowed to stand at room temperature and upon slow evaporation gave yellow crystals. The crystals that separated out were collected, washed with ether and dried over $P_4O_{10}$ *in vacuo*. Yield ~0.16 g; found (calc): C, 59.87 (60.38); H, 4.01 (4.22); N, 19.25 (19.56); IR data ($cm^{-1}$): 1597, 1515, 1229, 416, 520.

## 2.4. X-ray crystallography

Single crystals of compound **1** suitable for X- ray diffraction were obtained by slow evaporation of its solution in a 1:1:1 mixture of $CH_3OH$, $CHCl_3$ and $CH_2Cl_2$. Single crystals of compound **5** were obtained by slow evaporation of its solution in a 1:1 mixture of $CH_3OH$ and $CH_3CN$, and of compound **6** by slow evaporation of its solution in a 1:1:1:1 mixture of DMF, $CHCl_3$, $CH_3CN$ and $CH_3OH$. X-ray diffraction measurements were carried out on a CRYSALIS CCD diffractometer with graphite-monochromated Mo Kα ($\lambda$ = 0.71073 Å) radiation. The program CRYSALIS RED was used for data reduction and cell refinement [8]. The structure was solved by direct methods using SHELXS [9] and refined by full-matrix least-squares refinement on $F^2$ using SHELXL [10]. The N–H hydrogen atoms were located from difference Fourier maps and refined isotropically. The remainder of the H-atoms were included in calculated positions and refined as riding atoms using default SHELXL parameters. Compound **6** is non-centrosymmetric and its Flack *x* parameter is 0.001(12). As this value is near 0, with small standard uncertainty, the absolute structure given by the structure refinement is likely correct [11]. The structures of the compounds were

**Table 1**
Crystal data and structure refinement parameters for $[Zn(HL)Br_2]$ (**1**), $[ZnL_2]$ (**5**) and $[ZnL_2] \cdot 0.3H_2O$ (**6**)

| | **1** | **5** | **6** |
|---|---|---|---|
| Empirical formula | $C_{18}H_{15}Br_2N_5OZn$ | $C_{36}H_{28}N_{10}O_2Zn$ | $C_{36}H_{28}N_{10}O_2Zn \cdot 0.3H_2O$ |
| Formula weight | 542.54 | 698.05 | 702.85 |
| Temperature, K | 120(2) | 120(2) | 120(2) |
| Wavelength, Å | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | monoclinic | monoclinic | orthorhombic |
| Space group | $P2_1/n$ | $P2_1/n$ | $P2_12_12_1$ |
| *Unit cell dimensions* | | | |
| $a$ (Å) | 7.3466(3) | 11.0982(2) | 8.5993(4) |
| $b$ (Å) | 14.5893(4) | 16.6320(3) | 17.0904(6) |
| $c$ (Å) | 18.5267(5) | 17.8826(4) | 22.3002(11) |
| $\alpha$ (°) | 90 | 90 | 90 |
| $\beta$ (°) | 98.315(3) | 98.690(2) | 90 |
| $\gamma$ (°) | 90 | 90 | 90 |
| $V$ (Å$^3$) | 1964.85(11) | 3262.97(11) | 3277.4(3) |
| $Z$ | 4 | 4 | 4 |
| $D_{calc}$ (Mg/m$^3$) | 1.834 | 1.421 | 1.424 |
| Absorption coefficient (mm$^{-1}$) | 5.335 | 0.803 | 0.801 |
| $F(000)$ | 1064 | 1440 | 1450 |
| Crystal size (mm$^3$) | 0.32 × 0.28 × 0.26 | 0.26 × 0.21 × 0.19 | 0.18 × 0.11 × 0.08 |
| $\theta$ range for data collection (°) | 3.01–25.00 | 2.99–25.00 | 2.99–25.00 |
| Index ranges | $-8 \leqslant h \leqslant 8$, $-17 \leqslant k \leqslant 17$, $-21 \leqslant l \leqslant 22$ | $-13 \leqslant h \leqslant 12$, $-19 \leqslant k \leqslant 18$, $-21 \leqslant l \leqslant 21$ | $-10 \leqslant h \leqslant 10$, $-20 \leqslant k \leqslant 20$, $-26 \leqslant l \leqslant 26$ |
| Reflections collected | 16909 | 30049 | 31407 |
| Independent reflections | 3445 [$R$(int) = 0.0341] | 5729 [$R$(int) = 0.0358] | 5772 [$R$(int) = 0.1000] |
| Refinement method | full-matrix least-squares on $F^2$ | full-matrix least-squares on $F^2$ | full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 3445/0/252 | 5729/0/450 | 5772/0/454 |
| Goodness-of-fit on $F^2$ | 1.058 | 1.073 | 1.010 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1$ = 0.0273, $wR_2$ = 0.0532 | $R_1$ = 0.0306, $wR_2$ = 0.0638 | $R_1$ = 0.0500, $wR_2$ = 0.0661 |
| $R$ indices (all data) | $R_1$ = 0.0507, $wR_2$ = 0.0632 | $R_1$ = 0.0444, $wR_2$ = 0.0711 | $R_1$ = 0.0741, $wR_2$ = 0.0734 |
| Largest difference in peak and hole (e A$^{-3}$) | 0.362 and −0.262 | 0.272 and −0.290 | 0.608 and −0.415 |

$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.
$wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

plotted using the program ORTEP [12]. The crystallographic data along with the structural refinements are given in Table 1.

## 3. Results and discussion

### 3.1. Synthesis of complexes

Di-2-pyridyl ketone $N^4$-phenyl-3-semicarbazone (HL) reacts with zinc(II) halides in a 1:1 molar ratio to form **1** and **2**, complexes of the type $Zn(HL)X_2$ where X = Br and Cl. Complexes **3** and **4** were consistent with the general formula ZnLY where Y = OAc and $N_3$ and for complexes **5** and **6**, the composition $ZnL_2$ was obtained. For the preparation of complexes **3** and **5**, $Zn(OAc)_2 \cdot 2H_2O$ and HL were taken in 1:1 and 1:2 ratios, respectively, and for complexes **4** and **6**, $Zn(OAc)_2 \cdot 2H_2O$, HL and $NaN_3$ were taken in 1:1:2 and 1:1:1 ratios, respectively. In complex **6**, however, the azide added was not coordinated and $ZnL_2 \cdot H_2O$ was obtained accidentally, though the yield was much lower. Although the molecular formulae of **5** and **6** are same, the crystallographic parameters are different.

### 3.2. Description of the crystal structures of $Zn(HL)Br_2$ (1), $ZnL_2$ (5) and $ZnL_2 \cdot 0.3H_2O$ (6)

The molecular structure of complex **1**, along with the atom numbering scheme, is presented in Fig. 2. The compound crystallizes in the monoclinic crystal system with the space group $P2_1/n$. In this compound, the Zn atom is coordinated by an azomethine nitrogen (N2), pyridyl nitrogen (N1), ketoxy oxygen (O1) and two bromide ions (Br1 and Br2). The bond distances to Zn are in the order $Zn–N_{(azo)} < Zn–N_{(py)} < Zn–O_{(ketoxy)} < Zn–Br1 < Zn–Br2$. The bond lengths, $Zn–N_{(py)}$, 2.154(3) Å and $Zn–N_{(azo)}$, 2.130(3) Å are very similar compared to other Zn complexes of thiosemicarbazones [13–15]. The Zn–Br bond distances are 2.3561(5) and 2.4026(6) Å, but there is a difference of 0.0465 Å between the Zn–Br bonds of $[Zn(HL)Br_2]$. The basal plane could involve either Br1 or Br2 with the semicarbazone moiety, but because Zn–Br1 is marginally shorter and it can be designated as the apical position. The Zn atom is displaced by a distance of 0.8335 Å above the basal plane and elongated towards Br1. Selected bond lengths and bond angles are given in Table 2.

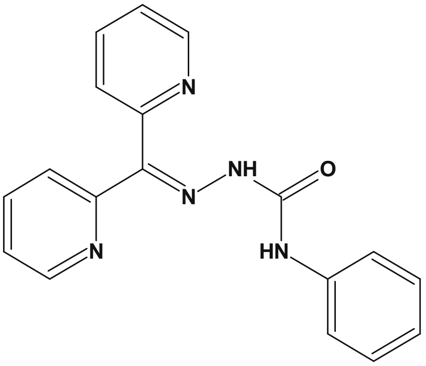

**Fig. 1.** Structure of HL.

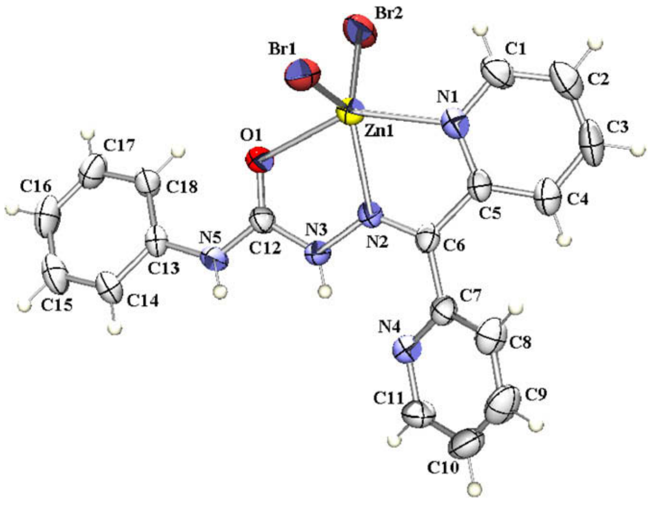

**Fig. 2.** Molecular structure of $Zn(HL)Br_2$.

According to Addison et al., for five coordinated complexes, the angular structural parameter ($\tau$) is used to propose an index of trigonality. The value of $\tau$ is defined by an equation represented by $\tau = (\beta - \alpha)/60$, where $\beta$ is the greatest basal angle and $\alpha$ is the second greatest angle; $\tau$ is 0 for rectangular pyramidal forms and 1 for trigonal bipyramidal forms [16,17]. However, in the case of five-coordinate systems, the structures vary from near regular trigonal bipyramidal (RTB) to near square based pyramidal (SBP). The $\tau$ value for the compound **1** of 0.27 indicates that the coordination geometry around Zn(II) is best described as a distorted square based pyramidal geometry [18].

The deviations from the least-square plane through the O1, N1, N2 and Br2 atoms comprising the square plane are 0.3697, 0.5336, −0.6794 and −0.0054 Å, respectively, and the Zn1 atom is deviated by 0.8335 Å in the direction of the Br1 atom. Ring puckering analysis and least square plane calculations show that the rings Cg(1) comprising of atoms Zn1, O1, C12, N3 and N2 and Cg(2) comprising of atoms Zn1, N1, C5, C6 and N2 adopt a twisted conformation [Cg(1) on N2–Zn1 and Cg(2) on C5–C6] [19]. In the crystal packing four molecules are present and two of them are complementary to each other (Fig. 3). In the unit cell π–π, C–H···π and hydrogen

**Table 2**
Selected bond lengths (Å) and bond angles (°) for $[Zn(HL)Br_2]$ (**1**), $[ZnL_2]$ (**5**) and $[ZnL_2] \cdot 0.3H_2O$ (**6**)

| 1 | 5 | 6 |
|---|---|---|
| *Bond lengths* | | |
| Zn1–N2 2.130(3) | Zn1–N7 2.0716(17) | Zn1–N2 2.073(3) |
| Zn1–N1 2.154(3) | Zn1–N2 2.0851(17) | Zn1–N7 2.077(3) |
| Zn1–O1 2.243(2) | Zn1–O1 2.0950(14) | Zn1–O1 2.097(3) |
| Zn1–Br1 2.3561(5) | Zn1–O2 2.1234(13) | Zn1–O2 2.099(3) |
| Zn1–Br2 2.4026(6) | Zn1–N1 2.1499(17) | Zn1–N1 2.155(3) |
| O1–C12 1.233(3) | Zn1–N6 2.2047(16) | Zn1–N6 2.221(3) |
| N1–C1 1.328(4) | O1–C12 1.257(2) | O1–C12 1.252(4) |
| N1–C5 1.345(4) | O2–C30 1.257(2) | O2–C30 1.256(4) |
| N2–C6 1.287(4) | N5–C12 1.363(3) | N1–C1 1.339(4) |
| N2–N3 1.355(4) | N5–C13 1.403(3) | N1–C5 1.352(5) |
| N3–C12 1.369(4) | N3–N2 1.352(2) | N2–C6 1.296(5) |
| | | N2–N3 1.347(4) |
| *Bond angles* | | |
| N2–Zn1–N1 73.88(10) | N7–Zn1–N2 165.27(6) | |
| N2–Zn1–O1 72.60(9) | N7–Zn1–O1 109.11(6) | N2–Zn1–N7 167.20(14) |
| N1–Zn1–O1 146.06(9) | N2–Zn1–O1 76.14(6) | N2–Zn1–O1 76.08(11) |
| N2–Zn1–Br1 129.81(8) | N7–Zn1–O2 76.17(6) | N7–Zn1–O1 109.42(11) |
| N1–Zn1–Br1 99.40(7) | N2–Zn1–O2 118.01(6) | N2–Zn1–O2 115.77(12) |
| O1–Zn1–Br1 97.86(6) | O1–Zn1–O2 91.14(5) | N7–Zn1–O2 76.30(12) |
| N2–Zn1–Br2 114.29(8) | N7–Zn1–N1 99.93(6) | O1–Zn1–O2 90.11(10) |
| N1–Zn1–Br2 101.82(8) | N2–Zn1–N1 75.49(6) | N2–Zn1–N1 75.84(12) |
| O1–Zn1–Br2 96.60(6) | O1–Zn1–N1 150.95(6) | N7–Zn1–N1 99.40(12) |
| Br1–Zn1–Br2 115.75(2) | O2–Zn1–N1 96.65(6) | O1–Zn1–N1 151.17(11) |
| C12–O1–Zn1 114.11(19) | N7–Zn1–N6 74.92(6) | O2–Zn1–N1 96.25(11) |
| | N2–Zn1–N6 90.96(6) | N2–Zn1–N6 92.80(13) |
| | O1–Zn1–N6 96.57(6) | N7–Zn1–N6 75.15(13) |
| | O2–Zn1–N6 151.03(6) | O1–Zn1–N6 98.13(11) |
| | N1–Zn1–N6 90.05(6) | O2–Zn1–N6 151.42(11) |
| | C12–O1–Zn1 111.16(13) | N1–Zn1–N6 89.61(11) |
| | | C12–O1–Zn1 110.7(3) |

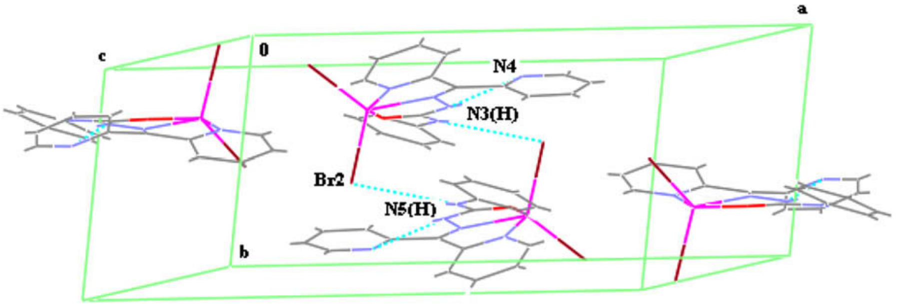

**Fig. 3.** Partial unit cell packing diagram for compound **1** with intra- and intermolecular hydrogen bonding interactions shown as dotted lines.

bonding interactions were observed. The $\pi$–$\pi$ interaction is perceived at 4.0873 Å for Cg(1)–Cg(1)$^{a}$ [Cg(1) = Zn1–O1–C12–N3–N2; $a = 1 - x, 1 - y, 1 - z$]. Only one C–H···$\pi$ interaction is shown in the unit cell and that is between C(8)–H(8)···Cg(5)$^{b}$ [Cg(5) = C(13)–C(14)–(15)–C(16)–C(17)–C(18); $d_{\text{H–Cg}}$ = 2.95 Å; $b = 1 - x, 1 - y, 1 - z$]. One intra- and one intermolecular hydrogen bonding interaction were observed, *ie*, N3(H) and N4 of the same molecule and N5(H) of one molecule with Br2 of the other molecule [N(3)–H(3 N)···N(4), D–H = 0.80(3) Å, H···A = 2.04(3) Å, D···A = 2.669(4) Å, D–H···A = 135(3)°; N(5)–(H5N)···Br(2)$^{c}$, D–H = 0.70(3) Å, H···A = 2.68(3) Å, D···A = 3.374(3) Å, D–H···A = 170(3)°, $c = 1 - x, 1 - y, 1 - z$].

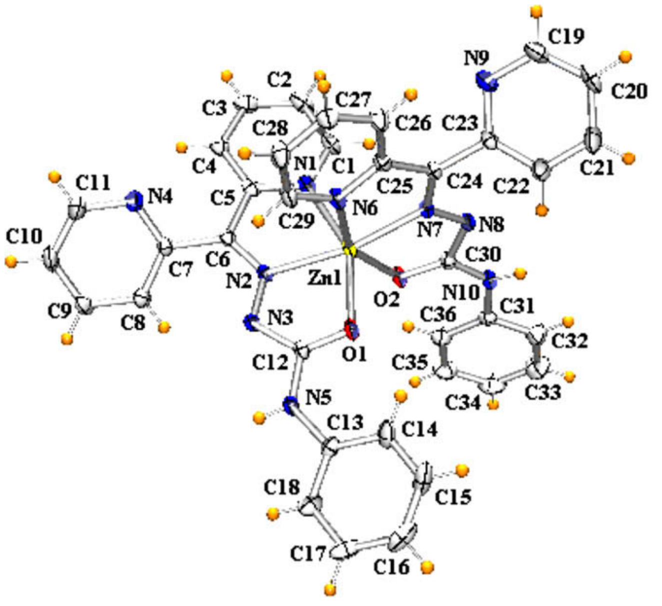

**Fig. 4.** Molecular structure of $ZnL_2$.

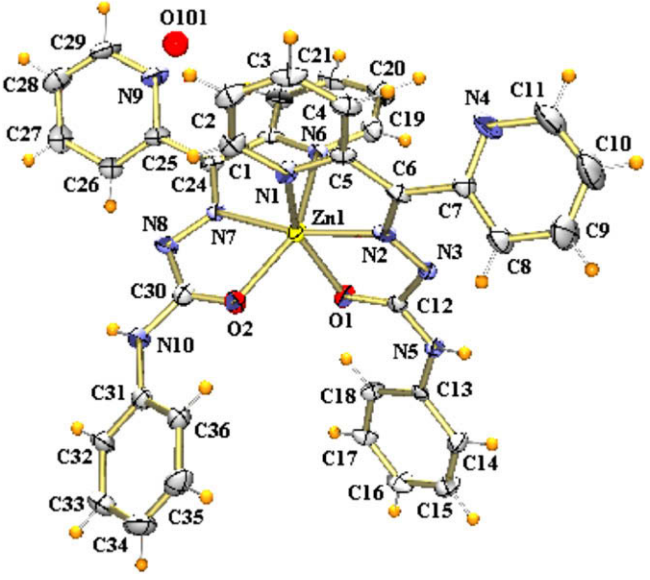

**Fig. 5.** Molecular structure of $ZnL_2 \cdot 0.3H_2O$.

Figs. 4 and 5 show the molecular structures of compounds **5** and **6** along with the atom numbering schemes. Compound **5** crystallizes in the monoclinic crystal system with the space group $P2_1/n$, while compound **6** in the orthorhombic crystal system with the space group $P2_12_12_1$. In both the compounds [$ZnL_2$], the Zn atom is six coordinate in which both ligands are coordinated in their deprotonated enolate forms *via* the pyridine nitrogen, azomethine nitrogen and enolate oxygen atoms. The ligands with their donor atoms are arranged around the zinc ion in a meridional fashion and both compounds are polymorphic. In compound **5**, atoms O1, O2, N1 and N6 lie in the equatorial plane, and N2 and N7 occupy the axial positions, while in compound **6**, atoms O1, O2, N1 and N6 lie in the equatorial plane, and N2 and N7 occupy the axial positions of the distorted octahedron. In both compounds **5** and **6**, the atoms Zn1, O1, O2, N1, N6 do not deviate significantly from the least square plane [0.0034 Å for **5** and 0.0015 Å for **6**]. Each of the semicarbazone fragments {(O1 and N1, O2 and N6 for **5**); (O1 and N1, O2 and N6 for **6**)} are coordinated to the Zn centre with an angle of 150.95(6)°, 151.03(6)° and 151.17(11)°, 151.42(11)°, respectively, for **5** and **6**, having a large distortion from an ideal octahedron (180°). The planes containing Zn1, O1, N1, N2, N7 (plane 1) and Zn1, O2, N2, N6, N7 (plane 2) are deviated from the central metal atom (Zn1) by 0.0837 and 0.0248 Å, respectively, in compound **5**, similarly in compound **6**, the planes containing Zn1, O2, N7, N6, N2 (plane 3) and Zn1, O1, N2, N1, N7 (plane 4) are deviated from the central metal atom (Zn1) by 0.0314 and 0.0610 Å, respectively. The dihedral angle formed by the planes 1 and 2 is 85.81(0.04)° for compound **5** and by the planes 3 and 4 in compound **6** is 85.69 (0.08)°, consistent with a nearly 90° octahedral angle. Selected bond lengths and bond angles are given in Table 2.

In compound **5**, when viewed along *a* axis, the molecules are arranged in an opposite manner and are interconnected through N5(H) and N3 of the same molecule with N8 and N10(H) of the nearby molecule, respectively (Fig. 6) [D–H···A, N(5)–H(5)···N(8)$^{d}$; D–H = 0.84(3) Å; H···A = 2.13(3) Å; D···A = 2.961(2) Å; D–H···A = 170.(2)°; Symmetry code, $d = 1/2 - x, 1/2 + y, 3/2 - z$; D–H···A, N(10)–H(10)···N(3)$^{e}$; D–H = 0.83(2) Å; H···A = 2.21(2) Å; D···A = 3.023(2) Å; D–H···A = 170.(2)°; Symmetry code, $e = 1/2 - x, -1/2 + y, 3/2 - z$]. Intramolecular hydrogen bonding interactions were also observed i.e., C4(H) with N4 and C8(H) with N3 and C14(H) with O1 [D–H···A, C(4)–H(4)···N(4); D–H = 0.93 Å; H···A = 2.42 Å; D···A = 2.984(3) Å; D–H···A = 119°;

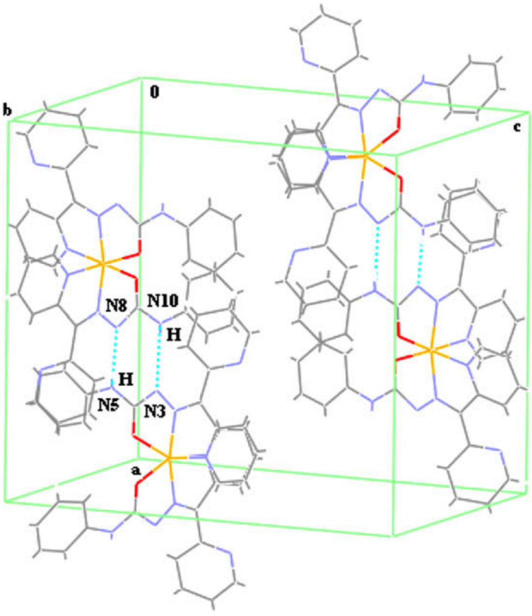

**Fig. 6.** Partial unit cell packing diagram for compound **5** with intermolecular hydrogen bonding interactions shown as dotted lines.

**Table 3**
Interaction parameters of the compounds [Zn(HL)Br$_2$] (**1**), [Zn(L)$_2$] (**5**) and [Zn(L)$_2$] · 0.3H$_2$O (**6**)

| Cg(I)–Res(1)···Cg(J) | Cg–Cg(Å) | α ° | β ° |
|---|---|---|---|
| *π···π Interactions* | | | |
| Cg(1) [1] → Cg(1)$^{a}$ | 4.0874 | 0.02 | 31.75 |

Equivalent position codes: $^{a}$= 1 – *x*, 1 – *y*, 1 – *z*
Cg(1) = Zn(1), O(1), C(12), N(3), N(2)

| XH(I)···Cg(J) | H···Cg (Å) | X–H···Cg (°) | X···Cg (Å) |
|---|---|---|---|
| *CH···π interactions* | | | |
| C(8)–H(8)[ 1] → Cg(5)$^{b}$ | 2.95 | 118 | 3.447(4) |

Equivalent position codes: $^{b}$= 1 – *x*, 1 – *y*, 1 – *z*
Cg(1) = C(13), C(14), C(15), C(16), C(17), C(18)

| D–H···A | D–H | H···A | D···A | D–H···A |
|---|---|---|---|---|
| *H bonding* | | | | |
| [Zn(HL)Br$_2$] (**1**) | | | | |
| N(3)–H(3N)···N(4) | 0.80(3) | 2.04(3) | 2.669(4) | 135(3) |
| N(5)–H(5N)···Br(2)$^{c}$ | 0.70(3) | 2.68(3) | 3.374(3) | 170(3) |
| [Zn(L)$_2$] (**5**) | | | | |
| N(5)–H(5N)···N(8)$^{d}$ | 0.84(3) | 2.13(3) | 2.961(2) | 170(2) |
| N(10)–H(10N)···N(3)$^{e}$ | 0.83(2) | 2.21(2) | 3.023(2) | 170(2) |
| C(4)–H(4)···N(4) | 0.93 | 2.42 | 2.984(3) | 119 |
| C(8)–H(8)···N(3) | 0.93 | 2.56 | 2.940(3) | 105 |
| C(14)–H(14)···O(1) | 0.93 | 2.32 | 2.901(3) | 120 |
| [Zn(L)$_2$]0.3H$_2$O (**6**) | | | | |
| N(5)–H(5N)···N(8)$^{f}$ | 0.84(3) | 2.15(3) | 2.992(5) | 179(5) |
| N(10)–H(10N)···N(3)$^{g}$ | 0.84(3) | 2.18(3) | 3.018(5) | 176(3) |
| C(4)–H(4)···N(4) | 0.95 | 2.45 | 3.041(6) | 120 |
| C(14)–H(14)···O(1) | 0.95 | 2.36 | 2.921(5) | 118 |
| C(22)–H(22)···N(9) | 0.95 | 2.61 | 3.026(5) | 107 |

Equivalent position codes: $^{c}$= 1 – *x*, 1 – *y*, 1 – *z*.
$^{d}$= 1/2 – *x*, 1/2 + *y*, 3/2 – *z*; $^{e}$= 1/2 – *x*, –1/2 + *y*, 3/2 – *z*; $^{f}$= 1 – *x*, 1/2 + *y*, 1/2 – *z*; $^{g}$ = 1 – *x*, –1/2 + *y*, 1/2 – *z*.
(D = donor, A = acceptor, Cg = centroid, α = dihedral angles between planes I and *J*, *β* = angle Cg(1)–Cg(J).

D–H···A, C(8)–H(8)··N(3)i; D–H = 0.93 Å; H···A = 2.56 Å; D···A = 2.940(3) Å; D–H···A = 105°; D–H···A, C(14)–H(14)···O(1); D–H = 0.93 Å; H···A = 2.32 Å; D···A = 2.901(3) Å; D–H···A = 120°]. In compound **6**, two intermolecular hydrogen bonding interactions are observed i.e., N5(H) and N8 and with N10(H) and N3, which are arranged in an opposite manner (Fig. 7) [D–H···A, N(5)–H(5)···N(8)$^{f}$; D–H = 0.84(3) Å; H···A = 2.15(3) Å; D···A = 2.992(5) Å; D–H···A = 179(5)°; Symmetry code, f = 1 – *x*, 1/2 + *y*, 1/2 – *z*; D–H···A, N(10)–H(10)···N(3)$^{g}$; D–H = 0.84(3) Å; H···A = 2.18(3) Å; D···A = 3.018(5) Å; D–H···A = 176(3)°; Symmetry code, *g* = 1 – *x*, –1/2 + *y*, 1/2 l– *z*]. Intramolecular hydrogen bonding interactions were also observed i.e., C4(H) with N4 and C14(H) with O1 and C22(H) with N9 [D–H···A, C(4)–H(4)···N(4); D–H = 0.95 Å; H···A = 2.45 Å; D···A = 3.041(6) Å; D–H···A = 120°; D–H···A, C(14)–H(14)···O(1); D–H = 0.95 Å; H···A = 2.36 Å; D···A = 2.921(5) Å; D–H···A = 118°; D–H···A, C(22)–H(22)···N(9); D–H = 0.95 Å; H···A = 2.61 Å; D···A = 3.026(5) Å; D–H···A = 107°] (Table 3).

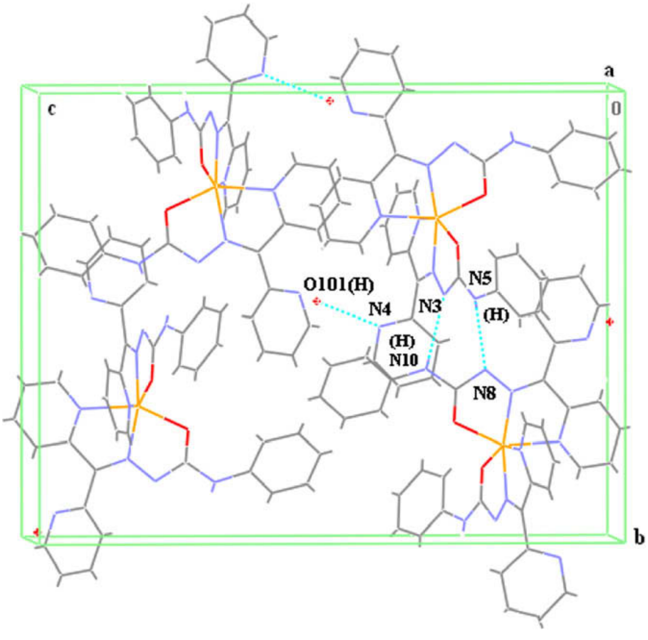

**Fig. 7.** Intermolecular hydrogen bonding interactions of compound **6**.

### 3.3. Infrared and electronic spectral studies

The infrared spectral data of the zinc(II) complexes are given in Table 4. The $\nu_a$(NH) vibrations of the imino group are observed at *ca.* 3369 cm$^{-1}$ in the IR spectrum of HL. The lack of an N–H stretching vibration in the spectra of the complexes ZnL(OAc) and ZnLN$_3$ endorses the ligand coordination to zinc(II) ion in the deprotonated enolate form. However in the complexes Zn(HL)Br$_2$ and Zn(HL)Cl$_2$ the presence of bands at 3239 and 3369 cm$^{-1}$, corresponding to $\nu$(NH) vibrations, indicates that the semicarbazone is coordinated in the neutral form. A strong band at 1591 cm$^{-1}$ in the IR spectrum of HL corresponds to the $\nu$(N3–C6) stretching, which suffers a positive shift on complexation. Coordination of the azomethine nitrogen atom is also consistent with the presence of a band in the 404–420 cm$^{-1}$ region, assignable to $\nu$(Zn–N) for these complexes

**Table 4**
IR spectral assignments for the ligand and the zinc(II) complexes

| Compound | $\nu$(NH) | $\nu$(C=N) | $\nu$(CO) | $\nu$(N=C) | $\nu$(N–N) | $\nu$(Zn–N) | $\nu$(Zn–O) |
|---|---|---|---|---|---|---|---|
| HL | 3369 | 1591 | 1718 | | 1129 | | |
| Zn(HL)Br$_2$ (**1**) | 3239 | 1597 | 1661 | | 1147 | 407 | |
| Zn(HL)Cl$_2$(**2**) | 3369 | 1597 | 1667 | | 1153 | 404 | |
| ZnL(OAc) (**3**) | | 1597 | | 1521 | 1156 | 414 | 516 |
| ZnLN$_3$(**4**) | | 1595 | | 1518 | 1148 | 404 | 502 |
| ZnL$_2$(**5**) | | 1597 | | 1515 | 1223 | 420 | 518 |
| ZnL$_2$ · H$_2$O (**6**) | | 1597 | | 1515 | 1229 | 416 | 520 |

**Table 5**
Electronic spectral assignments for the ligand and the zinc(II) complexes

| compound | $\pi$–$\pi^*$ | n–$\pi^*$ | MLCT |
|---|---|---|---|
| HL | 40000 | 30770 | |
| Zn(HL)Br$_2$ (**1**) | 37630 | 31840 | 24220 |
| Zn(HL)Cl$_2$ (**2**) | 37460 | 31450 | 24280 |
| ZnL(OAc) (**3**) | 37410 | 31350 | 24280 |
| ZnLN$_3$ (**4**) | 37200 | 32250 | 24210 |
| ZnL$_2$ (**5**) | 37280 | 32230 | 24230 |
| ZnL$_2$ · H$_2$O (**6**) | 37270 | 32240 | 24210 |

[20–22]. A band at 1718 cm$^{-1}$ in the ligand has significant contribution from the C═O stretching vibration and it is shifted to 1667 cm$^{-1}$ in Zn(HL)Cl$_2$ and 1661 cm$^{-1}$ in Zn(HL)Br$_2$ confirming the keto form of HL in these complexes. In complexes **3**–**6**, the bands at 502–520 cm$^{-1}$ are assignable to $\nu$(Zn–O), consistent with oxygen coordination. The spectra of the complexes exhibit a systematic shift in the position of the $\nu$(N–N) bands in the region 1129–1229 cm$^{-1}$. A medium band around 601 cm$^{-1}$, indicating an out-of-plane pyridyl ring vibration in the uncomplexed ligand, shifts to higher frequencies on complexation which confirms the coordination of the ligand to the metal via the pyridine nitrogen [23–26]. Compound ZnLN$_3$ exhibits strong bands at 2076 and 1302 cm$^{-1}$ corresponding to the asymmetric and symmetric stretching of the coordinating azido group. For the complex ZnL(OAc) the asymmetric and symmetric stretching vibrations of the acetate group appear at 1562 and 1433 cm$^{-1}$ respectively. The presence of a band at 3440 cm$^{-1}$ for ZnL$_2$ · H$_2$O indicates the presence of the H$_2$O molecule.

The electronic spectral data of the zinc(II) complexes are given in Table 5. The ligand HL has an absorption at 40000 cm$^{-1}$ due to the intra-ligand $\pi$–$\pi^*$ transitions of the pyridyl ring and imine function of the semicarbazone moiety. Another band at 30770 cm$^{-1}$ for HL corresponding to a n–$\pi^*$ transition of the amide function, which undergoes a small blue shift on complexation, indicating coordination via the pyridyl nitrogen with a reduction in intensity [27]. The shift of the $\pi$–$\pi^*$ bands to the longer wavelength region is the result of the C═O bond being weakened and the conjugated system being enhanced after the formation of the complexes. The metal–ligand CT bands are found around 24200 cm$^{-1}$.

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## Appendix A. Supplementary data

CCDC 648484, 648485 and 648486 contain the supplementary crystallographic data for **1**, **5** and **6**. 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2008.08.014.

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