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Spectrochimica Acta Part A 69 (2008) 726–732
SPECTROCHIMICA ACTA PART A
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Synthesis, spectral and structural studies of zinc(II) complexes of salicylaldehyde *N*(4)-phenylthiosemicarbazone

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Received 27 March 2007; accepted 10 May 2007

Abstract

Five Zn(II) complexes of salicylaldehyde *N*(4)-phenylthiosemicarbazone (H_2L) have been synthesized and physicochemically characterized. Out of the five Zn(II) complexes, one is binuclear $\{[(ZnL)_2]\cdot 3C_2H_5OH$ (**1**)$\}$ and the other four are mononuclear $\{[Zn(HL)_2]\cdot C_2H_5OH$ (**2**), $[ZnLbipy]\cdot 1/2H_2O$ (**3**), $[ZnLphen]\cdot H_2O$ (**4**) and $[ZnLdmbipy]$ (**5**)$\}$ in nature. In complex **2**, IR band due to ν(Zn–O) is absent and also the –OH signal due to the phenolic –OH group appears at $\delta = 11.38$ ppm obtained from the ^{1}H NMR spectrum supports the existence of free –OH group. Complexes **3**–**5** are heterocyclic base adducts and their IR spectra display bands characteristic of coordinated heterocyclic bases. The molecular structure of one of the complex **3** is resolved by single crystal X-ray diffraction studies. The complex **3** is orthorhombic with a space group $P2_1cn$. The Zn(II) in **3** is five coordinated and is having an approximately trigonal bipyramidal geometry with distortion from square based pyramid (TBDSBP).

Keywords: Salicylaldehyde; Thiosemicarbazone; Zn(II) complex; 2,2′-Bipyridine; 1,10-Phenanthroline; 4,4′-Dimethyl 2,2′-bipyridine; Crystal structure

1. Introduction

Thiosemicarbazones and their metal complexes show significant biological activity [1] and possess medicinal properties [2], which are dependent upon the chemical nature of the moiety attached to the C=S carbon atom. The biological activity of Zn(II) complexes of thiosemicarbazones mainly 2-pyridylketone thiosemicarbazone and *p*-isopropylbenzaldehyde thiosemicarbazone were reported earlier [3,4]. Zinc atom has either a structural or analytical role in several proteins. It has been recognized as an important cofactor in biological molecules, either as a structural template in protein folding or as a Lewis acid catalyst that can readily adopt 4-, 5- or 6- coordination [5]. Zinc is able to play a catalytic role in the activation of thiols as nucleophiles at physiological pH. Mononuclear zinc complexes may serve as model compounds for zinc enzymes such as phospholipase C, bovine lens leucine aminopeptidase, ATPases, carbonic anhydrases and peptide deformylase. Binuclear cores are versatile at active sites of many metalloenzymes and play essential role in biological systems.

The zinc(II) ion is known to have a high affinity towards nitrogen and sulfur donor ligands. Dowling and Perkin investigated Zn(II) complexes with mixed N, O and S coordination to understand the reactivity of the pseudotetrahedral zinc center in proteins [6]. Complexes of group 12 metals, mainly zinc, can provide an interesting range of stoichiometries depending on the preparative salt. Here, we report the synthesis and characterization of five Zn(II) complexes of salicylaldehyde *N*(4)-phenylthiosemicarbazone using infrared, electronic and ^{1}H NMR studies. It also describes the single crystal X-ray diffraction studies of the first heterocyclic base adduct of Zn(II) thiosemicarbazone complex with five coordinated geometry.

2. Experimental

2.1. Materials

All compounds used for the synthesis of salicylaldehyde *N*(4)-phenylthiosemicarbazone (H_2L) and their metal complexes were purified by standard methods and solvents were purified by distillation. $Zn(OAc)_2\cdot 2H_2O$ (S.D.Fine chemicals), 2,2′-bipyridine (bipy) (Central drug house), 1,10-phenanthroline (phen) (Ranboxy fine chemicals) and 4,4′-dimethyl 2,2′-

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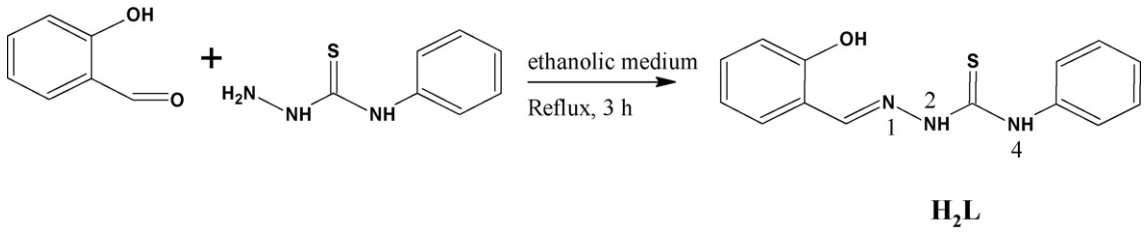
doi:10.1016/j.saa.2007.05.025



Scheme 1.

bipyridine (dmbipy) (E-Merck) were used. The reagents used were of analar grade and used without further purification.

2.2. Synthesis of the ligand and their Zn(II) complexes

Synthesis of the ligand H_2L (Scheme 1) was carried out by adapting the procedure of Klayman et al. and also by us [7,8].

2.2.1. $[(ZnL)_2]\cdot 3C_2H_5OH$ (**1**)

To a solution of H_2L (1 mmol, 0.271 g) in hot ethanol was added an ethanolic solution of $Zn(OAc)_2\cdot 2H_2O$ (1 mmol, 0.219 g) with constant stirring. The stirring was continued for about an hour when yellow compound separated was filtered, washed with ethanol and ether and dried *in vacuo* over P_4O_{10}.

2.2.2. $[Zn(HL)_2]\cdot C_2H_5OH$ (**2**)

A solution of $Zn(OAc)_2\cdot 2H_2O$ (1 mmol, 0.219 g) in ethanol and a solution of H_2L (2 mmol, 0.542 g) in hot ethanol were mixed and refluxed for 4 h. On cooling, yellow solid separated was filtered, washed with ethanol and ether and dried *in vacuo* over P_4O_{10}.

2.2.3. $[ZnLbipy]\cdot 1/2H_2O$ (**3**)

To a solution of H_2L (1 mmol, 0.271 g) in hot ethanol was added an ethanolic solution of $Zn(OAc)_2\cdot 2H_2O$ (1 mmol, 0.219 g) with constant stirring. This was followed by the addition of the base 2,2′-bipyridine (1 mmol, 0.156 g) in the solid form. The stirring was continued for about an hour when yellow crystalline compound formed was filtered, washed with ethanol and ether and dried *in vacuo* over P_4O_{10}.

2.2.4. $[ZnLphen]\cdot H_2O$ (**4**)

To a solution of H_2L (1 mmol, 0.271 g) in hot ethanol was added an ethanolic solution of $Zn(OAc)_2\cdot 2H_2O$ (1 mmol, 0.219 g) with constant stirring. This was followed by the addition of the base 1,10-phenanthroline (1 mmol, 0.198 g) in the solid form. The stirring was continued for about an hour when yellow compound began to separate. This was filtered, washed with ethanol and ether and dried *in vacuo* over P_4O_{10}.

2.2.5. [ZnLdmbipy] (**5**)

To a solution of H_2L (1 mmol, 0.271 g) in hot ethanol was added an ethanolic solution of $Zn(OAc)_2\cdot 2H_2O$ (1 mmol, 0.219 g) with constant stirring. This was followed by the addition of the base 4,4′-dimethyl 2,2′-bipyridine (1 mmol, 0.184 g) in the solid form. The stirring was continued for about an hour when yellow compound began to separate. This was filtered, washed with ethanol and ether and dried *in vacuo* over P_4O_{10}.

2.3. Physical measurements

Elemental analyses were performed on a Vario ELIII elemental analyzer at SAIF, Cochin University of Science and Technology, Kochi-22, India. The FT-IR spectra were recorded on a Thermo Nicolet AVATAR 370 DTGS FTIR spectrometer using KBr pellets in the range 4000–400 cm^{-1} at SAIF, Cochin University of Science and Technology, Kochi-22, India. Electronic spectra were recorded on a GENESYS^{TM} 10 series spectrophotometer in DMF solution. The ^1H NMR spectra were recorded on a Brucker DRX 500 MHz instrument using $CDCl_3$ as the solvent and TMS as the internal reference at Sophisticated Instruments Facility, Indian Institute of Science, Bangalore. Single crystal X-ray crystallographic study of one of the compounds was carried out using the Argus (Nonius, MACH3 software) at National Single Crystal X-Ray Diffraction Facility, IIT, Bombay, India.

2.4. X-ray crystallography

A yellow block crystal of the compound [ZnLbipy] having approximate dimensions 0.40 mm × 0.35 mm × 0.20 mm was sealed in a glass capillary and intensity data were measured at 293(2) K. The data acquisition and cell refinement were done using the Argus (Nonius, MACH3 software) [9]. The Maxus (Nonius software) were used for data reduction [10]. The structure was solved by direct methods and full-matrix least-squares refinement using SHELX97 [11] package. The positions of all the non-hydrogen atoms were included in the full-matrix least-squares refinement using SHELX97 program and all the hydrogen atoms were fixed in calculated positions. The structure of the compound **3** was plotted using the program Diamond Version 3.0 [12] and PLATON [13]. The crystal data and structure refinement parameters for [ZnLbipy] are given in Table 1.

3. Results and discussion

3.1. Synthesis

The colors, partial elemental analyses and magnetic moments of the complexes are presented in Table 2. The elemental analyses data are consistent with the general composition $(ML)_2$, $M(HL)_2$ and MLB, where M is the zinc atom, L is the doubly deprotonated thiosemicarbazone ligand and B is the bidentate

Table 1
Crystal data and structure refinement parameters for [ZnLbipy]

Empirical formula	$C_{24}H_{19}N_5OSZn$
Formula weight	490.87
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_1cn$
Unit cell dimensions	$a = 9.8250(16)$ Å, $b = 10.5580(6)$ Å, $c = 20.7990(12)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$
Volume	2157.5(4) Å^3
Z	4
Density (calculated)	1.511 Mg/m^3
Absorption coefficient	1.263 mm^{-1}
$F(0\,0\,0)$	1008
Crystal size	0.40 mm × 0.35 mm × 0.20 mm
θ range for data collection	1.96–24.96°
Index ranges	$-11 \le h \le 0$, $-12 \le k \le 0$, $-24 \le l \le 0$
Reflections collected	2012
Independent reflections	2012 [R(int) = 0.0000]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2012/1/293
Goodness-of-fit on F^2	1.017
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0383$, $wR_2 = 0.0681$
R indices (all data)	$R_1 = 0.0923$, $wR_2 = 0.0795$
Largest diff. peak and hole	0.324 and −0.380 e Å^{-3}

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

heterocyclic bases *viz*. bipy, phen or dmbipy. All the zinc complexes are yellow in color. Elemental analyses data shows both compounds **1** and **2** having ethanol molecules and compounds **3** and **4** having water molecules present as solvents of crystallizations. In compound **5**, there is neither ethanol nor water of crystallization present in it. The complexes are insoluble in most of the common polar and non-polar solvents. The complexes are soluble in DMF, $CHCl_3$ and DMSO.

3.2. Crystal structure of the compound [ZnLbipy]

The molecular structure of the compound **3** along with the atom numbering scheme is represented in Fig. 1 and selected bond lengths and bond angles are summarized in Table 3. Suitable pale yellow crystals were obtained from a solution of **3** in a mixture of CH_3OH and CH_3CN. The compound **3** is orthorhombic with a space group $P2_1cn$. This complex is mononuclear and five coordinated. In the complex [ZnLbipy], Zn(II) is located in an approximately trigonal bipyramidal geometry in which the

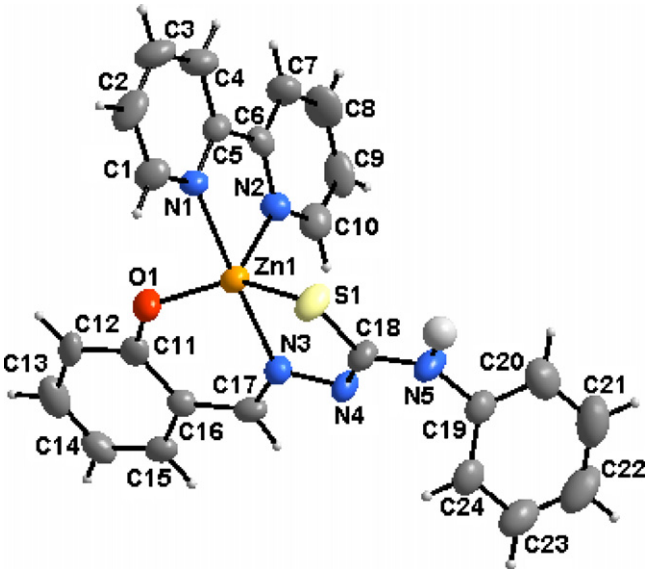


Fig. 1. Structure and labeling diagram of the compound **3**.

equatorial positions are occupied by the S(1), O(1), N(2) and the axial positions by N(1) and N(3) [Zn(1)–N(1), 2.164(5), Zn(1)–N(3), 2.098(5) Å] with the N(3)–Zn(1)–N(1) angle of 177.5(2)° being close to the 'ideal' value of 180° which is usual for such systems [14]. In a five-coordinate system, the angular structural parameter (τ) is used to propose an index of trigonality. The trigonality index τ of 0.53 {According to Addison et al, $\tau = (\beta - \alpha)/60$, where β = N(3)–Zn(1)–N(1) = 177.5(2)° and α = O(1)–Zn(1)–S(1) = 145.18(16)°; for perfect square pyramidal and trigonal bipyramidal geometries the values of τ are zero and unity, respectively [15]} indicates that the coordination geometry around zinc is intermediate between trigonal bipyramidal and square pyramidal geometries and is better described as trigonal bipyramidal distorted square based pyramid (TBDSBP) with zinc displaced 0.3225 Å above the N(1), N(3), O(1) and S(1) coordination plane and towards the elongated apical N(2) atom [16].

One of the reasons for the deviation from an ideal stereochemistry is the restricted bite angle imposed by both the $(L)^{2-}$ and bipy ligands. The bite angle around the metal *viz*. N(2)–Zn(1)–N(1) of 77.1(2)° may be considered normal, when compared with an average value of 77° cited in the literature [17–19]. The variation in Zn–N bond distances, Zn(1)–N(2), 2.097(5), Zn(1)–N(3), 2.098(5) and Zn(1)–N(1), 2.164(5) indicate differences in the strengths of the bonds

Table 2
Colors and partial elemental analyses data of Zn(II) complexes of H_2L ligand

Compound	Color	Found (calculated) (%)		
		C	H	N
$[(ZnL)_2]\cdot 3C_2H_5OH$ (**1**)	Yellow	50.14 (50.56)	5.08 (4.99)	10.55 (10.41)
$[Zn(HL)_2]\cdot C_2H_5OH$ (**2**)	Yellow	54.77 (55.25)	4.49 (4.64)	13.35 (12.89)
$[ZnLbipy]\cdot 1/2H_2O$ (**3**)	Yellow	57.92 (57.66)	3.88 (4.03)	14.02 (14.01)
$[ZnLphen]\cdot H_2O$ (**4**)	Yellow	58.63 (58.60)	3.96 (3.97)	13.13 (13.14)
[ZnLdmbipy] (**5**)	Yellow	59.90 (60.18)	4.58 (4.47)	13.38 (13.50)

Table 3
Selected bond lengths (Å) and bond angles (°) for [ZnLbipy]

Bond lengths	
Zn(1)–O(1)	1.958(5)
Zn(1)–N(2)	2.097(5)
Zn(1)–N(3)	2.098(5)
Zn(1)–N(1)	2.164(5)
Zn(1)–S(1)	2.3435(19)
S(1)–C(18)	1.738(7)
O(1)–C(11)	1.315(7)
N(3)–C(17)	1.276(7)
N(3)–N(4)	1.396(7)
N(4)–C(18)	1.308(7)
N(5)–C(18)	1.393(9)
N(5)–C(19)	1.414(9)
N(5)–H(105)	0.81(8)
Bond angles	
O(1)–Zn(1)–N(2)	104.3(2)
O(1)–Zn(1)–N(3)	89.19(19)
N(2)–Zn(1)–N(3)	100.8(2)
O(1)–Zn(1)–N(1)	92.68(19)
N(2)–Zn(1)–N(1)	77.1(2)
N(3)–Zn(1)–N(1)	177.5(2)
O(1)–Zn(1)–S(1)	145.18(16)
N(2)–Zn(1)–S(1)	110.34(15)
N(3)–Zn(1)–S(1)	81.30(15)
N(1)–Zn(1)–S(1)	98.10(14)
C(18)–S(1)–Zn(1)	92.5(2)
C(11)–O(1)–Zn(1)	129.0(4)
C(5)–N(1)–Zn(1)	114.0(4)
C(1)–N(1)–Zn(1)	126.9(4)
C(6)–N(2)–Zn(1)	117.1(4)
C(10)–N(2)–Zn(1)	125.0(5)
C(17)–N(3)–N(4)	115.5(5)
C(17)–N(3)–Zn(1)	126.2(5)
N(4)–N(3)–Zn(1)	118.0(4)
C(18)–N(4)–N(3)	110.9(5)
C(18)–N(5)–C(19)	126.5(7)

formed by each of the coordinating nitrogen atoms. The Zn–N bond lengths are shorter than those reported for mononuclear zinc(II) complexes, while there is no significant variation in the Zn–S bond lengths reported [20]. The dihedral angle formed

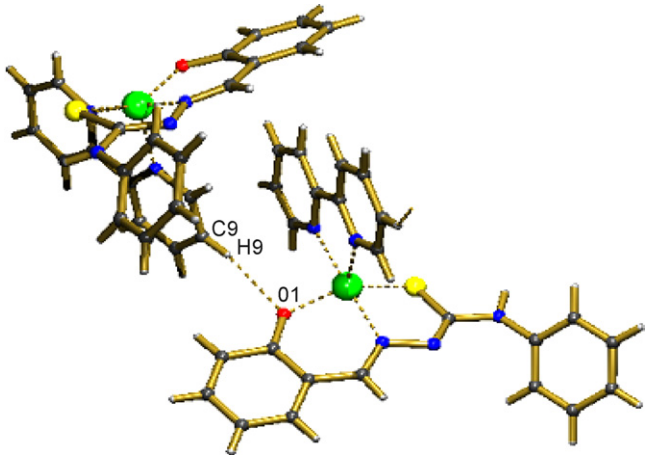


Fig. 3. Hydrogen bonding interactions for the compound **3**.

by the least square plane Cg(5) and Cg(7) is 4.78° for the compound **3**.

Ring puckering analyses shows that the ring Cg(3) comprising of atoms Zn(1), O(1), C(11), C(16), C(17) and N(3) with puckering amplitude (Q_T) = 0.1714 Å and the ring Cg(1) comprising of atoms Zn(1), S(1), C(18), N(4) and N(3) with puckering amplitude (Q_T) = 0.3742 Å [21]. The ring Cg(1) adopts an envelope on Zn(1) {The pseudorotation parameters $P = 159.1°$ and $\tau = 28.1°$ for Zn(1)–S(1) [22]}.

Fig. 2 shows the contents of the unit cell along the *a* axis. The assemblage of molecules in the respective manner in the unit cell is resulted by the π–π and CH–π interactions as depicted in Table 4. One intermolecular hydrogen bonding is observed, *i.e.*, [C(9)–H(9) and O(1)] (Fig. 3), but no classic hydrogen bonds were found. The centroid Cg(4) is involved in π–π interactions with pyridyl ring of the neighbouring unit at a distance of 3.8418 Å and the centroid Cg(5) with phenyl ring at a distance of 3.7274 Å, the CH–π interactions of the ring Cg(6) with the neighbouring molecules also contribute stability to the unit cell packing.

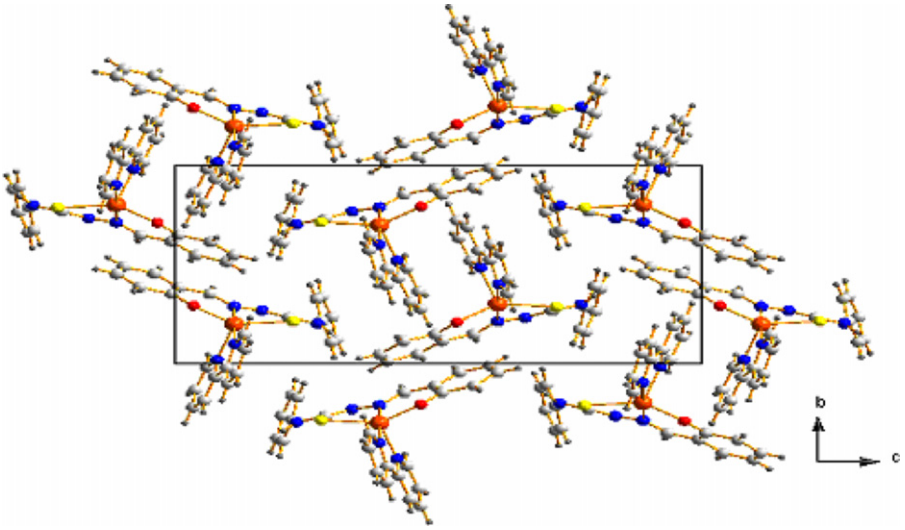


Fig. 2. Unit cell packing diagram of the compound **3** viewed along the *a* axis.

Table 4
Interaction parameters of the compound [ZnLbipy]

Cg(I)–Res(1)–Cg(J)	Cg–Cg (Å)	α (°)	β (°)
π–π interactions			
Cg(4)[1] → Cg(5)[a]	3.8418	23.58	5.95
Cg(5)[1] → Cg(4)[b]	3.8418	23.58	29.44
Cg(5)[1] → Cg(7)[c]	3.7274	4.78	18.80
Cg(7)[1] → Cg(5)[b]	3.7274	4.78	19.81

Eqivalent position codes: $a = -1/2 + x, -y, -z$, $b = 1/2 + x, -y, -z$, $c = -1/2 + x, -1/2 + y, 1/2 - z$, $d = 1/2 + x, 1/2 + y, 1/2 - z$
Cg(4) = N(1), C(1), C(2), C(3), C(4), C(5); Cg(5) = N(2), C(6), C(7), C(8), C(9), C(10); Cg(7) = C(19), C(20), C(21), C(22), C(23), C(24)

XH(I)–Cg(J)	H···Cg (Å)	X–H···Cg (°)	X···Cg (Å)
CH–π interactions			
C(4)–H(4)[1] → Cg(6)[a]	2.75	153	3.6078

Equivalent position codes: $a = -1/2 + x, -y, -z$

D···H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
H bonding				
C(9)–H(9)–O(1)	0.93	2.41	3.2456	149

D: donor, A: acceptor, Cg: centroid, α: dihedral angles between planes I and J, and β: angle Cg(I)–Cg(J).

3.3. Infrared spectra

Table 5 lists the tentative assignments of main IR bands of Zn(II) complexes for the ligand H_2L in 4000–50 cm^{-1} region. The spectrum of free ligand exhibits a medium band at 3146 cm^{-1}, which is assigned to ν(N–H) vibration. The absence of ν(N–H) band in the spectra of complexes provides a strong evidence for the ligand coordination around Zn(II) ion in its deprotonated form. On coordination of azomethine nitrogen, ν(C=N) shifts to lower wavenumbers by 10–20 cm^{-1}, as the band shifts from 1613 cm^{-1} in the uncomplexed thiosemicarbazone spectrum to *ca.*1598 cm^{-1} in the spectra of all the five Zn(II) complexes. Coordination of azomethine nitrogen is confirmed with the presence of new bands in the range 410–420 cm^{-1}, assignable to ν(Zn–N) for these complexes [23]. The ν(N–N) of the thiosemicarbazone is found at 1149 cm^{-1}. The increase in the frequency of this band in the spectra of the complexes, due to the increase in the bond strength, again confirms the coordination *via* the azomethine nitrogen.

The decrease in the stretching frequency of ν(CS) bond from 874 cm^{-1} in the thiosemicarbazone by 10–50 cm^{-1} upon complexation indicates coordination *via* its thiolato sulfur. In all the five Zn(II) complexes, another strong band is found at *ca.*1530–1550 cm^{-1}, which may be due to the newly formed ν(N=C) band. From this, it is clear that coordination *via* its thiolato sulfur takes place. In all the five complexes, except in **2**, phenolic oxygen is coordinated to copper by loss of the –OH proton. In complex **1**, the phenolic oxygen, on loss of the –OH proton, occupies the third and fourth (through bridging) coordination sites. This causes ν(C–O) to shift to higher wavenumbers (lower frequency) by 50–60 cm^{-1} from its position at 1255 cm^{-1} in the ligand spectra, which is consistent with a bridging phenolic oxygen [24]. A new band in the range 570–590 cm^{-1} in the spectra of the complexes is assignable to ν(Zn–O) [25]. In complex **2**, the band due to ν(Zn–O) is absent, which suggests that the phenolic –OH group is not coordinated to the metal in this complex. The non-involvement of the phenolic –OH group in a zinc(II) complex of a similar thiosemicarbazone is established by single crystal X-ray diffraction study [26]. Tentative structure of the complex **2** is shown in Fig. 4. The IR spectra of the complexes **3**, **4** and **5** display bands characteristic of coordinated heterocyclic bases [27,28]. In the spectrum of the thiosemicarbazone ligand, there is a sharp peak at 3336 cm^{-1}, which may be due to the presence of phenolic group. But, in the complexes **1**–**4**, no sharp peaks were observed at ∼3336 cm^{-1}, but there were broad bands in the 3200–3500 region. This is because of the presence of either the alcoholic group or the lattice water present in these complexes [29].

Table 5
Selected IR bands (cm^{-1}) with tentative assignments of Zn(II) complexes with H_2L ligand

Compound	ν(C=N)	ν(N=C)	ν(N–N)	ν(C–S)	ν(C–O)	ν(Zn–O)	ν(Zn–N)	Bands due to heterocyclic base
H_2L	1613	–	1149	1328, 874	1255	–	–	–
$[(ZnL)_2]\cdot 3C_2H_5OH$	1597	1548	1154	1316, 824	1200	573	417	–
$[Zn(HL)_2]\cdot C_2H_5OH$	1596	1542	1154	1327, 864	1204	–	421	–
$[ZnLbipy]\cdot 1/2H_2O$	1597	1534	1175	1316, 824	1245	587	411	1429, 758, 690
$[ZnLphen]\cdot H_2O$	1604	1534	1169	1309, 852	1239	588	420	1426, 751, 693
[ZnLdmbipy]	1597	1541	1169	1309, 837	1239	583	416	1432, 752, 694

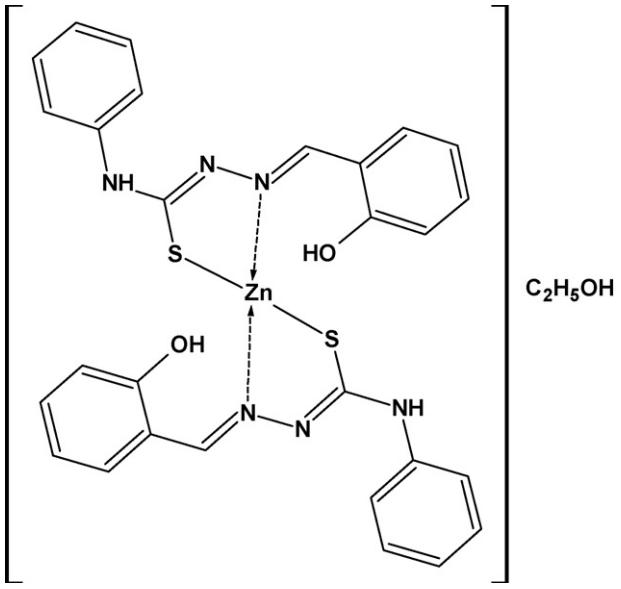


Fig. 4. Tentative structure of the compound **2**.

Table 6
Electronic spectral assignments (cm^{-1}) of the ligand H_2L and their Zn(II) complexes

Compound	π–π*	n–π*	MLCT
H_2L	32,250	29,060	–
$[(ZnL)_2]\cdot 3C_2H_5OH$	33,670	31,440, 30,300	27,240, 26,240
$[Zn(HL)_2]\cdot C_2H_5OH$	33,330	31,540, 30,300	27,470, 26,240
$[ZnLbipy]\cdot 1/2H_2O$	33,110	31,540, 30,300	27,390, 26,240
$[ZnLphen]\cdot H_2O$	33,440	31,940	26,170, 25,640
[ZnLdmbipy]	33,440	31,740, 30,300	27,390, 26,240

3.4. Electronic spectra

The electronic absorption bands of the Zn(II) complexes, recorded in DMF solution, are given in Table 6. The thiosemicarbazone (H_2L) has a ring $\pi \rightarrow \pi^*$ band at 32,250 cm^{-1} and a band at 29,060 cm^{-1} due to $n \rightarrow \pi^*$ transition associated with the azomethine linkage. This band in the complexes have shown a bathochromic shift due to the donation of a lone pair of electrons to the metal and hence the coordination of azomethine [30]. The absorption band centered around 29,060 cm^{-1} in the ligand was assigned to $n \rightarrow \pi^*$ of the thioamide chromophore, which suffers a blue shift in the complexes due to thioenolization.

The moderately intense broad bands for the complexes in the region 28,500–23,500 cm^{-1} are assigned to Zn(II) → S metal to ligand charge transfer transition (MLCT). The MLCT maxima for the phenolato complexes show line broadening, with a tail running into the visible part of the spectrum. This may result from Zn(II) to phenolate MLCT band being superimposed on the low energy side of Zn(II) → S MLCT [31]. Except this, the complexes show no appreciable absorptions in the region below 22,000 cm^{-1} in DMF solution, in accordance with the d^{10} electronic configuration of the Zn(II) ion.

Table 7
^{1}H NMR signals of H_2L and their Zn(II) complexes (δ, ppm)

Compound	–CH=N[1]	–[4]NH	Aromatic
H_2L	8.37	7.26	6.84–7.60
$[(ZnL)_2]\cdot 3C_2H_5OH$	–	7.26	–
$[Zn(HL)_2]\cdot C_2H_5OH$	8.72	7.26	6.85–7.9
$[ZnLbipy]\cdot 1/2H_2O$	8.7	7.26	6.5–7.6
$[ZnLphen]\cdot H_2O$	8.74	7.26	6.5–7.9
[ZnLdmbipy]	8.67	7.26	6.5–7.9

3.5. ^{1}H NMR spectra

The ^{1}H NMR signals of the ligand H_2L and their Zn(II) complexes recorded in $CDCl_3$ are listed in Table 7. The ligand has signals at $\delta = 11.36$, $\delta = 9.54$ and $\delta = 8.37$ ppm, which are due to –OH, –[2]NH and –CH=N[1], respectively. In the Zn(II) complexes, signal due to–[2]NH is absent supporting thioenolization [32]. The low field position of –[4]NH ($\delta = 7.26$ ppm) could be attributable to the deshielding caused by the phenyl group and the adjacent –N=C< of the system –N=C(SH)–NH–C_6H_5. In all the complexes, except in the spectrum of the complex $[Zn(HL)_2]\cdot C_2H_5OH$ (**2**), the–OH proton signals are absent. But in complex **2**, the –OH signal appears at $\delta = 11.38$ ppm, which

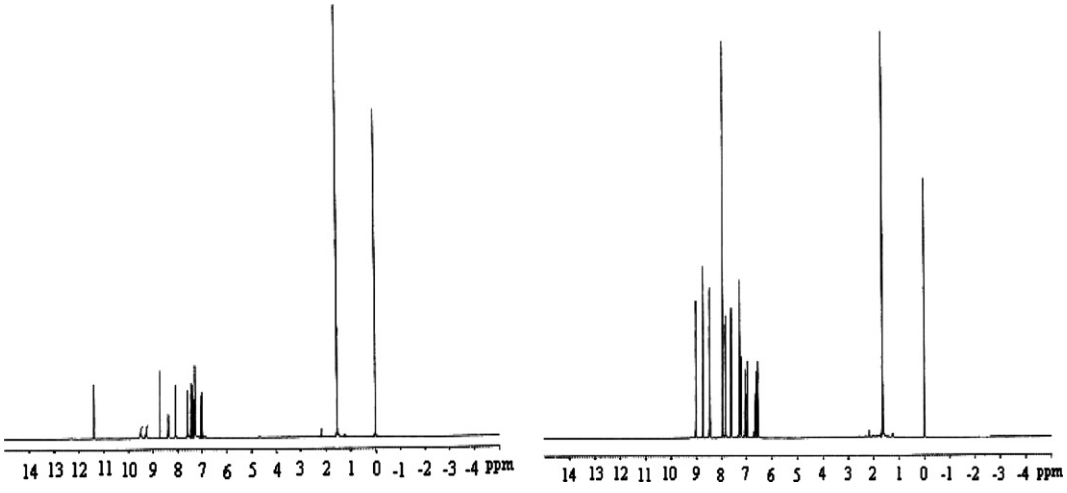


Fig. 5. ^{1}H NMR spectra of the compounds **2** and **4**.

supports for the existence of the phenolic –OH group in this complex. Considerable shift of characteristic signals occurs on complexation [33,34]. Representative spectra of the complexes **2** and **4** are presented in Fig. 5.

4. Supplimentary data

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data center, CCDC 283005 for compound [ZnLbipy]. Copies of this information may be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html [or from Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge, CB2, IEZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

The authors are indebted to SAIF, Cochin University of Science and Technology, Kochi, Kerala, India for elemental analyses and IR spectral analysis. We are thankful to National Single Crystal X-ray diffraction studies, IIT, Bombay, India for providing single crystal XRD results. The financial support by DST, New Delhi, India (No. SR/SI/IC-31/2002) is greatfully acknowledged.

References

[1] D.X. West, S.B. Padhye, P.B. Sonawane, Structure Bond. 76 (1991) 1.
[2] M.J.M. Campbell, Coord. Chem. Rev. 15 (1975) 279.
[3] Q. Li, H. Tang, Y. Li, M. Wang, L. Wang, C. Xia, J. Inorg. Biochem. 78 (2000) 167.
[4] J.M. Perez, A.I. Matesanz, A. Martine-Ambite, P. Navaro, C. Alonso, P. Souza, J. Inorg. Biochem. 75 (1999) 255.
[5] K. Peariso, C.W. Goulding, S. Huang, R.G. Matthews, J.E. Penner-Hahn, J. Am. Chem. Soc. 120 (1998) 8410.
[6] C. Dowling, G. Perkin, Polyhedron 15 (1996) 2463.
[7] D.L. Klayman, J.F. Bartosevich, T.S. Griffin, C.J. Mason, J.P. Scovill, J. Med. Chem. 22 (1979) 855.
[8] P. Bindu, M.R.P. Kurup, Trans. Met. Chem. 22 (1997) 578.
[9] B.V. Nonius, MACH3 Software, Delft, The Netherlands, 1997.
[10] G.M. Sheldrick, Acta Cryst. A 46 (1990) 467.
[11] G.M. Sheldrick, SHELXL97, SHELXS97, University of Gottingen, Germany, 1997.
[12] K. Brandenburg, Diamond Version 3.0, Crystal Impact GbR, Bonn, Germany, 1997–2004.
[13] A.L. Spek, ORTEP-III and PLATON, a Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 1999.
[14] G. Murphy, C.O. Sullivan, B. Murphy, B. Hathaway, Inorg. Chem. 37 (1998) 240.
[15] A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, J. Chem. Soc., Dalton Trans. (1984) 1349.
[16] D. Chakrabarthy, H. Nagase, M. Kamijo, T. Endo, H. Ueda, Anal. Sci. 21 (2005) x167.
[17] C.B. Castellani, G. Gatti, R. Millini, Inorg. Chem. 23 (1983) 4004.
[18] N.J. Ray, B.J. Hathaway, Acta Cryst. B 34 (1978) 3224.
[19] R.P. John, A. Sreekanth, V. Rajakannan, T.A. Ajith, M.R.P. Kurup, Polyhedron 23 (2004) 2549.
[20] C. Zhang, C. Janiak, J. Chem. Cryst. 31 (2001) 29.
[21] D. Cremer, J.A. Pople, J. Am. Chem. Soc. 97 (1975) 1354.
[22] S.T. Rao, E. Westhof, M. Sundaralingam, Acta Cryst. A 37 (1981) 421.
[23] E. Bermejo, A. Castineiras, L.M. Fostiak, I.G. Santos, J.K. Swearingen, D.X. West, Polyhedron 23 (2004) 2303.
[24] V.D. Khanolkar, D.D. Khanolkar, Indian J. Chem. 18A (1979) 315.
[25] R.P. John, Ph.D. Thesis, Cochin University of Science and Technology, 2001.
[26] L. Latheef, E. Manoj, M.R.P. Kurup, Polyhedron, in press.
[27] P. Bindu, M.R.P. Kurup, Indian J. Chem. 36A (1997) 1094.
[28] P.B. Sreeja, M.R.P. Kurup, Spectrochim. Acta A 61 (2004) 331.
[29] K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, 4th ed., Wiley–Interscience, New York, 1997, pp. 228.
[30] A.D. Naik, V.K. Revankar, Proc. Indian Acad. Sci. (Chem. Sci.) 113 (2001) 285.
[31] A. Castineiras, E. Bermejo, D.X. West, L.J. Ackerman, J. Valdes-Martinez, S. Hernandez-Ortega, Polyhedron 18 (1999) 1463.
[32] A. Castineiras, R. Carballo, T. Perez, Polyhedron 20 (2001) 441.
[33] A. Erxleben, Inorg. Chem. 40 (2001) 208.
[34] Z. Popovic, V. Roje, G. Pavlovic, D.M. Calogovic, M. Rajic, I. Leban, Polyhedron 23 (2004) 1293.