SYNTHESES, CRYSTAL STRUCTURES AND SPECTRAL ASPECTS OF ZINC(II) CHELATES DERIVED FROM ONS DONOR THIOSEMICARBAZONES

6.1. Introduction

Zinc is a bluish-white, lustrous, diamagnetic metal [1]. It is somewhat less dense than iron and has a hexagonal crystal structure [2]. The metal is hard and brittle at most temperatures but becomes malleable between 100 and 150 °C [1,3]. Zinc is a fair conductor of electricity [1]. Its melting point is the lowest of all the transition metals aside from mercury and cadmium [4]. Many alloys contain zinc, including brass, an alloy of zinc and copper. Zinc makes up about 75 ppm (0.0075%) of the earth's crust, making it the 24th most abundant element and has five stable isotopes. The most common zinc ore is sphalerite (zinc blende), a zinc sulfide mineral. Zinc production includes froth floatation of the ore, roasting and final extraction using electricity (electrowinning). Alchemists burned zinc in air to form what they called "philosopher's wool" or "white snow". The element was probably named by the alchemist Paracelsus after

the German word *Zinke*. German chemist Andreas Sigismund Marggraf is normally given credit for discovering pure metallic zinc in 1746.

Zinc is an essential mineral of exceptional biologic and public health importance [5]. In children it causes growth retardation, delayed sexual maturation, infection susceptibility and diarrhea. Enzymes with a zinc atom in the reactive center are widespread in biochemistry, such as alcohol dehydrogenase in humans. Consumption of excess zinc can cause ataxia, lethargy and copper deficiency.

The biological activity of Zn(II) complexes of thiosemicarbazones mainly 2-pyridyl ketone thiosemicarbazone and *p*-isopropylbenzaldehyde thiosemicarbazone were reported earlier [6,7]. 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 [8]. 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 [9]. The zinc(II) ion has been found to be of catalytic importance in enzymatic reactions [10]. The

enhancement of antitumor activity of some thiosemicarbazones in the presence of zinc(II) ions has been reported [11].

6.2. Experimental

6.2.1. Materials

Zinc(II) acetate dihydrate (E-Merck), 1,10-phenanthroline (phen), 2,2′-bipyridine (bipy), 4,4′-dimethyl-2,2′-bipyridine (4,4′-dmbipy), 5,5′-dimethyl-2,2′-bipyridine (5,5′-dmbipy) were used as received.

6.2.2. Syntheses of the thiosemicarbazones

The syntheses of thiosemicarbazones H_2L^1 and H_2L^2 are discussed already in Chapter 2.

6.2.3. Syntheses of the complexes

6.2.3.1. [(ZnL¹)₂] (18)

This complex was synthesized by refluxing a solution of H_2L^1 (0.190 g, 0.5 mmol) in 1:1 (v/v) mixture of DMF and methanol with a methanolic solution of $Zn(OAc)_2 \cdot 2H_2O$ (0.109 g, 0.5 mmol) for 3 hours. The complex formed was filtered, washed with methanol and dried *in vacuo*.

Elemental Anal. Found (Calcd.) (%) : C, 40.83 (40.61); H, 3.06 (2.73); N, 9.66 (9.47); S, 7.46 (7.23). Yield: 70%

6.2.3.2. [ZnL¹phen] (19)

Methanolic solution of zinc(II) acetate dihydrate (0.109 g, 0.5 mmol) was added to a stirred mixture of H_2L^1 (0.190 g, 0.5 mmol) in DMF and methanol (1:1 v/v) and 1,10-phenanthroline (0.099 g, 0.5 mmol) in methanol. The resultant homogenous yellow solution was refluxed for

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three hours.   The yellow product obtained was filtered, washed with methanol and dried *in vacuo*.

Elemental Anal. Found (Calcd.) (%) : C, 52.14 (51.98); H, 3.41 (3.23); N, 11.34 (11.23); S, 5.35 (5.14). Yield: 75%

6.2.3.3. [ZnL^{1}bipy] (20)

To a stirred mixture of H$_2$L^1 (0.190 g, 0.5 mmol) in DMF and methanol (1:1 v/v) and 2,2′-bipyridine (0.078 g, 0.5 mmol) in methanol, zinc(II) acetate dihydrate (0.109 g, 0.5 mmol) was added. The resultant yellow solution was refluxed for 3 hours and the yellow product separated out was filtered, washed with methanol and dried *in vacuo*.

Elemental Anal. Found (Calcd.) (%) : C, 50.35 (50.06); H, 3.64 (3.36); N, 11.73 (11.68); S, 5.35 (5.35). Yield: 77%

6.2.3.4. [ZnL^1(4,4′-dmbipy)]·DMF (21)

To a stirred mixture of H$_2$L^1 (0.190 g, 0.5 mmol) in DMF and methanol (1:1 v/v) and 4,4′-dimethyl-2,2′-bipyridine (0.092 g, 0.5 mmol) in methanol, methanolic solution of zinc(II) acetate dihydrate (0.109 g, 0.5 mmol) was added. The resultant yellow solution was refluxed for 3 hours and single crystals suitable for X-ray diffraction studies were obtained from mother liquor after three days.

Elemental Anal. Found (Calcd.) (%) : C, 51.30 (51.40); H, 4.54 (4.46); N, 11.56 (11.99); S, 4.84 (4.57). Yield: 83%

6.2.3.5. [ZnL^1(5,5'-dmbipy)] (22)

Methanolic solution of zinc(II) acetate dihydrate (0.109 g, 0.5 mmol) was added to a stirred mixture of H$_2$L^1 (0.190 g, 0.5 mmol) in DMF and methanol (1:1 v/v) and 5,5'-dimethyl-2,2'-bipyridine (0.092 g, 0.5 mmol) in methanol. The resultant yellow solution was refluxed for three hours. The yellow product obtained was filtered, washed with methanol and dried *in vacuo*.

Elemental Anal. Found (Calcd.) (%) : C, 51.45 (51.65); H, 3.57 (3.85); N, 11.31 (11.15); S, 4.97 (5.11). Yield: 78%

6.2.3.6. [(ZnL^2)$_2$] (23)

This complex was synthesized by refluxing a solution of H$_2$L^2 (0.193 g, 0.5 mmol) in 1:1 (v/v) mixture of DMF and methanol with a methanolic solution of Zn(OAc)$_2$·2H$_2$O (0.109 g, 0.5 mmol) for 3 hours. The complex formed was filtered, washed with methanol and dried *in vacuo*.

Elemental Anal. Found (Calcd.) (%) : C, 40.25 (40.06); H, 3.88 (4.03); N, 9.68 (9.34); S, 6.86 (7.13). Yield: 72%

6.2.3.7. [ZnL^{2}phen] (24)

Methanolic solution of zinc(II) acetate dihydrate (0.109 g, 0.5 mmol) was added to a stirred mixture of H$_2$L^2 (0.193 g, 0.5 mmol) in DMF and methanol (1:1 v/v) and 1,10-phenanthroline (0.099 g, 0.5 mmol) in methanol. The resultant homogenous yellow solution was refluxed for three hours. The yellow product obtained was filtered, washed with methanol and dried *in vacuo*.

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Elemental Anal. Found (Calcd.) (%) : C, 51.14 (51.48); H, 4.36 (4.16); N, 11.55 (11.12); S, 5.36 (5.09). Yield: 77%

6.2.3.8. [ZnL^{2}bipy] (25)

To a stirred mixture of H$_2$L^2 (0.193 g, 0.5 mmol) in DMF and methanol (1:1 v/v) and 2,2′-bipyridine (0.078 g, 0.5 mmol) in methanol, zinc(II) acetate dihydrate (0.109 g, 0.5 mmol) was added. The resultant yellow solution was refluxed for 3 hours and the yellow product separated out was filtered, washed with methanol and dried *in vacuo*.

Elemental Anal. Found (Calcd.) (%) : C, 49.69 (49.56); H, 4.66 (4.33); N, 11.87 (11.56); S, 5.51 (5.29). Yield: 69%

6.3. Results and discussion

Equimolar ratios of the thiosemicarbazones and the metal acetate yielded the light yellow colored complexes [(ZnL^1)$_2$] (**18**) and [(ZnL^2)$_2$] (**23**). The other compounds were prepared by using the heterocyclic bases like 1,10-phenanthroline, 2,2′-bipyridine, 4,4′-dimethylbipyridine and 5,5′-dimethylbipyridine. Single crystals of compound **21** could be isolated and the structure was established by single crystal XRD studies. The complexes were characterized by the following physico-chemical methods.

6.3.1. Elemental analyses

From the observed C, H, N and S values, the above stoichiometry of the complexes were proposed.

6.3.2. Molar conductivity

The molar conductivities of the complexes in DMF (10^{-3} M) was measured at 298 K with a Systronic model 303 direct reading conductivity bridge. The molar conductivity measurements showed that all the complexes are non-electrolytic in nature since the observed values are less than 10 ohm^{-1}cm^{2}mol^{-1} which are very much less than the value of 65-90 ohm^{-1}cm^{2}mol^{-1} reported for a 1:1 electrolyte in the same solvent [12].

Table 6.1. Molar conductivity of Zn(II) complexes

Compound	$\lambda_m{}^a$
[(ZnL^1)$_2$] (**18**)	2.0
[ZnL^{1}phen] (**19**)	4.0
[ZnL^{1}bipy] (**20**)	2.5
[ZnL^1(4,4′-dmbipy)]· DMF (**21**)	4.0
[ZnL^1(5,5′-dmbipy)] (**22**)	3.5
[(ZnL^2)$_2$] (**23**)	2.0
[ZnL^{2}phen] (**24**)	4.3
[ZnL^{2}bipy] (**25**)	3.0

^{a} = mho cm^2 mol^{-1}

6.3.3. Infrared spectra

To clarify the mode of bonding, the IR spectra of the thiosemicarbazones and their Zn(II) complexes were studied and assigned on the basis of a careful comparison of the latter with the thiosemicarbazones. The tentative IR spectral assignments are listed in Table 6.2. The IR spectra of the thiosemicarbazones exhibit a medium band

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at ~3305 cm^{-1} which is assigned to ^{2}NH vibration. It disappears in the spectra of complexes providing strong evidence for ligand coordination to the metal in the deprotonated thioiminolate form [13].   The band corresponding to azomethine bond, v(C=N), shifts to higher energy on coordination due to the combination of v(C=N) with the newly formed C=N bond which results from the loss of the thioamide hydrogen from the thiosemicarbazone moiety [14-18].   The involvement of this nitrogen in bonding is also supported by a shift in v(N–N) to higher frequencies. Coordination *via* the thioiminolate sulfur is indicated by the negative shift of the two bands assigned to v(C=S) and δ(C=S) vibrations. Some of the IR spectra of the Zn(II) complexes are depicted in Figs. 6.1-6.6.

Table 6.2. IR spectral assignments (cm^{-1}) of thiosemicarbazones and their Zn(II) complexes

Compound	v(O–H)	v(C=N)	v(C=N)^a	v(N–N)	v(C=S)/v(C–S), δ(C=S)/δ(C–S)	v(C–O)	v(Zn–O)	v(Zn–N)
H$_2$L^1	3441	1540	----	1071	1333, 857	1267	----	----
[(ZnL^1)$_2$] (**18**)	----	1603	1523	1112	1318, 833	1237	498	435
[ZnL^{1}phen] (**19**)	----	1595	1535	1102	1306, 766	1232	502	458
[ZnL^{1}bipy] (**20**)	----	1599	1481	1100	1306, 766	1228	502	454
[ZnL^1(4,4′-dmbipy)]·DMF (**21**)	----	1608	1539	1093	1316, 832	1228	502	460
[ZnL^1(5,5′-dmbipy)] (**22**)	----	1608	1539	1096	1316, 834	1237	504	470
H$_2$L^2	3454	1539	----	1067	1342, 851	1257	----	----
[(ZnL^2)$_2$] (**23**)	----	1597	1556	1101	1328, 811	1225	500	459
[ZnL^{2}phen] (**24**)	----	1589	1535	1110	1315, 806	1232	482	441
[ZnL^{2}bipy] (**25**)	----	1590	1542	1097	1322, 821	1233	480	436

^{a} = newly formed C=N bond
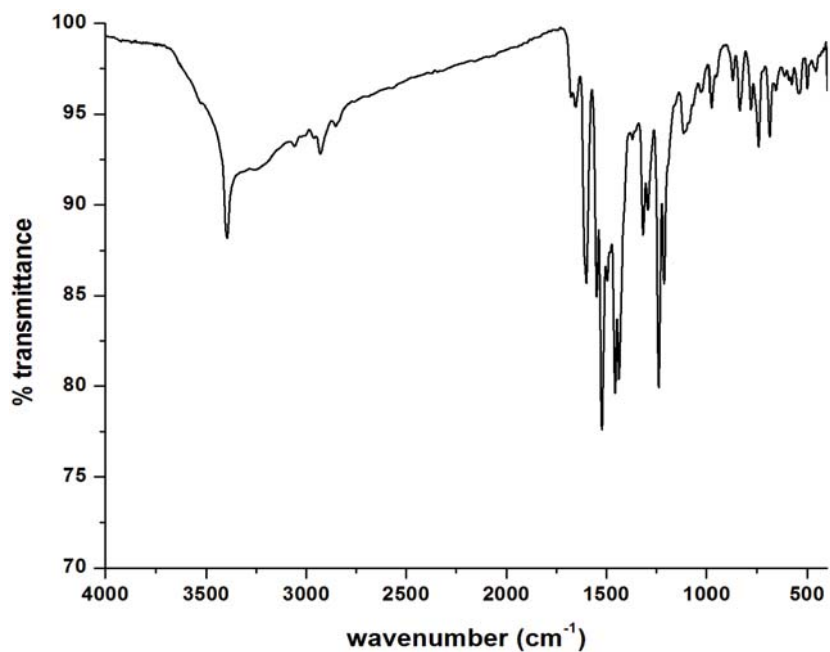
Fig. 6.1. Infrared spectrum of [(ZnL^1)$_2$] (18).
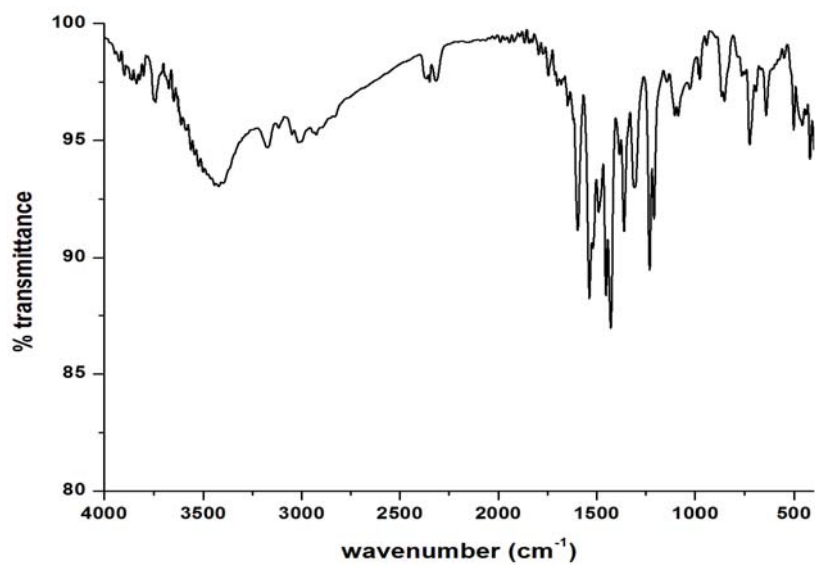
Fig. 6.2. Infrared spectrum of [ZnL^{1}phen] (19).

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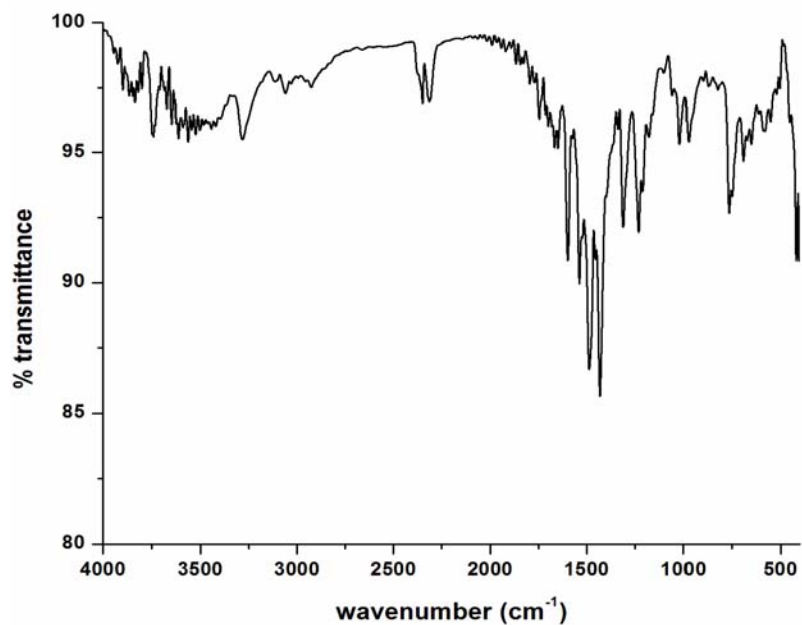Derived from Aldehyde based ONS Donor Thiosemicarbazones

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Fig. 6.3. Infrared spectrum of [ZnL¹bipy] (20).

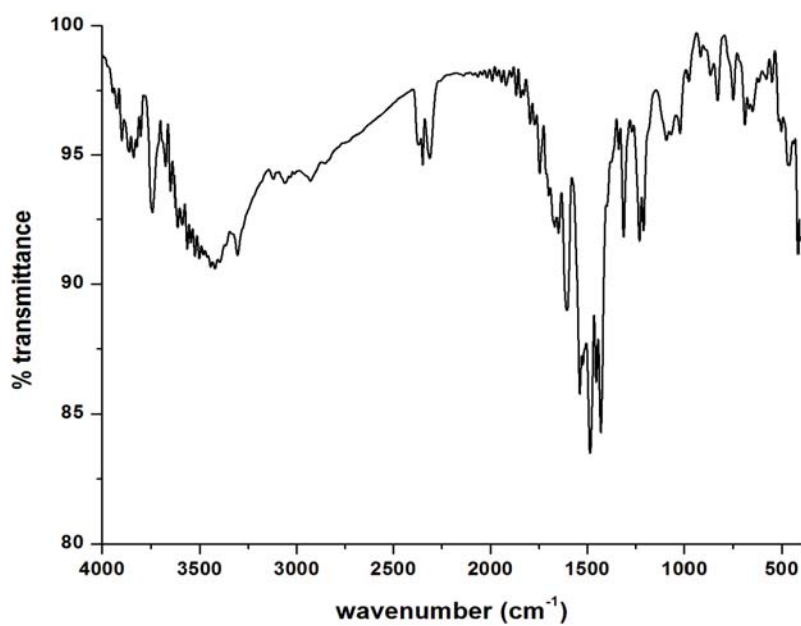**Fig. 6.4. Infrared spectrum of [ZnL^1(4,4′-dmbipy)]·DMF (21).**
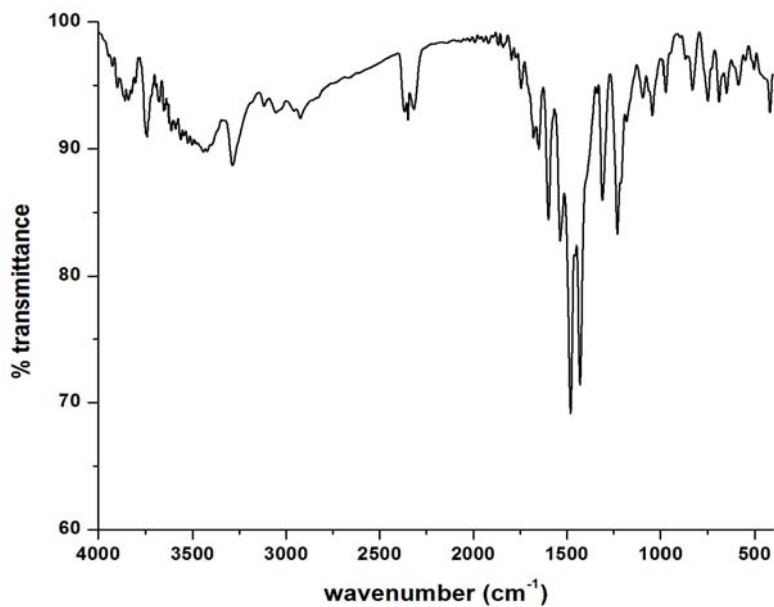
Fig. 6.5. Infrared spectrum of [ZnL^1(5,5′-dmbipy)] (22).

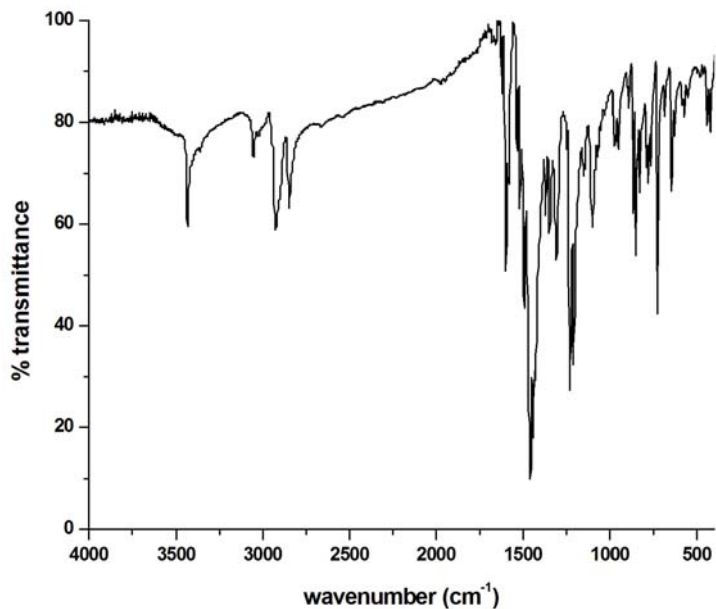**Fig. 6.6. Infrared spectrum of [ZnL^{2}phen] (24).**

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6.3.4. Electronic spectra

Electronic spectroscopy is an important and valuable tool for chemists to draw important information about the structural aspects of complexes. The UV-vis spectra of the Zn(II) complexes were studied in DMF. The bands in the range 28700-30590 cm^{-1} in the electronic spectra of thiosemicarbazones due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions suffered marginal shifts upon complexation. This may be due to the weakening of the C=S bond and the extension of conjugation upon complexation [19]. The shift occurs also due to coordination *via* phenolic oxygen and azomethine nitrogen [20] and is an indication of the enolization followed by the deprotonation of the ligands during complexation. In addition to this, a new band in the range 24300-25170 cm^{-1} is observed in the spectra of complexes and this can be assigned to the $O_{phenolate} \rightarrow$ Zn, $N_{azomethine} \rightarrow$ Zn and $S \rightarrow$ Zn LMCT transitions [21,22]. The electronic spectral data of the Zn(II) complexes are given in Table 6.3. Figs. 6.7 and 6.8 represent the electronic spectra of the complexes.

Table 6.3. Electronic spectral assignments (cm^{-1}) of thiosemicarbazones and their Zn(II) complexes

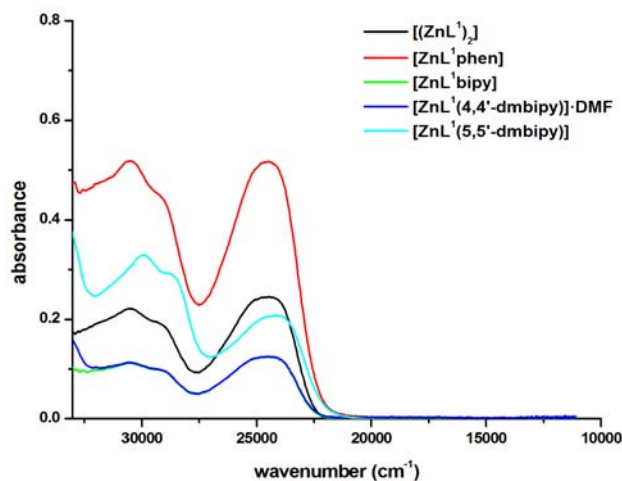| Compound	$n \rightarrow \pi^*/\pi \rightarrow \pi^*$	LMCT
H_2L^1	28770, 30490	----
[(ZnL^1)$_2$] (**18**)	29160, 30590	24600
[ZnL^{1}phen] (**19**)	29160, 30530	24480
[ZnL^{1}bipy] (**20**)	29100, 30590	24650
[ZnL^1(4,4'-dmbipy)]·DMF(**21**)	29100, 30590	24650
[ZnL^1(5,5'-dmbipy)] (**22**)	28700, 29960	24300
H_2L^2	29300, 30490	----
[(ZnL^2)$_2$] (**23**)	29620, 30980	25170
[ZnL^{2}phen] (**24**)	29670, 31040	25170
[ZnL^{2}bipy] (**25**)	29670, 30990	25170

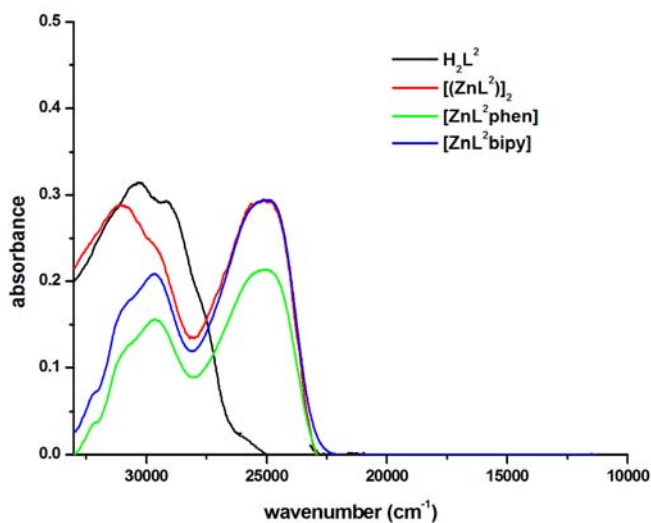**Fig. 6.7. Electronic spectra of Zn(II) complexes of H_2L^1.**

Fig. 6.8. Electronic spectra of Zn(II) complexes of H_2L^2.

6.3.5. X-ray crystallography

6.3.5a. Crystal structure of the compound [ZnL¹(4,4′-dmbipy)]·DMF (21)

Single crystals of the complex **21** suitable for X-ray diffraction studies were obtained by slow evaporation of the mother liquor over 3 days. The

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crystallographic data and structure refinement parameters for the complex are given in Table 6.4.

Table 6.4 Crystal data and structure refinement parameters for complex 21

Parameters	[ZnL^1(4,4'-dmbipy)]·DMF (21)
Empirical formula	C$_{30}$H$_{31}$BrN$_6$O$_3$SZn
Formula weight	700.95
Temperature	293 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	a = 15.2674(3) Å
	b = 12.2422(3) Å
	c = 22.3402(5) Å
	α = 90°
	β = 131.425(10)°
	γ = 90°
Volume	3130.90(12) Å^3
Z	4
Density (calculated)	1.487 Mg/m^3
Absorption coefficient	2.168 mm^{-1}
F(000)	1432
Crystal size	0.40 x 0.30 x 0.25 mm^3
θ range for data collection	2.47 to 26.31°
Limiting indices	-19 ≤ h ≤ 19,
	-15 ≤ k ≤ 15,
	-29 ≤ l ≤ 28
Reflections collected	52133
Independent reflections	14238 [R(int) = 0.0505]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14238 / 66 / 676
Goodness-of-fit on F^2	1.011
Final R indices [I > 2σ(I)]	R$_1$ = 0.0697, wR$_2$ = 0.1751
R indices (all data)	R$_1$ = 0.1204, wR$_2$ = 0.2105
Largest diff. peak and hole	1.22 and -1.64 e Å^{-3}

$R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$

$wR_2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2 / \Sigma w(F_o{}^2)^2]^{1/2}$

A yellow prism like crystal of the compound having approximate dimensions of 0.40 × 0.30 × 0.25 mm³ was selected. The unit cell parameters were determined and the data collections were performed on a Bruker SMART APEXII CCD diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation at the Sophisticated Analytical Instruments facility (SAIF), Cochin University of Science and Technology, Kochi-22, Kerala, India. The programs SAINT and XPREP were used for data reduction and APEX2 and SAINT were used for cell refinement [23]. The structure was solved by direct methods using SHELXS97 [24] and refined by full-matrix least-squares refinement on F^2 using SHELXL97 [25]. The molecular and crystal structures were plotted using DIAMOND version 3.2g [26] and X-SEED [27].

Carbon and nitrogen bound H-atoms were placed in calculated positions (C–H 0.93 to 0.96 Å, N–H 0.88 Å) and were included in the refinement in the riding model approximation, with U(H) set to 1.2 to 1.5 U(C,N). Omitted owing to bad disagreement was (0 1 1). All aromatic and pyridine rings were refined as rigid hexagons of 1.39 Å sides. One of the phenyl rings of the thiosemicarbazone is disordered over two positions in a 1:1 ratio. The temperature factors of the primed atoms were set to those of the unprimed ones but in the reverse order (*i.e.*, those of C11 to those of C15), and the pair of N–C$_{phenyl}$ distances were restrained to within 0.01 Å of each other. The molecules of DMF were each restrained to lie on a plane. The anisotropic temperature factors were restrained to be nearly isotropic. The final difference Fourier map had a peak at 0.91 Å from Br1 and a hole at 0.96 Å from Br2. The base scale factor was explicitly refined.

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The zinc homolog has been isolated as a 2,2'-bipyridine adduct [28]. The compound crystallizes as a DMF solvate. The asymmetric unit of the compound, $[Zn(C_{15}H_{12}BrN_3O_2S)(C_{12}H_{12}N_2)]C_3H_7NO$ (**21**) contains two independent molecules with a similar structure. In one molecule, Zn is displaced by 0.305(3) Å in the direction of the apical occupant (Fig. 6.9) whereas in the other, the displacement is 0.103(6) Å in the opposite direction (Fig. 6.10).
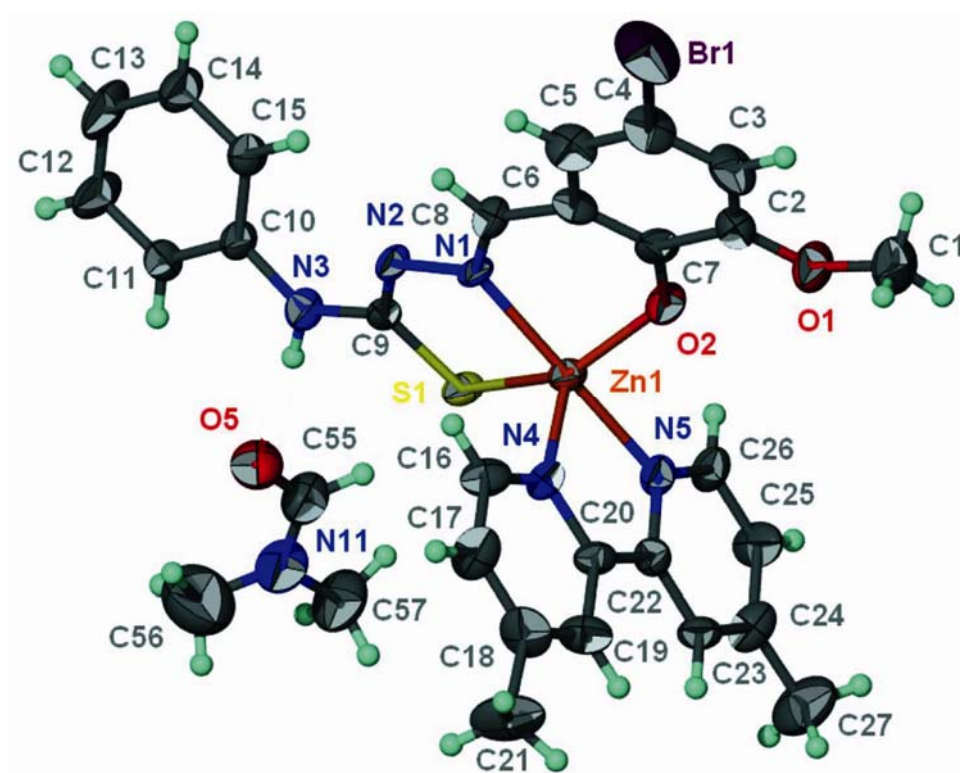

Fig. 6.9. **Thermal ellipsoid plot of one [ZnL[1](4,4′-dmbipy)]·DMF molecule at the 50% probability level; hydrogen atoms are drawn as spheres of arbitrary radius. The disorder in one of the phenyl rings is not shown.**

Fig. 6.10. Thermal ellipsoid plot of second [ZnL^1(4,4′-dmbipy)]·DMF molecule at the 50% probability level; hydrogen atoms are drawn as spheres of arbitrary radius. The disorder in one of the phenyl rings is not shown.
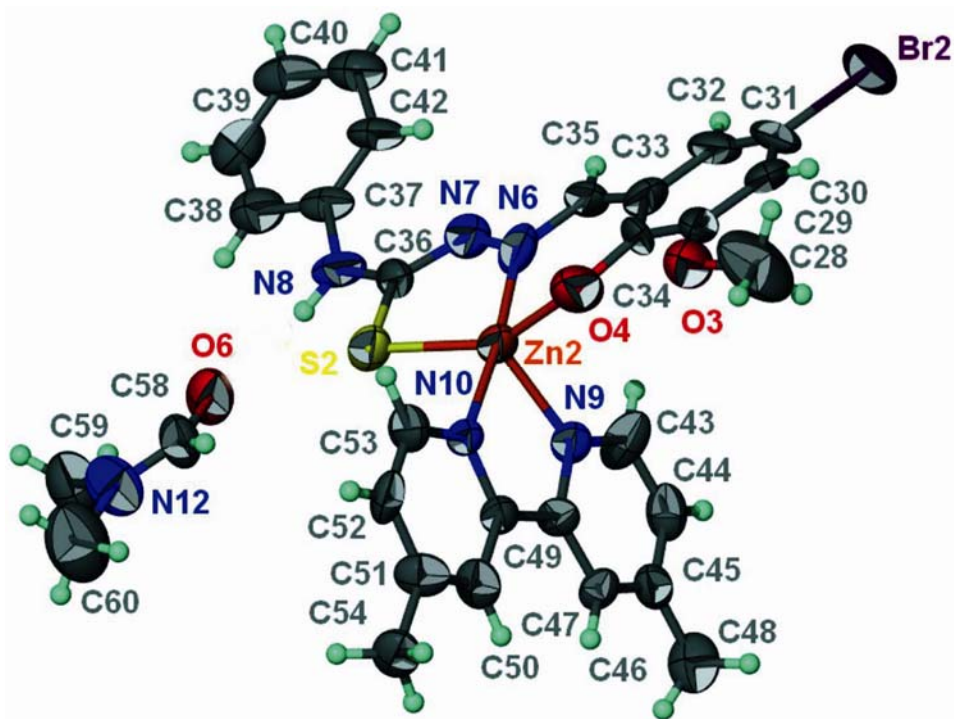
The metal center shows square pyramidal coordination. Substituents in the thiosemicarbazone as well as 2,2′-bipyridine do not perturb the square pyramidal coordination geometry in [Zn(C$_{12}$H$_{12}$N$_2$) (C$_{15}$H$_{12}$BrN$_3$O$_2$S)]·DMF. The doubly deprotonated Schiff base ligand O,N,S-chelates to the metal atom and the three coordinating atoms along with one N atom of the substituted 2,2′-bipyridine constitute the square plane of the distorted square pyramid surrounding the metal atom. The apical site is occupied by the second N atom of the substituted 2,2′-bipyridine. The secondary amine group of the Schiff base dianion forms a hydrogen bond to the O atom of the dimethylformamide solvent (Fig. 6.11). In the crystal, the phenyl ring

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of one of the two thiosemicarbazones is disordered over two positions in a 1:1 ratio. The crystal is found to be a racemic twin. The packing diagram of the compound is shown in Fig. 6.12. The coordination polyhedra present in the unit cell is shown in Fig. 6.13. Selected bond distances and bond angles are given in Table 6.5 and interaction parameters are given in Table 6.6.
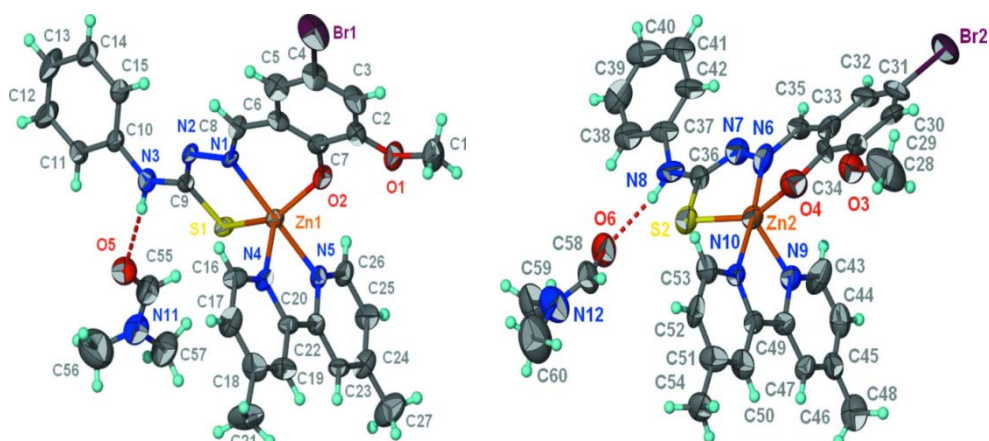

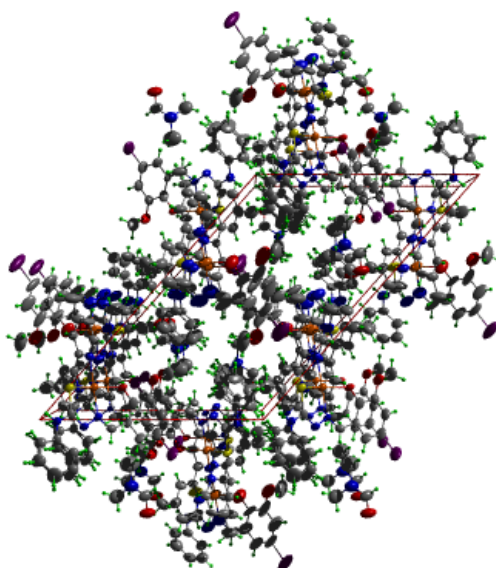**Fig. 6.11. Hydrogen bonding interactions shown as dotted lines.**
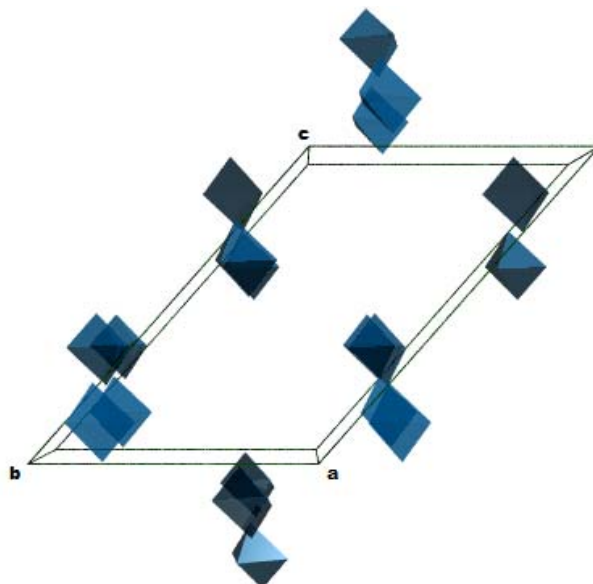

Fig. 6.12. Packing diagram along '*b*' axis.

Fig. 6.13. Coordination polyhedra in a unit cell.

Table 6.5 Selected bond lengths and angles for complex 21

Bond lengths (Å)		Bond angles (°)		Bond angles (°)	
Zn(1)–S(1)	2.353(2)	N(1)–Zn(1)–O(2)	87.7(2)	C(22)–N(5)–C(26)	120.0
Zn(1)–O(2)	1.987(6)	O(2)–Zn(1)–N(5)	93.9(2)	O(1)–C(2)–C(3)	124.2(5)
Zn(1)–N(1)	2.124(6)	N(1)–Zn(1)–N(5)	176.3(3)	N(1)–C(8)–C(6)	128.3(8)
Zn(1)–N(5)	2.134(4)	O(2)–Zn(1)–S(1)	148.2(2)	C(7)–O(2)–Zn(1)	126.8(4)
S(1)–C(9)	1.765(10)	O(2)–Zn(1)–N(4)	103.2(3)	C(9)–N(2)–N(1)	114.2(6)
N(1)–N(2)	1.388(9)	N(1)–Zn(1)–S(1)	82.0(2)	C(20)–N(4)–Zn(1)	114.9(3)
N(4)–C(16)	1.390	N(1)–Zn(1)–N(4)	104.9(3)	O(1)–C(2)–C(3)	124.2(5)
N(5)–C(26)	1.390	N(4)–Zn(1)–N(5)	78.0(2)	N(3)–C(9)–S(1)	111.4(7)
N(2)–C(9)	1.251(11)	N(5)–Zn(1)–S(1)	94.97(17)	C(9)–S(1)–Zn(1)	93.8(3)
N(1)–C(8)	1.246(11)	C(8)–N(1)–N(2)	117.1(7)	N(2)–N(1)–Zn(1)	119.5(5)
N(3)–C(9)	1.401(11)	C(9)–N(3)–C(10)	130.1(11)	C(16)–N(4)–Zn(1)	125.1(3)
Zn(1)–N(4)	2.088(4)				

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Table 6.6. Interaction parameters

H bonding				
D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
N(3)–H(3)···O(5)	0.88	2.07	2.950(10)	175
N(8)–H(8)···O(6)	0.88	2.07	2.950(10)	172
C(15)–H(15)···N(2)	0.93	2.39	2.954(17)	119
C(17)–H(17)···O(5)	0.93	2.52	3.089(10)	120
C(19)–H(19)···O(3)	0.93	2.35	3.168(14)	146
C(42)–H(42)···N(7)	0.93	2.31	2.917(15)	123
C(46)–H(46)···O(1)	0.93	2.34	3.204(11)	154

D = Donor, A = acceptor, Cg = Centroid

References

[1]   D.R. Lide, Handbook of Chemistry and Physics, 87th ed. CRC Press, Taylor & Francis, Boca Raton, Florida, 2006.

[2]   R.S. Lehto, Zinc, In Clifford A. Hampel, The Encyclopedia of the Chemical Elements, New York: Reinhold Book Corporation (1968) 822.

[3]   D.L. Heiserman, Element 30: Zinc, Exploring Chemical Elements and their Compounds. New York: TAB Books, 1992.

[4]   "Zinc Metal Properties", American Galvanizers Association, 2008.

[5]   K.M. Hambidge, N.F. Krebs, J. Nutr. 137 (2007) 1101.

[6]   Q. Li, H. Tang, Y. Li, M. Wang, L. Wang, C. Xia, J. Inorg. Biochem. 78 (2000) 167.

[7]   J.M. Perez, A.I. Matesanz, A. Martine-Ambite, P. Navaro, C. Alonso, P. Souza, J. Inorg. Biochem. 75 (1999) 255.

[8] K. Peariso, C.W. Goulding, S. Huang, R.G. Mathews, J.E. Penner-Hahn, J. Am. Chem. Soc. 120 (1998) 8410.

[9] C. Dowling, G. Perkin, Polyhedron 15 (1996) 2463.

[10] M.B. Ferrari, G.G. Fava, C. Pelizzic, P. Tarasconi, J. Chem. Soc., Dalton Trans. (1992) 2153.

[11] D. Solaiman, L. Saryan, D.H. Petering, J. Inorg. Biochem. 10 (1979) 135.

[12] W.J. Geary, Coord. Chem. Rev. 7 (1971) 81.

[13] V. Philip, V. Suni, M.R.P. Kurup, M. Nethaji, Spectrochim. Acta Part A 64 (2006) 171.

[14] G. Plesch, C. Friebel, Polyhedron 14 (1995) 1185.

[15] M. Joseph, V. Suni, M.R.P. Kurup, M. Nethaji, A. Kishore, S.G. Bhat, Polyhedron 23 (2004) 3069.

[16] M.A. Ali, M.T.H. Tarafdar, J. Inorg. Nucl. Chem. 39 (1977) 1785.

[17] M.J.M. Campbell, Coord. Chem. Rev. 15 (1975) 279.

[18] B.S. Garg, M.R.P. Kurup, S.K. Jain, Y.K. Bhoon, Transit. Met. Chem. 13 (1988) 247.

[19] I.-X. Li, H.-A. Tang, Y.-Z. Li, M. Wang, L.-F. Wang, C.-G. Xia, J. Inorg. Biochem. 78 (2000) 167.

[20] R.P. John, A. Sreekanth, M.R.P. Kurup, A. Usman, I.A. Razak, H.K. Fun, Spectrochim. Acta. 59A (2003) 1349.

[21] M.A. Ali, D.A. Chowdhary, M. Nazimuddin, Polyhedron 3 (1984) 595.

[22] V. Philip, V. Suni, M.R.P. Kurup, M. Nethaji, Polyhedron 24 (2005) 1133.

[24] G.M. Sheldrick, Acta Crystallogr., Sect. A 46 (1990) 467.

Crystal Structures and Spectral Aspects of Mixed Ligand Transition Metal Chelates
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[25] G.M. Sheldrick, SHELXL97 and SHELXS97, University of Göttingen, Germany, 1997.

[26] K. Brandenburg, Diamond Version 3.2g, Crystal Impact GbR, Bonn, Germany, 2010.

[27] L.J. Barbour, J. Supramol. Chem. 1 (2001) 189.

[28] E.B. Seena, M.R.P. Kurup, Spectrochim. Acta Part A 69 (2008) 726.

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