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SYNTHESIS, CHARACTERIZATION, AND BIOLOGICAL PROPERTIES OF BIVALENT TRANSITION METAL COMPLEXES OF Co(II), Cu(II), Ni(II), AND Zn(II) WITH SOME ACYLHYDRAZINE DERIVED FURANYL AND THIENYL ONO AND SNO DONOR SCHIFF BASE LIGANDS

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SYNTHESIS, CHARACTERIZATION, AND BIOLOGICAL PROPERTIES OF BIVALENT TRANSITION METAL COMPLEXES OF Co(II), Cu(II), Ni(II), AND Zn(II) WITH SOME ACYLHYDRAZINE DERIVED FURANYL AND THIENYL ONO AND SNO DONOR SCHIFF BASE LIGANDS

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ABSTRACT

Some acylhydrazine derived furanyl and thienyl ONO and SNO donor Schiff base ligands and their Co(II), Cu(II), Ni(II), and Zn(II) complexes have been prepared and characterized on the basis of elemental analyses, magnetic moments, molar conductances, and spectroscopic (electronic, IR, ^{1}H NMR, and ^{13}C NMR) data. All of the ligands function as tridentates and the deprotonated enolic form is preferred in the coordination.

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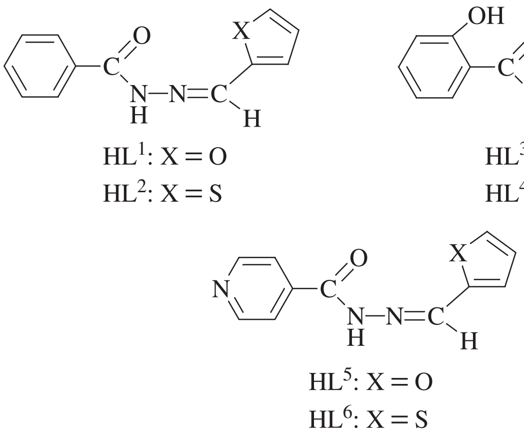


Figure 1. Proposed structures of schiff bases.

INTRODUCTION

Hydrazine and hydrazones have been actively investigated (1–5) because of their varied ligational behavior toward metal ions and their manifestation of novel structural features in their coordination chemistry. Certain acylhydrazines and their transition metal chemistry also have been a subject of many researchers (6–8) due to their significant properties as antibacterial and antifungal agents. The present investigation, therfore, was undertaken to better understand the ligational behavior of some novel acylhydrazine derived Schiff bases towards bivalent transition metal ions and their role in biological systems.

Accordingly, some novel benzoylhydrazine, salicyloylhydrazine, and nicotinoylhydrazine derived furanyl and thienyl Schiff bases (Fig. 1) and their Co(II), Cu(II), Ni(II), and Zn(II) complexes have been successfully synthesized and their characterization, ligational behavior, and biological properties are reported.

RESULTS AND DISCUSSION

Physical Properties

The Schiff bases (HL^1–HL^6) (Fig. 1) were prepared by reacting equimolar amounts of 2-furanecarboxaldehyde or 2-thiophenecarboxaldehyde with the respective benzoylhydrazine, salicyloylhydrazine, or nicotinoylhydrazine in ethanol. The structures of these Schiff base ligands were established with the help of their IR, ^{1}H NMR, ^{13}C NMR, and microanalytical data (Tables 1 and 4).

Table 1. Physical, Spectra, and Analytical Data of the Schiff Bases

Schiff Base Ligand	M.p (°C)	IR (cm^{-1})[a]	Calc. (Found) (%) C	H	N	Yield (%)
HL^1						
$C_{12}H_{10}N_2O_2$	145	3240 (s, NH), 1700 (m, NH + CN),	67.3	4.7	13.1	78
[214.0]		1635 (s, CH=N), 1020 (s, N–N),	(67.7)	(4.5)	(13.2)	
HL^2						
$C_{12}H_{10}N_2OS$	148	3245 (s, NH), 1705 (m, NH+CN),	62.6	4.3	12.2	82
[230.1]		1635 (s, CH=N), 1020 (s, N–N),	(62.9)	(4.7)	(12.5)	
HL^3		3365 (br, OH), 3245 (s, NH),	62.6	4.3	12.2	80
$C_{12}H_{10}N_2O_3$	135	1705 (m, NH + CN), 1630	(62.5)	(3.9)	(12.5)	
[230.0]		(s, CH–N), 1025 (s, N–N)				
HL^4		3365 (br, OH), 3240 (s, NH),	58.5	4.1	11.4	80
$C_{12}H_{10}N_2O_2S$	128	1705 (m, NH + CN), 1630	(58.8)	(4.0)	(11.3)	
[246.1]		(s, CH=N), 1025 (s, N–N)				
HL^5						
$C_{11}H_9N_3O_2$	138	3245 (s, NH), 1705 (m, NH + CN),	(61.4)	(4.2)	19.5	75
[215.0]		1635 (s, CH=N), 1025 (s, N–N)	(61.6)	(4.5)	(19.8)	
HL^6						
$C_{11}H_9N_3OS$	122	3245 (s, NH), 1700 (m, NH + CN),	57.1	3.9	18.2	81
[231.1]		1635 (s, CH=N), 1020 (s, N–N)	(57.5)	(4.1)	(18.5)	

[a] s: Sharp; m: Medium; br: Broad.

All of the metal complexes [(**1**)–(**24**)] (Table 2) of these Schiff bases were prepared by the stoichiometric reaction of the respective metal chlorides and the prepared Schiff base ligands in the molar ratio M:HL = 1:2. The proposed reaction between the Schiff base ligands and the metal salts is represented by the following equation:

$$MCl_2 + 2HL \longrightarrow [M(L)_2] + 2HCl$$

where M = Co(II), Cu(II), Ni(II), or Zn(II) and L = L^1, L^2, L^3, L^4, L^5, or L^6.

The complexes are intensely colored and stable solids, which decompose above 200°C without melting and are insoluble in common organic solvents like ethanol, methanol, chloroform, or acetone. DMSO and DMF, however, dissolved all of the complexes. Their elemental analyses data, solubility, and melting behavior suggest that they are monomers. Molar conductance values of the soluble complexes in DMF show low values (28–41 $ohm^{-1}\ cm^2\ mol^{-1}$) indicating (9) that they are all nonelectrolytic in nature.

Table 2. Physical and Analytical Data of the Metal(II) Complexes

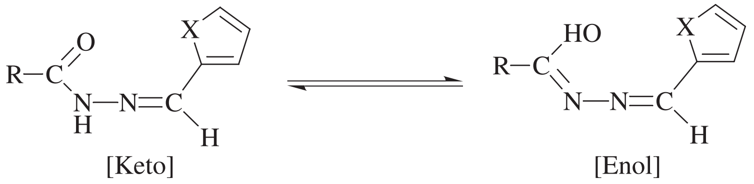
Complex		M.p. (°C)	B.M. (μ_{eff})	Yield (%)	Calc. (Found) (%)		
					C	H	N
(**1**)	$[Co(L^1)_2]$ $C_{24}H_{18}CoN_4O_4$ [484.9]	222–224	4.85	60	59.4 (59.7)	3.7 (3.5)	11.5 (11.6)
(**2**)	$[Cu(L^1)_2]$ $C_{24}H_{18}CuN_4O_4$ [489.5]	238–240	1.55	65	58.8 (59.1)	3.7 (3.6)	11.4 (11.5)
(**3**)	$[Ni(L^1)_2]$ $C_{24}H_{18}NiN_4O_4$ [484.7]	231–233	3.20	62	59.4 (59.0)	3.7 (3.5)	11.5 (11.8)
(**4**)	$[Zn(L^1)_2]$ $C_{24}H_{18}ZnN_4O_4$ [491.4]	228–230	Dia	58	58.6 (58.9)	3.7 (3.3)	11.4 (11.6)
(**5**)	$[Co(L^2)_2]$ $C_{24}H_{18}CoN_4O_2S_2$ [517.0]	225–227	4.93	60	55.7 (55.9)	3.5 (3.3)	10.8 (10.5)
(**6**)	$[Cu(L^2)_2]$ $C_{24}H_{18}CuN_4O_2S_2$ [521.6]	230–232	1.78	58	55.2 (55.0)	3.5 (3.6)	10.7 (10.5)
(**7**)	$[Ni(L^2)_2$ $C_{24}H_{18}NiN_4O_2S_2$ [516.8]	228–230	3.70	65	55.7 (55.9)	3.5 (3.1)	10.8 (10.5)
(**8**)	$[ZN(L^2)_2]$ $C_{24}H_{18}ZnN_4O_2S_2$ [523.5]	235–237	Dia	60	55.0 (55.5)	3.4 (3.1)	10.7 (10.8)
(**9**)	$[Co(L^3)_2]$ $C_{24}H_{18}CoN_4O_4$ [516.9]	232–234	4.90	62	55.7 (55.9)	3.5 (3.6)	10.8 (10.6)
(**10**)	$[Cu(L^3)_2]$ $C_{24}H_{18}CuN_4O_6$ [521.5]	226–228	1.60	62	55.2 (55.5)	3.5 (3.2)	10.7 (10.5)
(**11**)	$[Ni(L^3)_2]$ $C_{24}H_{18}NiN_4O_6$ [516.7]	225–227	3.50	60	55.7 (55.9)	3.5 (3.3)	10.8 (10.9)
(**12**)	$[Zn(L^3)_2]$ $C_{24}H_{18}ZnN_4O_6$ [523.4]	235–237	Dia	61	55.0 (54.8)	3.4 (3.6)	10.7 (10.6)
(**13**)	$[Co(L^4)_2]$ $C_{24}H_{18}CoN_4O_4S_2$ [549.0]	229–231	4.92	62	52.4 (52.5)	3.3 (3.0)	10.2 (10.1)

Table 2. *Continued*

Complex		M.p.	B.M.	Yield	Calc. (Found) (%)		
		(°C)	(μ_{eff})	(%)	C	H	N
(**14**)	$[Cu(L^4)_2]$ $C_{24}H_{18}CuN_4O_4S_2$ [553.6]	224–226	1.68	65	52.0 (52.2)	3.3 (3.4)	10.1 (10.5)
(**15**)	$[Ni(L^4)_2]$ $C_{24}H_{18}NiN_4O_4S_2$ [548.8]	228–230	3.30	63	52.5 (52.3)	3.3 (3.2)	10.1 (10.3)
(**16**)	$[Zn(L^4)_2]$ $C_{24}H_{18}ZnN_4O_4S_2$ [555.5]	232–234	Dia	58	51.8 (51.9)	3.2 (3.3)	10.8 (10.6)
(**17**)	$[Co(L^5)_2]$ $C_{22}H_{16}CoN_6O_4$ [486.9]	235–237	4.88	62	54.2 (54.5)	3.3 (3.6)	17.3 (17.1)
(**18**)	$[Cu(L^5)_2]$ $C_{22}H_{16}CuN_6O_4$ [491.5]	228–230	1.70	60	53.7 (53.9)	3.3 (3.5)	17.1 (17.6)
(**19**)	$[Ni(L^5)_2]$ $C_{22}H_{16}NiN_6O_4$ [486.7]	232–234	3.50	60	54.2 (54.1)	3.3 (3.3)	17.3 (17.1)
(**20**)	$[Zn(L^5)_2]$ $C_{22}H_{16}ZnN_6O_4$ [493.4]	230–232	Dia	60	53.5 (53.7)	3.2 (3.5)	17.0 (16.8)
(**21**)	$[Co(L^6)_2]$ $C_{22}H_{16}CoN_6O_2$ [519.0]	225–227	4.91	65	50.9 (51.2)	3.1 (3.3)	16.2 (16.0)
(**22**)	$[Cu(L^6)_2]$ $C_{22}H_{16}CuN_6O_2S_2$ [523.6]	228–230	1.75	62	50.4 (50.6)	3.1 (3.0)	16.0 (16.2)
(**23**)	$[Ni(L^6)_2]$ $C_{22}H_{16}NiN_6O_2S_2$ [518.8]	231–233	3.60	60	50.9 (50.8)	3.1 (3.3)	16.2 (16.0)
(**24**)	$[Zn(L^6)_2]$ $C_{22}H_{16}ZnN_6O_2S_2$ [525.5]	228–230	Dia	62	50.2 (50.5)	3.0 (3.2)	16.0 (16.4)

Model Studies

Examination of the physical molecular models of these Schiff base ligands, illustrated in Figure 1, show that in no case can the ligands exhibit quadridentate ONNO or ONNS and bidenate ON or SN behavior. It is capable of exhibiting either



R = Ph; X = O (L^1), R = Ph; X = S (L^2)
R = PhOH-*o*; X = O (L^3), R = PhOH-*o*; X = S (L^4)
R = Py; X = O (L^5), R = Py; X = S (L^6)

Figure 2. Possible flexidentate keto–enol forms of Schiff base ligands.

tridentate monobasic (flexidentate keto–enol form) (Fig. 2) or neutral tridentate behavior.

In its enol form, the ligand can function like an enol with ONO or ONS donor sites by either the deprotonated hydroxyl group of the enol, ν(OH), the nitrogen of hydrazine, ν(N–N), and the heteroatom (X) of the furanyl or thienyl groups. The keto form however, acts as tridentate ONO or ONS donors showing coordination through the keto oxygen (C=O), azomethine nitrogen (HC=N), and the heteroatom (X).

The physical model studies further showed that the phenolic OH of the Schiff base ligands HL^3 and HL^4 could not participate stereochemically in the coordination because of their planar structures in which all atoms are sp^2-hybridized (Fig. 1). Moreover, the presence of OH protons in the ^{1}H NMR spectra of HL^3 and HL^4 confirmed that the hydroxyl group is not involved in the coordination. Also, the molecular model studies revealed that nitrogen of pyridine in ligands HL^5 and HL^6 could not get involve in the coordination due to its stereochemically out of plane geometry.

Infrared Spectra

The IR spectra of the Schiff bases and their metal(II) complexes were recorded in KBr and are summerized in Tables 1 and 3 with some tentative assignments of important characteristic bands. All the Schiff bases showed the absence of bands at ~1735 and 3420 cm^{-1} due to characteristic carbonyl ν(C=O) and $\nu(NH_2)$ stretching vibrations of the respective aldehydes and amines (starting materials). Instead, a new band at ~3240 cm^{-1} and sharp bands at ~3215, 1700, 1635, and 1020 cm^{-1} assigned (10,11) to amide-I [ν(CO–NH)], amide-II [ν(NH + CN)], azomethine [ν(HC=N)] linkage, and ν(N–N) modes appeared, respectively. It suggested that hydrazino amine and aldehyde moieties of the starting

Table 3. IR and UV–vis Data of the Metal(II) Complexes

No.	IR (cm^{-1})	λ_{max} (cm^{-1}) (ε)[a]
(**1**)	1625 (s, HC=N), 1245 (s, C–O), 1025 (m, N–N), 455 (m, M–O)	20920 (24), 28570
(**2**)	1625 (m, HC=N), 1240 (s, C–O), 1030 (m, N–N), 460 (m, M–O)	14925 (32), 16390 (46), 27250
(**3**)	1630 (s, HC=N), 1240 (m, C–O), 1030 (m, N–N), 455 (m, M–O)	16670 (14), 27780
(**4**)	1625 (s, HC=N), 1245 (s, C–O), 1025 (m, N–N), 455 (m, M–O)	27555 (CT)
(**5**)	1630 (s, HC=N), 1245 (s, C–O), 1025 (m, N–N), 460 (m, M–O), 360 (m, M–S)	20922 (23), 28575
(**6**)	1630 (s, HC=N), 1242 (m, C–O), 1025 (m, N–N), 455 (m, M–O), 365 (m, M–S)	14920 (31), 16395, (48), 27250
(**7**)	1625 (m, HC=N), 1240 (m, C–O), 1030 (m, N–N), 455 (m, M–O), 365 (m, M–S)	16665 (16), 27785
(**8**)	1625 (s, HC=N), 1245 (m, C–O), 1025 (m, N–N), 460 (m, M–O), 360 (s , M–S)	27550 (CT)
(**9**)	3365 (br, OH), 1625 (m, HC=N), 1245 (s, C–O), 1025 (m, N–N), 455 (m, M–O)	20925 (25), 28585
(**10**)	3365 (br, OH), 1630 (m, HC=N), 1245 (m, C–O), 1030 (m, N–N), 455 (m, M–O)	14922 (31), 16395, (46), 27255
(**11**)	3365 (br, OH), 1625 (s, HC=N), 1240 (s, C–O), 1025 (m, N–N), 455 (m, M–O)	16675 (14), 27785
(**12**)	3365 (br, OH), 1630 (s, HC=N), 1240 (m, C–O), 1025 (m, N–N), 455 (m, M–O)	27555 (CT)
(**13**)	3365 (br, OH), 1630 (s, HC=N), 1242 (s, C–O), 1025 (m, N–N), 460 (m, M–O), 365 (m, M–S)	20922 (25), 28580
(**14**)	3365 (br, OH), 1625 (s, HC=N), 1245 (s, C–O), 1025 (m, N–N), 460 (m, M–O), 365 (m M–S)	14925 (32), 16392, (45), 27255
(**15**)	3365 (br, OH), 1625 (s, HC=N), 1240 (s, C–O), 1025 (m, N–N), 455 (m, M–O), 365 (m M–S)	16670 (13), 27785
(**16**)	3365 (br, OH), 1625 (s, HC=N), 1245 (s, C–O), 1030 (m, N–N), 455 (m, M–O), 365 (m M–S)	27585 (CT)
(**17**)	1625 (s, HC=N), 1245 (s, C–O), 1025 (m, N–N), 460 (m, M–O)	20920 (27), 28575
(**18**)	1625 (s, HC=N), 1245 (s, C–O), 1025 (m, N–N), 455 (m, M–O)	14925 (32), 16390, (45), 27250
(**19**)	1625 (m, HC=N), 1245 (m, C–O), 1030 (m, N–N), 455 (m, M–O)	16665 (12), 27780,
(**20**)	1630 (m, HC=N), 1240 (s, C–O), 1025 (m, N–N), 455 (m, M–O)	27580 (CT),
(**21**)	1625 (s, HC=N), 1245 (s, C–O), 1025 (m, N–N), 460 (m, M–O), 365 (m, M–S)	20922 (25), 28580,
(**22**)	1630 (s, HC=N), 1240 (s, C–O), 1025 (m, N–N), 455 (m, M–O), 360 (m, M–S)	14920 (30), 16395, (46), 27255
(**23**)	1630 (s, HC=N), 1245 (s, C–O), 1030 (m, N–N), 455 (m, M–O), 360 (m, M–S)	16670 (14), 27780,
(**24**)	1625 (s, HC=N), 1240 (s, C–O), 1025 (m, N–N), 455 (m, M–O), 365 (m, M–S)	27580 (CT)

s: Sharp; m: Medium; br = Broad.

[a] ε: Molar extinction coefficient (L mol^{-1} cm^{-1}).

reagents no longer exist and have been condensed and converted into their respective Schiff bases. The physical molecular model studies and the comparison of the IR spectra of the Schiff bases and their metal complexes indicated that the Schiff bases are coordinated to the metal atom by three sites, thus suggesting that the ligands act as tridentates. The band appearing at ∼3240 cm^{-1} due to the amide-I band was substantially shifted to lower frequency (20–30 cm^{-1}) relative to the free ligand values, and the bands due to ν(C=O) were completely missing in the spectra of the complexes, suggesting (12) enolization of the Schiff bases on complexation. This is also supported by the fact that no band for ν(OH) in the spectra of the Schiff base ligands and also in the complexes is observed except the phenolic ν(OH) at 3365 cm^{-1} in the Schiff base ligands HL^3 and HL^4 and their complexes. Instead, a band due to ν(C−O) at about ∼1245 cm^{-1} was observed for all the title complexes, which supports the observation of their enolization during coordination. These facts suggest that the Schiff bases remain in the keto form in the solid state but in solution, both the keto and enol forms remain in equilibrium (13) (Fig. 2) and during complexation, deprotonation occurs from the enol form. This coordination through the deprotonated enolized oxygen results in a ν(NCO) band manifested in the region at ∼1245 cm^{-1}. The amide-II band was split, displaced to higher frequency and reduced in intensity. A shift to higher frequency (5–10 cm^{-1}) of the ν(N−N) band at ∼1020 cm^{-1} and its splitting indicated (14) coordination of the azomethine nitrogen. Moreover, the shift to lower frequency (5–10 cm^{-1}) of the band due to the azomethine ν(CH=H) linkage at ∼1635 cm^{-1} also indicated involvement of azomethine group in coordination.

The new, weak, low-frequency bands at ∼360 and ∼455 cm^{-1} were assigned (15) to metal-sulfur ν(M−S) in the thienyl derived and metal-oxygen ν(M−O) in the furanyl derived ligands. These bands were only observable in the spectra of the metal complexes and not in the spectra of their Schiff bases, which in turn confirmed the participation of the heteroatoms (S and O) in the coordination.

NMR Spectra

The NMR spectra of the free ligands and some of their metal complexes have been recorded in DMSO-d_6. The features of the free ligands and some of their complexes are shown in Table 4. NMR spectra of the free ligands support the conclusions derived from the IR spectra. The ligands exhibit aromatic and heteroaromatic proton signals at δ 4.5–7.9 ppm as expected. The signals for the NH proton appeared at δ 11.4 ppm (s, br) in the spectra of the free Schiff base ligands; these signals are absent in the spectra of their metal complexes. This indicated (16) that the Schiff bases are coordinated to the metal ions in the enolic form by deprotonation.

Table 4. NMR Spectral Data of the Schiff Base Ligands and Selected Complexes

No	^{1}H NMR(DMSO-d$_6$) (ppm)	^{13}C NMR (DMSO-d$_6$) (ppm)
HL^1	4.5–4.7 (m, 1H, furanyl), 4.8 (dd, 1H, $J(^{1}\text{H}{-}^{1}\text{H}) = 1.8$, $J(^{1}\text{H}{-}^{1}\text{H}) = 1.7$ Hz, furanyl), 5.8 (m, 1H, furanyl), 7.2 (s, 1H, HC=N) 7.5–7.7 (m, 2H, Ph), 7.8–7.9 (m, 3H, Ph), 10.8 (s, 1H, NH).	104.5, 112.6, 121.3, 123.2 (furanyl), 124.8, 126.7, 129.1, 137.3 (Ph), 152.4 (HC=N), 187.4 (C=O).
HL^2	4.6–4.7 (m, 1H, thienyl), 4.7 (dd, 1H, $J(^{1}\text{H}{-}^{1}\text{H}) = 2.1$, $J(^{1}\text{H}{-}^{1}\text{H}) = 2.0$ Hz, thienyl), 5.8 (m, 1H, thienyl), 7.3 (s, 1H, HC=N), 7.5–7.7 (m, 2H, Ph), 7.8–7.9 (m, 3H, Ph), 10.9 (s, 1H, NH).	104.6, 112.5, 121.4, 123.2 (thienyl), 125.0, 126.5, 129.3, 137.4 (Ph), 152.4 (HC=N), 187.4 (C=O).
HL^3	4.5–4.7 (m, 1H, furanyl), 4.8 (dd, 1H, $J(^{1}\text{H}{-}^{1}\text{H}) = 1.8$, $J(^{1}\text{H}{-}^{1}\text{H}) = 1.7$ Hz, furanyl), 5.8 (m, 1H, furanyl), 7.2 (s, 1H, HC=N), 7.4–7.5 (m, 1H, Ph), 7.6–7.8 (m, 2H, Ph), 7.9–8.1 (m, 1H, Ph), 10.8 (s, 1H, NH), 12.4 (s, 1H, OH−Ph).	104.5, 112.6, 121.3, 123.2 (furanyl), 124.8, 126.7, 130.3, 176.7 (Ph), 152.4 (HC=N), 187.4 (C=O).
HL^4	4.5–4.7, (m, 1H, thienyl), 4.9 (dd, 1H, $J(^{1}\text{H}{-}^{1}\text{H}) = 2.1$, $J(^{1}\text{H}{-}^{1}\text{H}) = 2.0$ Hz, thienyl), 5.7 (m, 1H, thienyl), 7.4 (s, 1H, HC=N), 7.4–7.5 (m, 1H, Ph), 7.6–7.8 (m, 2H, Ph), 7.9–8.2 (m, 1H, Ph), 10.9 (s, 1H, NH), 12.3 (s, 1H, OH−Ph).	104.5, 112.8, 121.5, 123.3 (thienyl), 124.7, 126.9, 130.4, 176.6 (Ph), 152.4 (HC=N), 187.5 (C=O).
HL^5	4.5–4.7 (m, 1H, furanyl), 4.7 (dd, 1H, $J(^{1}\text{H}{-}^{1}\text{H}) = 1.8$, $J(^{1}\text{H}{-}^{1}\text{H}) = 1.7$ Hz, furanyl), 5.9 (m, 1H, furanyl), 7.5 (s, 1H, HC=N), 7.6–7.8 (m, 2H, Py), 8.3–8.5 (m, 2H, Py), 10.7 (s, 1H, NH).	104.4, 112.6, 121.4, 123.0 (furanyl), 126.8, 167.8 (Py), 152.4 (HC=N), 187.4 (C=O).
HL^6	4.6–4.8 (m, 1H, thienyl), 4.9 (dd, 1H, $J(^{1}\text{H}{-}^{1}\text{H}) = 2.1$, $J(^{1}\text{H}{-}^{1}\text{H}) = 2.0$ Hz, thienyl), 5.8 (m, 1H, thienyl), 7.3 (s, 1H, HC=N), 7.7–7.9 (m, 2H, Py), 8.4–8.6 (m, 2H, Py), 10.8 (s, 1H, NH).	104.5, 112.6, 121.3, 123.2 (thienyl), 126.7, 167.8 (Py), 152.4 (HC=N), 187.5 (C=O).
(**1**)	4.6–4.8 (m, 1H, furanyl), 4.9 (dd, 1H, $J(^{1}\text{H}{-}^{1}\text{H}) = 1.9$, $J(^{1}\text{H}{-}^{1}\text{H}) = 1.8$ Hz, furanyl), 5.9 (m, 1H, furanyl), 7.4 (s, 1H, HC=N), 7.6–7.7 (m, 2H, Ph), 7.9–8.2 (m, 3H, Ph).	104.6, 112.7, 121.5, 123.3 (furanyl), 124.9, 126.8, 129.2, 137.5 (Ph), 152.8 (HC=N), 190.1 (C–O).
(**5**)	4.7–4.8 (m, 1H, thienyl), 4.9 (dd, 1H, $J(^{1}\text{H}{-}^{1}\text{H}) = 2.2$, $J(^{1}\text{H}{-}^{1}\text{H}) = 2.1$ Hz, thienyl), 6.1 (m, 1H, thienyl), 7.6 (s, 1H, HC=N), 7.7–7.8 (m, 2H, Ph), 7.9–8.1 (m, 3H, Ph).	104.8, 112.6, 121.6, 123.3 (thienyl), 125.2, 126.6, 129.3, 137.5 (Ph), 152.7 (HC=N), 190.3 (C–O).
(**9**)	4.6–4.8 (m, 1H, furanyl), 4.9 (dd, 1H, $J(^{1}\text{H}{-}^{1}\text{H}) = 1.9$, $J(^{1}\text{H}{-}^{1}\text{H}) = 1.8$ Hz, furanyl), 5.9 (m, 1H, furanyl), 7.5 (s, 1H, HC=N), 7.6–7.7 (m, 1H, Ph), 7.8–7.9 (m, 2H, Ph), 8.1–8.3 (m, 1H, Ph), 12.6 (s, 1H, OH−Ph).	104.6, 112.8, 121.5, 123.3 (furanyl), 124.9, 126.8, 130.5, 176.9 (Ph), 152.8 (HC=N), 190.2 (C−O).
(**13**)	4.6–4.8 (m, 1H, thienyl), 5.1 (dd, 1H, $J(^{1}\text{H}{-}^{1}\text{H}) = 2.2$, $J(^{1}\text{H}{-}^{1}\text{H}) = 2.1$ Hz, thienyl), 5.8 (m, 1H, thienyl), 7.5 (s, 1H, HC=N), 7.6–7.7 (m, 1H, Ph), 7.8–7.9 (m, 2H, Ph), 8.1–8.3 (m, 1H, Ph), 12.2 (s, 1H, OH−Ph).	104.7, 112.8, 121.6, 123.5 (thienyl), 124.8, 126.9, 130.5, 176.8 (Ph), 152.8 (HC=N), 190.3 (C−O).

(*continued*)

Table 4. *Continued*

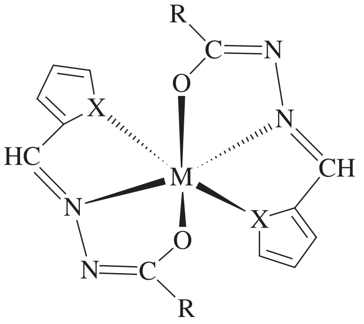
No	^{1}H NMR(DMSO-d$_6$) (ppm)	^{13}C NMR (DMSO-d$_6$) (ppm)
(**17**)	4.6–4.8 (m, 1H, furanyl), 4.9 (dd, 1H, $J(^1H–^1H) = 1.9$, $J(^1H–^1H) = 1.8$ Hz, furanyl), 5.9 (m, 1H, furanyl), 7.7 (s, 1H, HC=N), 7.9–8.1 (m, 2H, Py), 8.4–8.6 (m, 2H, Py).	104.5, 112.8, 121.5, 123.3 (furanyl), 126.8, 167.9 (Py), 152.8 (HC=N), 190.2 (C–O).
(**21**)	4.7–4.9 (m, 1H, thienyl), 5.1 (dd, 1H, $J(^1H–^1H) = 2.2$, $J(^1H–^1H) = 2.1$ Hz, thienyl), 5.9 (m, 1H, thienyl), 7.4 (s, 1H, HC=N), 7.8–8.1 (m, 2H, Py), 8.5–8.7 (m, 2H, Py).	104.6, 112.8, 121.5, 123.3 (thienyl), 126.9, 167.9, (Py) 152.8 (HC=N), 190.3 (C–O).

In the complexes, the aromatic and heteroaromatic proton signals appeared downfield, as expected, due to increased conjugation on coordination (17). ^{13}C NMR spectra (Table 4), likewise, showed similar diagnostic features (18) for the free ligands as well as their complexes as expected. Furanyl and thienyl carbons were found in the range 104.5–123.2 ppm, aromatic carbons at 124.8–137.3 ppm and the azomethine carbon signal was found at 152.4 ppm. Similarly, the presence of the C = O signal at ~187.4 ppm in the spectra of the ligands and the absence of this signal in the spectra of the complexes and appearance of a signal at lower values supported the evidence that the ligands act in an enolized form. However, due to solubility problems it was not possible to obtain NMR spectra of all the complexes and only a representative spectrum of the cobalt(II) complex of each ligands was taken and reported in Table 4.

Magnetic Moments and Electronic Spectra

UV–vis spectral bands of the complexes are recorded in Table 3. The cobalt(II) complexes show magnetic moment values of 4.85–4.93 B.M. at room temperature. These high values of the magnetic moments and the stoichiometries suggest a coordination number of six for the central cobalt(II) ion and an octahedral geometry. The electronic spectra of these complexes are also consistent with their octahedral environment around the cobalt(II) ion. The spectra display two bands at ~20,920 and ~28,570 cm^{-1} attributed to $^4T_{1g} \rightarrow {}^4T_{1g}$ and $^4T_{1g} \rightarrow {}^4T_{2g}$ transitions, respectively, in a high-spin octahedral geometry (19,20).

The copper(II) complexes exhibit magnetic moments of 1.55–1.78 B.M., respectively, at room temperature. These values are quite close to the spin-allowed values expected for a S =1/2 system and may be indicative of a distorted octahedral geometry around copper(II) ions. These copper(II) complexes deisplay a broad band at ~14,920 cm^{-1} due to $^2B_{1g} \rightarrow {}^2E_g$ and two bands at ~16,390 and



R = Ph; X = O (L^1)
R = Ph; X = S (L^2)
R = PhOH-*o*; X = O (L^3)
R = PhOH-*o*; X = S (L^4)
R = Py; X = O (L^5)
R = Py; X = S (L^6)
M = Co(II), Cu(II), Ni(II) or Zn(II)

Figure 3. Proposed structure of the metal(II) complexes.

~27,250 cm^{-1} assigned to d–d transitions and a charge transfer band, respectively, of a distorted octahedral environment (21,22).

The electronic spectra of the nickel(II) complexes exhibited absorption bands at ~16,670 and ~27,780 cm^{-1}, attributable to $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P), transitions, respectively, in an octahedral geometry (23,24). The calculated values of the ligand field parameters lie in the range reported for an octahedral structure. Also, the values of the magnetic moment (3.2–3.7 B.M.) may be taken as additional evidence for their octahedral structure.

The diamagnetic zinc(II) complexes did not show any d–d bands and their spectra are dominated only by charge transfer bands. The charge transfer band at 27,550 cm^{-1} was assigned to the transition $^2E_g \rightarrow {}^2T_{2g}$, possibly in an octahedral environment (20).

On the basis of the above observations, it is tentatively suggested that all of the complexes show an octahedral geometry (Fig. 3) in which the two ligands act as tridentates. These possibly accommodate themselves around the metal atom in such a way that a stable chelate ring is formed giving, in turn, stability to the formed metal complexes.

Antibacterial Properties

The title Schiff bases and their metal(II) chelates were evaluated for their antibacterial activity against the standard bacterial strains of a) *Escherichia coli*, b) *Staphylococcus aureus*, and c) *Pseudomonas aeruginosa*. The compunds were tested at a concentration of 30 μg/0.01 mL in DMF solution, using the paper disc diffusion method as earlier reported (25,26). The inhibition zones were measured in mm and the results are reproduced in Table 5. The inhibition zones are the clear

Table 5. Antibacterial Activity Data of the Schiff Bases and Its Metal(II) Complexes

Schiff Base/ Complex	Microbial Species[a]		
	a	b	c
HL^1	++	++	++
HL^2	++	+	+
HL^3	++	+	++
HL^4	++	++	+
HL^5	++	+	++
HL^6	+	++	++
(**1**)	+++	++	+++
(**2**)	+++	+++	++
(**3**)	+++	++	++++
(**4**)	+++	++	+++
(**5**)	++++	+++	+++
(**6**)	+++	+++	++
(**7**)	++++	++	+++
(**8**)	++	+++	++++
(**9**)	+++	+++	++
(**10**)	+++	+++	+++
(**11**)	+++	+++	+++
(**12**)	+++	++++	++
(**13**)	++	++	+++
(**14**)	+++	+++	+++
(**15**)	+++	++++	++
(**16**)	++	+++	+++
(**17**)	++++	+++	++
(**18**)	+++	+++	++
(**19**)	+++	+++	+++
(**20**)	++	+++	++
(**21**)	+++	++++	+++
(**22**)	+++	+++	+++
(**23**)	++++	+++	++
(**24**)	+++	+++	+++

[a] a: *E. coli*; b: *S. aureus*; c: *P. aeruginosa.*

Inhibition zone diameter mm (% inhibition): +, 6–10 (27–45%); ++, 10–14 (45–64%); +++, 14–18 (64–82%); ++++, 18–22 (82–100%). Percent inhibition values are relative to the inhibition zone (22 mm) with 100% inhibition.

zones around the discs, which were measured in mm. All the Schiff bases were found to be biologically active and their metal(II) complexes showed significantly enhanced antibacterial activity against one or more bacterial species in comparison to the free Schiff bases. It is, however, known (27–29) that chelation tends to make the ligands act as more powerful and potent bactericidal agents, thus killing more of the bacteria than the parent Schiff bases do. It is suspected that factors such as solubility, conductivity, dipole moment, and cell permeability mechanisms (influenced by the presence of metal ions) may be the possible reasons for increasing this activity.

EXPERIMENTAL

Material and Methods

All chemicals and solvents used were of Analar grade. All metal(II) salts used were the dichlorides. 2-Furanecarboxaldehyde, 2-thiophenecarboxaldehyde, benzoylhydrazine, nicotinoylhydrazine, and salicyloylhydrazine were obtained from Merck. IR spectra were obtained as KBr discs on a Philips Analytical PU 9800 FTIR spectrophotometer. ^{1}H-NMR and ^{13}C NMR spectra were recorded on a Bruker 250-MHz spectrometer in DMSO-d_6. UV-vis spectra were obtained in DMF on a Hitachi U-2000 double-beam spectrophotometer. C, H, and N analyses were carried out by Butterworth Laboratories Ltd. (U.K). Conductances of the metal complexes were determined in DMF on a Hitachi YSI-32 model conductometer. Magnetic measurements were doen on the solid complexes using the Gouy method. Melting points were recorded on a Gallenkamp apparatus and are uncorrected.

Preparation of Schiff Base Ligands

***N*-(2-Furanylmethylene)benzoylhydrazine (HL^1).** 2-Furanecarboxaldehyde (0.83 mL, 0.97 g, 0.01 mol) in absolute ethanol (20 mL) was added to a stirred ethanol solution (20 mL) of benzoylhydrazine (1.4 g, 0.01 mol). Then 2–3 drops of conc. H_2SO_4 were added and the mixture was refluxed for 1 h. The reaction mixture was then cooled and left for 24 h at room temperature. During this period, a yellow solid was formed. It was recrystallized from hot ethanol; Yield, 1.1 g.

***N*-(2-Thienylmethylene)benzoylhydrazine (HL^2).** 2-Thiophenecarboxaldehyde (0.93 mL, 1.12 g, 0.01 mol) in absolute ethanol (20 mL) was added to a stirred ethanol solution (20 mL) of benzoylhydrazine (1.4 g, 0.01 mol). Then

2–3 drops of conc. H_2SO_4 were added and the mixture was refluxed for 1 h. The reaction mixture was then cooled and left for 24 h at room temperature. During this period, a light yellow solid was formed, which was recrystallized from hot ethanol to give the desired product; Yield 1.3 g.

All other Schiff base ligands were prepared following the same above method.

Preparation of Metal Complexes

An ethanol solution (20 mL) of the appropriate metal(II) chloride salt (0.001 mol) was added to a magnetically stirred ethanol solution (15 mL) of the respective Schiff base (0.002 *M*). The mixture was refluxed for 2 h, then coolded to room temperature, filtered and reduced to nearly half of its volume. The concentrated solution was left standing overnight at room temperature, which resulted in the formation of a solid product. The product thus obtained was filtered, washed with ethanol, then the ether, and dried. Crystallization in aqueous ethanol (50%) gave the desired metal complexes.

Antibacterial Studies

Preparation of discs. The ligand/complex (30 μg) in DMF (0.01 mL) was applied to a paper disc, (prepared from blotting paper, (3-mm diameter) with the help of a micropipette. The discs were left in an incubator for 48 h at 37°C and then applied to the bacteria grown on agar plates.

Preparation of agar plates. Minimal agar was used for the growth of specific bacterial species. For the preparation of the agar plates for *E. coli*, MacConkey agar (50 g) obtained from Merck Chemical Company, was suspended in freshly distilled water (1 L). It was allowed to soak for 15 min and the boiled on a water bath until the agar was completely dissolved. The mixture was autoclaved from 15 min at 120°C and then poured into previously washed and sterilized Petri dishes and stored at 40°C for inoculation.

Procedure of inoculation. Inoculation was done with the help of a platinum wire loop, which was made red hot in a flame, cooled and then used for the application of bacterial strains.

Application of discs. Sterilized forceps were used for the application of the paper disc on the earlier inoculated agar plates. When the discs were applied, they were incubated at 37°C for 24 h. The zone of inhibition was then measured (diameter in mm) around the disc.

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