2-(Benzothiazol-2-yl)-N'-(2,5-dihydroxybenzylidene)acetohydrazide의 Mn(II), Ni(II), Co(II), Cu(II) 및 Zn(II) 착물의 합성, 특성 및 생물학적 연구

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Synthesis, Characterization and Biological Studies of New Mn(II), Ni(II), Co(II), Cu(II) and Zn(II) of 2-(benzothiazol-2-yl)-N'-(2,5-dihydroxybenzylidene)acetohydrazide

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요 약. 2-(Benzothiazol-2-yl)-N'-(2,5-dihydroxybenzylidene)acetohydrazide 에대한새로운일련의 Mn(II), Ni(II), Co(II), Cu(II) 및 Zn(II) 착물을 합성하여 그 특성을원소분석, IR, UV-vis, ^{1}H-NMR, 질량분석, ESR, 자기수자율 및 몰 전기전도도측정에 의하여조사하였다. 이들 착물의기하구조가사각평면 또는 팔면체임을 분광학적 데이터 및 자기적 측정으로부터알았다. 이 리간드와 해당착물의세균에(Aspergillus nigar 및 Fusarium oxysporium) 대한생물학적활성을조사하였다. 그 결과, 금속착물 들은리간드 및 금속이온 모두에비해 더 큰 활성을나타내었다.

주제어: Benzothiazol, Acetohydrazide, 착물, 살균활성, ESR 분광학

ABSTRACT. New series of Mn(II), Ni(II), Co(II), Cu(II) and Zn(II) of the 2-(benzothiazol-2-yl)-N'-(2,5-dihydroxyben-zylidene) acetohydrazide have been synthesized and characterized by elemental analysis, IR, UV-vis, ^{1}H-NMR, mass and ESR spectra, magnetic susceptibility and molar conductivity measurements. The spectral data and magnetic measurements of the complexes indicate that, the geometries are either square planar or octahedral. The biological activity of the ligand and its complexes against fungi (Aspergillus nigar and Fusarium oxysporium) were investigated. The metal complexes exhibited higher activity than both the parent ligand and the corresponding metal ion.

Keywords: Benzothiazol, Acetohydrazide, Complexes, Fungicidal activities, ESR spectroscopy

INTRODUCTION

Biomaterial science has expanded rapidly in the past few decades, in basic and medical field. Coordination chemistry is also contributing to the development of biomaterials[1] and biomaterial science. The synthesis, structural investigation and reactions of transition metal Schiff bases showed a special attention, due to their biological activities as antitumoral, antifungal and antiviral activities.[2] Thus, hydrazones are also interesting from the point of view of pharmacology. Also hydrazone derivatives are found to possess antimicrobial,[3] antitubercular,[4] anticonvulsant[5] and antiinflammatory[6] activities. Particularly, the antibacterial and antifungal properties of bisacylhydrazone and their complexes with transition metal ions were studied and reported.[7] In addition, complexes of salicylaldehide benzoylhydrazone were shown to be a potent inhibitor of DNA synthesis and cell growth.[8] This hydrazone showed a mild bacteriostatic activity and a range of analogues has been investigated as potential oral ion chelating drugs for genetic disorders such as thalasemia.[9,10] Interest is focused on the preparation and characterization of the related ligands and their metal complexes. The present paper describes the synthesis and characterization of 2-(benzo-thiazol-2-yl)-N'-(2,5-dihy-droxybenzylidene) acetohydrazide and its Mn(II), Ni(II), Co(II), Cu(II) and Zn(II) complexes. The coordination behavior of the hydrazone ligand towards metal ions was investigated via IR, UV-vis, ESR as well as conductivity and magnetic moments

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measurements. The fungicidal activities of the ligand and its complexes were investigated against Aspergillus nigar and Fusarium oxysporium.

EXPERIMENTAL

Materials

Reagents grade chemicals were used without further purification. 2-(benzothiazol-2-yl)acetohydrazide was synthesized according to the literature.[11]

Physical Measurements

C, H, N, S and Cl contents were analyzed at the Micro-analytical Laboratory, Faculty of Science, Cairo University, Egypt (*Table* 1). The metal ion contents of the complexes were also determined by the previously reported methods.[12-15] IR spectra of the ligand and its metal complexes were measured using KBr discs with a Jasco FT/IR 300E Fourier transform infrared spectrophotometer covering the range 400 - 4000 cm^{-1} and in the 500 - 100 cm^{-1} region using polyethylene-sandwiched Nujol mulls on a Perkin Elmer FT-IR 1650 spectrophotometer. ^{1}H NMR spectrum was obtained on Brucker Advance 400-DRX spectrometers. Chemical shifts (ppm) are reported relative to TMS. The electronic spectra of the ligand and its complexes were obtained in Nujol mulls and in saturated DMSO solutions using a Shimadzu UV-240 UV-visible recording spectrophotometer. Mass spectra of the solid ligand and its metal complexes were recorded using JEUL JMS-AX-500 mass spectrometer provided with data system. Molar conductivities of the metal complexes in DMSO (10^{-3} M) were measured using a dip cell and a Bibby conductimeter MC1 at room temperature. The resistance measured in ohms and the molar conductivities were calculated according to the equation: $\Lambda = V \times K \times Mw/g \times \Omega$, where, molar conductivity (ohm^{-1} cm^2 mol^{-1}); V, volume of the complex solution (mL); K, cell constant 0.92 cm^{-1}; Mw, molecular weight of the complex; g, weight of the complex; and Ω, resistance measured in ohms. Magnetic moments at 298 K were determined using the Gouy method with Hg[Co (SCN)$_4$] as calibrant. The solid ESR spectra of the complexes were recorded with ELEXSYS E500 Brucker spectrometer in 3-mm Pyrex Tubes at 298 K. Diphenyl-picrylhydrazide (DPPH) was used as a g-marker for the calibration of the spectra. TLC confirmed the purity of the prepared compounds.

Synthesis of the ligand

A hot solution of 2-(benzothiazol-2-yl)acetohydrazide (2.1 g,1.0 mmol) in ethanol (20 mL) was added to a hot solution of 2,5-dihydroxybenzaldehyde (1.4 mg, 1.0 mmol) in ethanol (25 mL) and the mixture was refluxed for two hours. The volume of the reaction mixture was reduced to half and the formed yellow precipitate is filtered of, washed with cold methanol, recrystalized from methanol and dried under vacuum over anhydrous CaCl$_2$. ^{1}H NMR (400 MHz, d_6-DMSO): δ = 12.22 (s, 1H, OH), 12.07 (s, 1H, OH), 10.98 (s, 1H, NH), 8.44 (s, 1H, N=CH), 8.02-6.95 (aromatic, 7H), 4.25 (s, 2H, CH$_2$).

Synthesis of the metal complexes

Complexes (**2**), (**3**), (**4**), (**6**), (**7**) and (**8**) were prepared by mixing a hot methanolic solution of Co(Cl)$_2$·6H$_2$O, Co(NO$_3$)$_2$·6H$_2$O, Co(CH$_3$COO)$_2$·4H$_2$O, Mn(Cl)$_2$·4H$_2$O, Mn(NO$_3$)$_2$·6H2O, Mn(CH$_3$COO)$_2$·4H$_2$O with a hot ethanolic solution of the ligand in molar ratio (1 Ligand:1 Metal). The reaction mixture was then refluxed for 2 - 4 h, depending on the metal salt used. The precipitates formed were filtered off, washed with ethanol, then with diethyl ether and dried under vacuum over anhydrous CaCl$_2$.

Complexes (**5**) and (**9**)-(**17**) were prepared by mixing a hot methanolic solution of Co(CH$_3$COO)$_2$·4H$_2$O, Mn(CH$_3$-COO)$_2$·4H$_2$O, Mn(Cl)$_2$·4H$_2$O, Mn(NO$_3$)$_2$·6H$_2$O, Zn(Cl)$_2$, Zn(CH$_3$COO)$_2$·2H$_2$O, Zn(NO$_3$)$_2$·6H$_2$O, Cu(NO$_3$)$_2$·2.5H$_2$O, Ni(NO$_3$)$_2$·6H$_2$O, Cu(CH$_3$COO)$_2$·H$_2$O, with a hot ethanolic solution of the ligand in molar ratio (2 Ligand:1 Metal). The reaction mixture was then refluxed for 2 - 4 h, depending on the metal salt used. The precipitates formed were filtered off, washed with ethanol, then with diethyl ether and dried under vacuum over anhydrous CaCl$_2$.
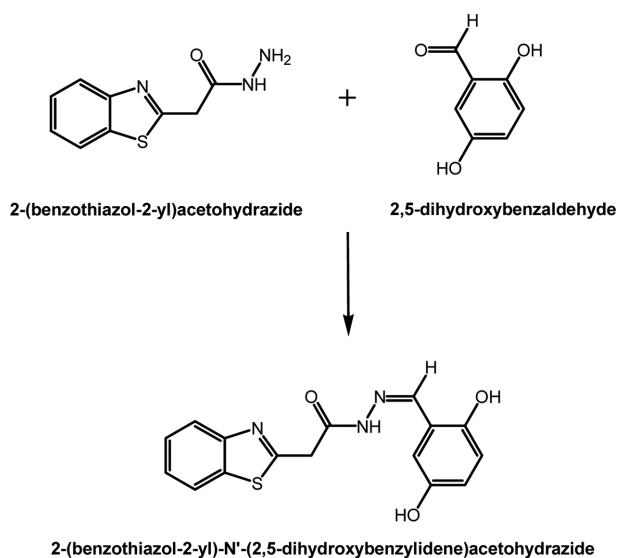
Typical Procedure for the biological activity

The fungicidal activities of the ligand and its metal complexes were evaluated using the agar plate technique[17] on Aspergillus niger and Fusarium oxysporium. The tested compounds were dissolved in DMSO to give a 10,000 ppm stock solution. From the stock solution the required concentration levels (l00, 200, 500 ppm) were prepared by appropriate dilutions. To ensure proper setting of the medium solutions were placed in Petri dishes and a stand for l h to. Spores were taken from an eight-day-old culture of the fungi. The selectorial bodies were planted at the centers of each Petri dish. The inoculated dishes were kept in an incubator at 27 ^{o}C the diameters of the resulting fugi colonies were measured with a millimeter scale after three and five days for Aspergillus niger and Fusarium oxysporium respectively.

RESULTS AND DISCUSSION

The elemental and physical data of the ligand H$_3$L and its

Table **1.** Analytical and physical data of the ligand H_3L and its metal complexes

| No. | Ligand/Complexes | Color | FW | Yield (%) | Anal./Found (calc.) (%) | | | | | | Molar conductance Λm ($\Omega^{-1} cm^2 mol^{-1}$) |
					C	H	N	S	Cl	M	
1	H_3L	Yellow	327.4	79	58.7(58.7)	4.1(4.0)	12.8(12.8)	9.7(9.8)	-	-	-
2	$H_2LCoCl(H_2O)_2$	Brown	456.8	71	42.0(42.1)	3.7(3.5)	9.3(9.2)	7.0(7.0)	7.6(7.8)	12.8(12.9)	10
3	$H_2LCo(ONO_2)(H_2O)_2$	Brown	483.3	70	39.7(39.8)	3.4(3.3)	11.7(11.6)	6.5(6.6)	-	12.2(12.2)	12
4	$H_2LCo(OC(O)CH_3)$	red	444.3	76	48.6(48.7)	3.5(3.4)	9.5(9.5)	7.2(7.2)	-	13.2(13.3)	9
5	$(H_2L)_2Co$	orange	711.6	79	54.0(54.0)	3.5(3.4)	11.9(11.8)	9.0(9.0)	-	8.2(8.3)	11
6	$H_2LMnCl(H_2O)_2$	Brown	452.8	85	42.4(42.4)	3.6(3.6)	9.4(9.3)	7.1(7.1)	7.5(7.8)	12.0(12.1)	6
7	$H_2LMn(ONO_2)(H_2O)_2$	Brown	479.3	87	40.0(40.1)	3.5(3.4)	11.7(11.7)	6.7(6.7)	-	11.5(11.5)	13
8	$H_2LMn(OOCCH_3)(H_2O)$	Brown	458.4	81	47.1(47.2)	3.9(3.7)	9.2(9.2)	7.0(7.0)	-	11.9(12.0)	7
9	$(H_3L)_2Mn(OC(O)CH_3)_2$	Brown	827.7	77	52.2(52.2)	4.0(3.9)	10.3(10.2)	7.8(7.8)	-	6.5(6.6)	8
10	$(H_3L)_2MnCl_2$	Brown	780.6	89	49.2(49.2)	3.4(3.4)	10.9(10.8)	8.1(8.2)	9.0(9.1)	6.9(7.0)	15
11	$(H_3L)_2Mn(ONO_2)_2$	Brown	833.7	72	46.1(46.1)	3.2(3.1)	13.5(13.4)	7.7(7.7)	-	6.5(6.6)	14
12	$(H_2L)_2Zn(H_2O)_2$	Yellow	754.1	81	50.9(51.0)	3.8(3.7)	11.1(11.1)	8.4(8.5)	-	8.6(8.7)	6
13	$(H_3L)_2Zn(OC(O)CH_3)_2$	Yellow	838.2	89	51.5(51.6)	4.0(3.9)	10.1(10.0)	7.6(7.7)	-	7.6(7.8)	14
14	$(H_2L)_2Zn$	Yellow	718.1	91	53.5(53.5)	3.5(3.4)	11.7(11.7)	8.8(8.9)	-	9.1(9.1)	7
15	$(H_2L)_2Cu(H_2O)_2$	Green	752.3	90	51.0(51.1)	3.8(3.8)	11.3(11.2)	8.5(8.5)	-	8.4(8.5)	5
16	$(H_2L)_2Ni(H_2O)_2$	Brown	747.4	92	51.4(51.4)	3.7(3.8)	11.3(11.2)	8.6(8.6)	-	7.9(7.9)	8
17	$(H_3L)_2Cu(OC(O)CH_3)_2$	Green	836.4	91	51.5(51.7)	4.1(3.9)	10.2(10.1)	7.7(7.7)	-	7.5(7.6)	11

2-(benzothiazol-2-yl)acetohydrazide   **2,5-dihydroxybenzaldehyde**

2-(benzothiazol-2-yl)-N'-(2,5-dihydroxybenzylidene)acetohydrazide

Fig. **1.** Schematic representation for the formation of the Schiff base ligand H_3L.

complexes (*Table* 1) are compatible with the proposed structures (*Fig.* 1 and 2A-B) and showed that the stoichiometry of the complexes obtained is 1:1, 1:2 (metal: ligand).

Mass spectrum of the ligand

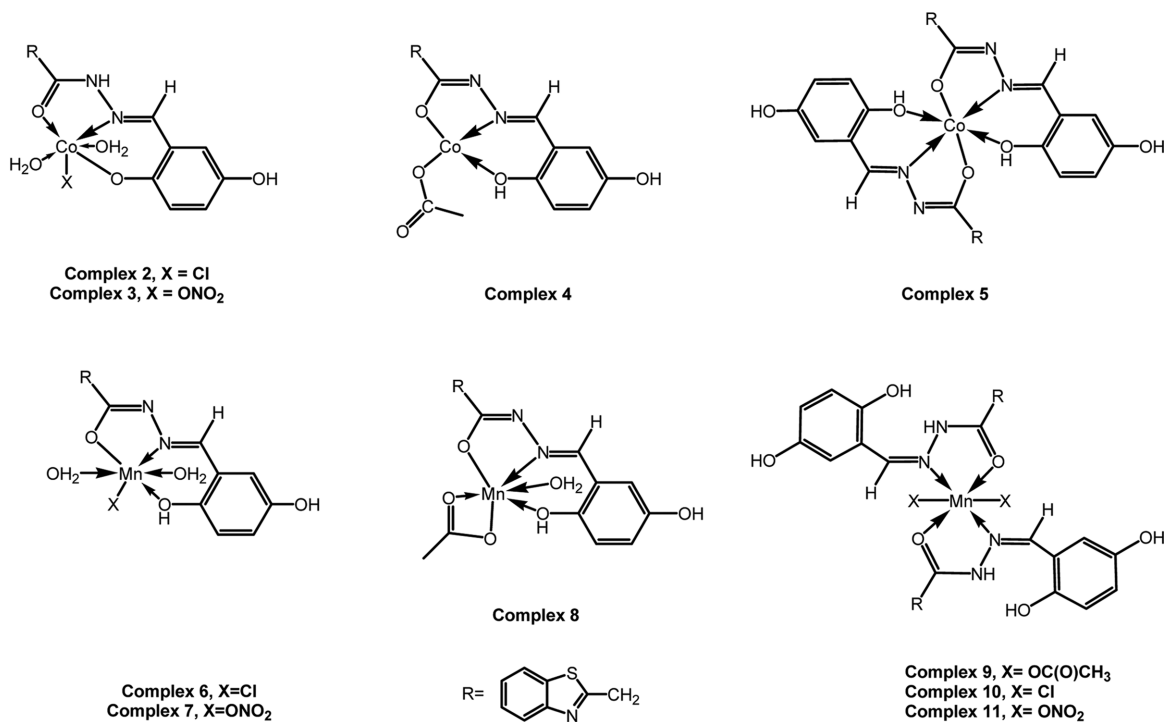The mass spectrum of the ligand revealed the molecular ion peaks at m/e 327 which is coincident with the formulae weight (327.36) for the ligand and supports the identity of its structure.
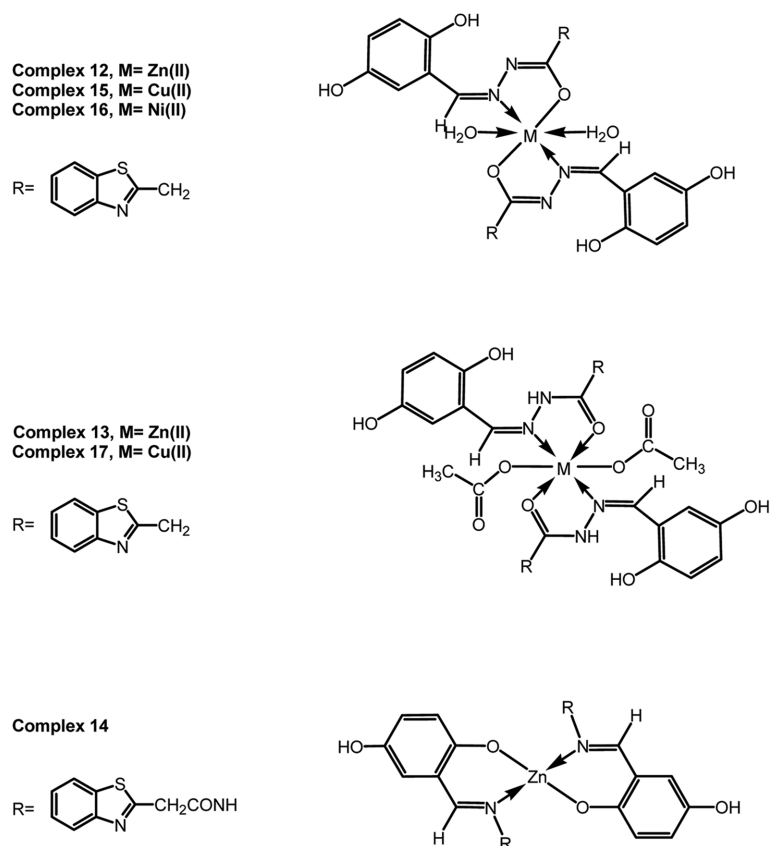
Infrared spectra

The infrared spectrum of the ligand showed a strong band located at 1680 cm^{-1}, which is assigned to carbonyl group ν(C=O), whereas the broad medium bands at 3280, 3260 and 3200 cm^{-1} are assigned to the (OH), (NH) group respectively. These observations confirmed the ketonic form of the ligand in the solid state. On the other hand the relatively strong bands at 1625, 1222, 1115 cm^{-1} are assigned to ν(C=N), ν(C-OH) and ν(N-N) groups respectively. By comparison of the IR spectra of complexes (**2**)-(**17**) with that of the free ligand (*Table* 2), it was concluded that, the ligand has different modes of coordination.

1) The ligand behaves as monobasic tridentate ligand. It bonded to metal ions through the ketonic carbonyl (C=O), azomethine (C=N) and deprotonated phenolic groups as in complexes (**2**) and (**3**). this mode of bonding was suggested by the following evidence: (i) the disappearance of the band for the phenolic OH, indicating the subsequent deprotonation of the phenolic proton prior to coordination,[18] (ii) the shift of υ(C=N) to lower frequency (15 - 16 cm^{-1}) together with its weak appearance, which indicates the coordination of the azomethine nitrogen,[19,20] (iii) the band due to the carbonyl group is weakened and shifted to lower wave number by 13 - 15 cm^{-1}, (iv) the occurrence of the

(A)

Complex 2, X = Cl
Complex 3, X = ONO₂

Complex 4

Complex 5

Complex 6, X=Cl
Complex 7, X=ONO₂

Complex 8

R= [benzothiazole]-CH₂

Complex 9, X= OC(O)CH₃
Complex 10, X= Cl
Complex 11, X= ONO₂

(B)

Complex 12, M= Zn(II)
Complex 15, M= Cu(II)
Complex 16, M= Ni(II)

R= [benzothiazole]-CH₂

Complex 13, M= Zn(II)
Complex 17, M= Cu(II)

R= [benzothiazole]-CH₂

Complex 14

R= [benzothiazole]-CH₂CONH

Fig. 2. The proposed structures of metal complexes.

Table **2.** IR frequencies of the bands (cm⁻¹) of ligand H₃L and its Metal Complexes and their assignments

No.	$\nu(H_2O)$	$\nu(OH)$	$\nu(NH)$	$\nu(C=O)$	$\nu(C=N)$	$\nu(C=N)_{ring}$	$\nu(C\text{-}O)$	$\nu(N\text{-}N)$	$\nu_s(Coo)$, $\nu_{as}(Coo)$, $\tilde{\Delta}\nu(NO_3)(D)$	$\nu(M\text{-}N)$	$\nu(M\text{-}O)$	$\nu(M\text{-}Cl)$
1	-	3280s, 3260s	3200s	1680 v.s	1625s	1572s	1222m	1115m	-	-	-	-
2	3445br	3260s	3205s	1665s	1610m	1573s	1235m	1141m	-	535m	660w	375m
3	3451br	3262s	3206s	1667s	1609m	1569s	1231m	1139m	1468, 1380, 1030, 710, (88)	520w	665w, 230m	-
4	-	3269sh, 3259s	-	-	1613m, 1628m	1571s	1229m	1137m	1560m, 1359m, (201)	590m	655w, 645m	-
5	-	3270sh, 3265m, 3259s	-	-	1614m, 1611m, 1633m	1569s	1230m	1131m	-	545m	655m	-
6	3447br	3267m, 3259s	-	-	1608m, 1631m	1570s	1228m	1132m	-	534m	615m	365m
7	3455br	3265m, 3261s	-	-	1613m, 1624m	1571s	1234m	1142m	1460,1372,1060,718, (88)	540m	608m, 240m	-
8	3450br	3271m, 3260s	-	-	16014m, 1630m	1569s	1235m	1139m	1551m, 1454m, (97)	532m	650m, 658m	-
9	-	3281s, 3259s	3203s	1669s	1608m	1570s	1223m	1127m	1557m, 1354m, (203)	521m	642m, 649m	-
10	-	3280s, 3262s	3198s	1668s	1611m	1571s	1220m	1134m	-	535m	645m	370
11	-	3279s, 3263s	3201s	1665s	1609m	1569s	1221m	1139m	1463, 1375, 1045, 720, (88)	560m	618m, 235m	-
12	3451br	3278s, 3261s	-	-	1612m, 1630m	1573s	1220m	1124m	-	541m	633m	-
13	-	3281s, 3263s	3201s	1664s	1607m	1570s	1220m	1120m	1563m, 1361m, (202)	539m	651m	-
14	-	3261s	3202s	1682 v.s	1609m	1571s	1234m	1126m	-	551m	647m	
15	3450br	3280s, 3262s	-	-	1614m, 1629m	1570s	1222m	1127m	-	551m	623m	-
16	3450br	3282s, 3260s	-	-	1611m, 1632m	1571s	1221m	1134m	-	548m	645m	-
17	-	3279s, 3261s	3203s	1668s	1612m	1572s	1220m	1125m	1560m, 1355m, (205)	544m	641m	-

υ(N-N) band at higher wave number, (v) the band due to phenolic C-O stretching vibrations are upward shifted due to O-metal coordination,[21] (vi) the simultaneous appearance of new bands in the 520 - 535 and 660 - 665 cm⁻¹ regions due to the υ(M-N) and υ(M-O) vibrations, respectively.[22,23]

2) The ligand behaves as monobasic tridentate ligand. Itbonded to metal ions through the enolic carbonyl (C-O), azomethine (C=N) and phenolic groups as in complexes (**4**), (**5**), (**6**), (**7**) and (**8**). this mode of bonding was suggested by the following evidence: (i) the band due to the phenolic OH group is weakened and shifted to lower wave number by 10 - 15 cm⁻¹, (ii) the shift of υ(C=N) to lower frequency (15 - 16 cm⁻¹) together with its weak appearance, which indicates the coordination of the azomethine nitrogen,[19,20] (iii) the disappearance of the band due to the carbonyl and the amine groups with the appearance of a new band due to the new υ(C=N) found at higher wave number, (iv) the occurrence of the υ(N-N) band at higher wave number, (v) the band due to phenolic C-O stretching vibrations

are upward shifted due to O-metal coordination,[21] (vi) the simultaneous appearance of new bands in the 540 - 590 and 608 - 655 cm⁻¹ regions due to the υ(M-N) and υ(M-O) vibrations, respectively.[22,23]

3) The ligand behaves as neutral bidentate ligand. It coordinated to the metal ions through the ketonic carbonyl (C=O) and azomethine (C=N) groups as in complexes (**9**), (**10**), (**11**), (**13**) and (**17**). This mode of coordination was suggested by the following evidence: (i) the band due to the phenolic OH group retained its intensity and place, (ii) the shift of υ(C=N) to lower frequency (13 - 18 cm⁻¹) together with its weak appearance, which indicates the coordination of the azomethine nitrogen,[19,20] (iii) the band due to the carbonyl group is weakened and shifted to lower wave number by 11 - 16 cm⁻¹, (iv) the occurrence of the υ(N-N) band at higher wave number, (v) the simultaneous appearance of new bands in the 520 - 535 and 660 - 665 cm⁻¹ regions due to the υ(M-N) and υ(M-O) vibrations, respectively.[22,23]

4) The ligand behaves as monobasic bidentate ligand. It

bonded to metal ions through the enolic carbonyl (C-O) and azomethine (C=N) groups as in complexes (**12**), (**15**) and (**16**). This mode of bonding was suggested by the following evidence: (i) the band due to the phenolic OH group retained its intensity and place, (ii) the shift of υ(C=N) to lower frequency (11 - 14 cm^{-1}) together with its weak appearance, which indicates the coordination of the azomethine nitrogen[19,20] (iii) the disappearance of the band due to the carbonyl and the amine (NH) groups with the appearance of a new band due to the new υ(C=N) found at higher wave number, (iv) the occurrence of the υ(N-N) band at higher wave number, (v) the simultaneous appearance of new bands in the 541 - 551 and 623 - 645 cm^{-1} regions due to the υ(M-N) and υ(M-O) vibrations, respectively.[22,23]

5) The ligand behaves as monobasic bidentate ligand. It bonded to metal ions through the azomethine (C=N) and deprotonated phenolic groups as in complex (**14**). This mode of bonding was suggested by the following evidence: (i) the disappearance of the band for the phenolic OH, indicating the subsequent deprotonation of the phenolic proton prior to coordination,[24] (ii) the shift of υ(C=N) to lower frequency (16 cm^{-1}) together with its weak appearance, which indicates the coordination of the azomethine nitrogen,[19,20] (iii) the band due to υ(C=O) group retained its intensity and place, (iv) the occurrence of the υ(N-N) band at higher wave number, (v) the band due to phenolic C-O stretching vibration is upward shifted due to oxygen-metal coordination,[21] (vi) the simultaneous appearance of new bands at 551 and 647 cm^{-1} due to the υ(M-N) and υ(M-O) vibrations, respectively.[22,23]

The IR spectra of complexes (**2**), (**3**), (**6**), (**7**), (**8**), (**12**), (**15**) and (**16**) showed bands in 3445 - 3455, 1605 - 1620, 940 - 965 and 610 - 635 cm^{-1} regions due to OH stretching, HOH deformation, H_2O rocking and H_2O wagging, respectively.[24,25] This confirmed the presence of coordinated water molecules in these complexes. The appearance of two characteristic bands in the 1563 - 1551 cm^{-1} and 1454 - 1370 cm^{-1} regions, in case of complexes (**4**), (**8**), (**9**), (**13**) and (**17**) were attributed to υ_{asym}(COO^{-}) and υ_{sym}(COO^{-}), respectively, indicating the participation of the carboxylate oxygen in the complexes formation. The mode of coordination of carboxylate group has often been deduced from the magnitude of the observed separation between the υ_{asym}(COO^{-}) and υ_{sym}(COO^{-}). The separation value (Δ) between υ_{asym}(COO^{-}) and υ_{sym}(COO^{-}) in complexes (**4**), (**9**), (**13**) and (**17**) was more than 200 cm^{-1} (201 - 205 cm^{-1}), suggesting the coordination of carboxylate group in a monodentate fashion.[26] In case of complex (**8**), Δ was found to be 97 cm^{-1} which correlated to a bidentate behavior (*Table* 2).[27] The spectrum of the

complexes (**3**), (**7**) and (**11**) showed bands in the ranges 1468 - 1460 cm^{-1} (υ_1), 1060 - 1030 cm^{-1} (υ_2), 1380 - 1372 cm^{-1} (υ_4) and 710 - 720 cm^{-1} (υ_5) with υ_1-υ_4 separation of 88 cm^{-1}, characteristic of monodentate nitrato group.[28] Complexes (**2**) and (**6**) showed bands at 375, 365 and 370 cm^{-1}, due to coordinated chlorine atom.[28]

Molar conductance data

The molar conductivities (Δ) of the metal complexes in DMSO (10^{-3} M) are found to be in the 8 - 15 Ω^{-1}cm^{2}mol^{-1} range. These low values indicate that, all these complexes are non-electrolytes due to the absence of any counter ions in their structures.[29,30]

Electronic spectra and magnetic moments

Cobalt (II) Complexes: In Nujol mull, the electronic spectra of the cobalt(II) complexes (**2**), (**3**) and (**5**) gave three bands in the 645 - 655 nm, 580 - 595 nm and 530 - 540 nm ranges which can be assigned to the $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(\nu1)$ and $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)(\nu2)$ and $^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)(\nu3)$ transitions, respectively, suggesting an octahedral geometry around Co(II) ion.[14,31] The magnetic moment of these complexes was found in the 4.62 - 4.96 B.M. range, consistent with octahedral geometry. While complex (**4**) showed magnetic moment value of 2.11 B.M.,[32] which correspond to a low spin square planar geometry.[13] It gave electronic absorption band at 720 nm which can be assigned to $^2Eg \rightarrow {}^2A_{1g}$ transition.[13,33]

Copper (II) complexes: The UV-vis spectra of the Cu(II) complexes (**15**) and (**17**), in Nujol mull, showed two band in the 565 - 590 nm and 540 - 570 nm ranges which can be assigned to the $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively indicating that the copper(II) have tetragonal distorted octahedral geometry.[14,31] The magnetic moments are 1.73 and 181 B.M. corresponding to one unpaired electron in an octahedral geometry.

Nickel (II) complex: In Nujol mull, the absorption spectral bands of Ni(II) complex **16** showed two spin allowed transitions: $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ appearing at 880 and 620 nm, consistent with a typical Ni(II) in an octahedral environment.[12,13] The magnetic moment value was found to be 3.2 B.M. as expected for octahedral nickel complexes.[12,13]

Manganese(II) complexes: The spectra of Mn(II) complexes (**6**)-(**11**) showed bands in the Nujol mull, located at 450 - 498 and 550 - 595 nm ranges. These peaks were

Table **3.** The electronic absorption spectral bands (nm) and magnetic moment (B.M.) for the ligand H3L and its complexes

No.	Ligand/Complexes	λ_{max} (nm)	μ_{eff} (B.M.)
1	H_3L	230, 300	-
2	$H_2LCoCl(H_2O)_2$	240, 310, 450, 530, 590, 650	4.75
3	$H_2LCo(ONO_2)(H_2O)_2$	237, 300, 410, 480, 540, 595, 645	4.62
4	$H_2LCo(OC(O)CH_2)$	247, 320, 410, 720	2.11
5	$(H_2L)_2Co$	240, 350, 420, 495, 535, 580, 655	4.96
6	$H_2LMnCl(H_2O)_2$	245, 290, 325, 410, 480, 560	6.18
7	$H_2LMn(ONO_2)(H_2O)_2$	235, 300, 415, 470, 570	5.81
8	$H_2LMn(OOCCH_2)(H_2O)$	240, 300, 340, 400, 498, 595	6.31
9	$(H_3L)_2Mn(OC(O)CH_3)_2$	230, 300, 315, 380, 495, 590	6.10
10	$(H_3L)_2MnCl_2$	245, 310, 380, 450, 595	5.80
11	$(H_3L)_2Mn(ONO_2)_2$	250, 320, 405, 495, 550	5.82
12	$(H_2L)_2Zn(H_2O)_2$	240, 290, 320, 415	Diamagnetic
13	$(H_3L)_2Zn(OC(O)CH_3)_2$	245, 330, 450	Diamagnetic
14	$(H_2L)_2Zn$	250, 320, 360, 415	Diamagnetic
15	$(H_2L)_2Cu(H_2O)_2$	240, 325, 405, 580, 690	1.73
16	$(H_2L)_2Ni(H_2O)_2$	250, 350, 410, 620, 880	3.2
17	$(H_3L)_2Cu(OC(O)CH_3)_2$	260, 350, 410, 605, 670	1.81

Table **4.** ESR parameters for copper(II) and manganese(II) complexes

No.	$g_\parallel$	$g_\perp$	g_{iso}	G	ΔE_{xy} (cm^{-1})	E_{xz} (cm^{-1})	$K_\perp^2$	$K_\parallel^2$	K^2	$g_\parallel/A_\parallel$
6			2.14							
8			2.10							
9			2.18							
15	2.17	2.05	2.09	4.2	14.492	22.727	0.66	0.36	0.56	200
17	2.27	2.07	2.13	5.1	14.925	22.2220	0.91	0.60	0.81	194

assigned to the $^6A_{1g} \rightarrow {}^4T_{2g}(D)$ and $^6A_{1g} \rightarrow {}^4T_{1g}(G)$ transitions respectively indicating octahedral geometry.[34-37] The magnetic moments of the manganese complexes found to be in the 5.80 - 6.31 B.M. range (*Table* 3) indicating a high spin man-ganese(II) complexes.[38]

Electron spin resonance

The X-band ESR spectra of the polycrystalline samples of the copper(II) complexes are recorded at room tempera-ture (298 K) and the data are given in *Table* 4. The spectra of all complexes are of axial shape type with $g_\parallel > g_\perp$ cha-racteristic of complexes with $^2B_1(d_{x2-y2})$ orbital ground state. The isotropic g values were calculated according to the equation $g_{iso} = 1/3[g_\parallel + 2 g_\perp]$ and the results are given in *Table* 4. Both complexes exhibit $g_\parallel < 2.3$, suggesting covalent bond character around the copper(II) ions.[39] The exchange coupling interaction parameter (G) between copper(II) ions is explained by Hathaway expression $G = (g_\parallel-2)/(g_\perp-2)$.[40] If the values G < 4.0, a considerable exchange coupling is present in solid state but if G > 4.0, the exchange interaction is negligible which is typically the case for complexes (**15**) and (**17**). The $g_\parallel/A_\parallel$ is taken as an indication

for the stereochemistry of the copper(II) complexes. Addison has suggested that this ratio may be an empirical indication of the tetrahedral distortion of the square planar geometry.[41] The values of $g_\parallel/A_\parallel$ quotient in the range (105 - 135 cm^{-1}) are expected for copper complexes within perfectly square based geometry and those higher than 150 cm^{-1} for tetrahedrally distorted complexes. The values for the copper complexes (**15**) and (**17**) are associated with a tetragonally distorted field around the copper(II) centers. For copper(II) complexes with $^2B_1$ ground state, the g-values can be related to the parallel ($k_\parallel$) and perpendicular ($k_\perp$) components of the orbital reduction factor (k) as follow:[42]

$$k_\parallel^2 = (g_\parallel - 2.0023)\Delta E_2/8\lambda_0 \qquad (1)$$

$$k_\perp^2 = (g_\perp - 2.0023)\Delta E_1/2\lambda_0 \qquad (2)$$

$$k^2 = (k_\parallel^2 + 2 k_\perp^2)/3 \qquad (3)$$

Where λ_0 is the spin orbit coupling of the free copper(II) ion (-828 cm^{-1}), ΔE_1 and ΔE_2 are the electronic transitions

Table 5. Fungicidal activities of various concentrations of the ligand and its metal complexes on the growth (G) of Aspergillus niger and Fusarium oxysporum as indicated by the percentage of growth inhibition (I) (the data are mean values of three replicates)

Compound No.	Aspergillus niger						Fusarium oxysporum					
	100 ppm		200 ppm		500 ppm		100 ppm		200 ppm		500 ppm	
	G (mm)	I (%)	G (mm)	I (%)	G (mm)	I (%)	G (mm)	I (%)	G (mm)	I (%)	G (mm)	I (%)
1	36.4	5.8	3 1.2	28.1	21. 0	36.6	35.0	6.5	30.1	9.7	23.0	31.9
3	79.0	2.6	77.0	6.0	74.2	8.6	71.6	1.5	70.1	4.3	71.0	4.5
6	39.8	8.7	38.2	22.3	23.2	40.9	40.5	7.5	38.6	11.3	23.9	40.1
14	81 .1	1.3	80.1	1.3	80.0	2.6	75.0	1.3	73.1	1.4	70.0	2.7
15	82 .0	1.3	81.2	1.4	80.0	2.5	71.0	5.9	68.0	5.5	66.0	1.2
16	8 1.0	1.3	78.3	3.6	75.0	8.4	72.0	1.4	70.0	4.2	70.0	4.3

$^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2B_{2g}$, respectively.

The calculated values of $k_{\parallel}^2$, $k_{\perp}^2$ and k^2, *Table* 4, showed that, $k_{\parallel}^2 < k^2$ which is a good evidence for the assumed $^2B_1$ ground state for the complexes. Furthermore, for ionic environment, $k = 1$, and for covalent environment k is less than 1. The lower values of k than the unity (0.56 and 0.81) are indicative of their covalent nature, which in agreement with the conclusion obtained from the values of g_{II}.[43,44]

The ESR, spectra for the manganese complexes (**6**), (**8**) and (**9**) are characteristic of a monomer, d^5, Mn(II) configuration and having an isotropic type with $g_{iso} = 2.14$, 2.10 and 2.18 respectively, indicating octahedral structure.[44]

Biological activity

The biological activity of the ligand and its metal complexes were tested against fungi (Aspergillus nigar and Fusarium oxysporium). The biological data in *Table* 5, indicates that, the biological activities of the ligand and its complexes increase as the concentration increases. However, the complexes displayed a higher activity against Aspergillus nigar than the ligand. Complexes of cobalt(II) and copper(II) showed higher activity against Fusarium oxysporum than the ligand at all used concentrations. However, the manganese(II) complexes showeded a moderate activity against Fusarium oxysporiurn in comparison to the ligand alone while the inhibitory effect of the complexes of nickel(II) and zinc(II) was not clearly manifested against this fungal strain. On the other hand, aqueous ions of the all tested metals showed a significant lower growth inhibition than that of the studied complexes.[17]

Clearly, the metal complexes in most cases exhibit higher activities in comparison to either the parent ligand or corresponding aqueous metal ions. Due to the complex formation between the aqueous metal salt (cations) and the anionic constituents of the fungal cell wall, the metal uptake decreases and hence toxicity decreases. But in case of metal complexes, since the metal cation is already coordinated to a ligand, it easily entre into the fungal cells and hence exert higher metal toxicity. The toxicity of the metal ions on the metafolic activity of the fungal cells is resulting from the complex and inactivation of cellular functional macromolecules. The differential toxicity of the different metal ions was extensively studies and attributed to the chemical properties of the metal ions such as electron negativity and stability of the complex.

CONCLUSIONS

The ligand H3L and its corresponding Co(II), Cu(II), Ni(II), Mn(II) and Zn(II) complexes have been synthesized and spectrally characterized. The ligand acted either as monobasic tridentate, monobasic bidentate or neutral bidentate ligand. All prepared complexes showed either octahedral or square planar geometries. The biological activity of the ligand and its metal complexes were tested against fungi (Aspergillus nigar and Fusarium oxysporium). The biological activities of the cobalt(II) and copper(II) complexes are higher than the ligand and also the corresponding aqueous ions.

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