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RESEARCH ARTICLE

ANTIBACTERIAL EVALUATION OF ETHOXY-OXIME SCHIFF BASE LIGAND AND ITS METAL COMPLEXES

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ABSTRACT

New octahedral Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes of ethoxy-oxime ligand have been prepared and characterized using elemental analyses, IR, UV-Vis spectra, Magnetic moments, Conductances, ¹H-NMR and Mass spectra (ligand and its Zn(II) complex), Thermal analyses (DTA and TGA) and ESR measurements. The IR data show that, the ligand behaves as monobasic bidentate or neutral bidentate. Molar conductances in DMSO indicate that, the complexes are non-electrolytes. ESR spectra of solid Cu(II) complexes at room temperature show axial type ($d_{x^2-y^2}$) with covalent bond character. The antibacterial activity of the ligand and its metal complexes has been investigated on bacteria strains by disc diffusion method and micro broth dilution assays.

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INTRODUCTION

Recently, many researchers have focused their interests on transition metal complexes because of their extensive applications in wide ranging areas (Boerner *et al.*, 2005). It is well known that, metal ions present in complexes accelerate the drug action and the efficacy of the organic therapeutic agents (Siddiqi, 2010). The pharmacological efficiencies of metal complexes depend on the nature of the metal ions and the type of the ligands (Siddiqi *et al.*, 1966). It is declared in the literature that, different ligands and different complexes synthesized from same ligands with different metal ions possess different biological properties (Serbest *et al.*, 2001). So, there is an increasing requirement for the discovery of new complexes having antimicrobial activities. It is found that, the bioactivity of oximes was related to the coordination mode of the oxime site (N and O coordination modes) (Kukushkin *et al.*, 1992 and Baghlaf *et al.*, 1987) as well as to the bridging capacity of the coordinated oximato group to metal ions (Coacio *et al.*, 1995; Ruiz *et al.*, 1993). The bridging oxygen atom of the oximato group serves as a binding site for

developing supermolecular structures (Aly *et al.*, 1998). In this paper, we prepared and characterized new ethoxy-oxime ligand and its metal complexes. Also, the bioefficacy of these complexes were examined against the growth of microorganisms in terms of their antimicrobial potential.

Experimental

MATERIALS AND METHODS

All the reagents were of the best grade available and used without further purification. C, H, N and Cl analyses were determined at the Analytical Unit of Cairo University, Egypt. A standard method [gravimetric] was used to determine metal (II) ion (Vogel, 1951). All complexes were dried under vacuum over P₄O₁₀. The IR spectra were measured as KBr and CeBr pellets using a Perkin-Elmer 683 spectrophotometer (4000-200 cm⁻¹). Electronic spectra (900-200 nm) were recorded on a Perkin-Elmer 550 spectrophotometer. The conductance of (10⁻³ M, DMSO) of the complexes were measured at 25°C with a Bibby conductimeter type MCl. ¹H-NMR spectra (ligand and its Zn(II) complex) were obtained with Perkin-Elmer R32-90-MHz spectrophotometer using TMS as internal standard. Mass spectra (ligand and its Zn(II)

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complex) were recorded using JEULJMS-AX-500 mass spectrometer provided with data system. The thermal analyses (DTA and TGA) were carried out in air on a Shimadzu DT-30 thermal analyzer from 27 to 800°C at a heating rate of 10°C per minute. Magnetic susceptibilities were measured at 25°C by the Gouy method using mercuric tetrathiocyanato cobalt (II) as the magnetic susceptibility standard. Diamagnetic corrections were estimated from Pascal's constant (Lewis *et al.*, 1960). The magnetic moments were calculated from the equation: $\mu_{eff} = 2.84\sqrt{\chi_M^{corr} \cdot T}$. The ESR spectra of solid complexes at room temperature were recorded using a varian E-109 spectrophotometer, DPPH was used as a standard material. The T.L.C of the ligand and its complexes confirmed their purity.

Preparation of the ligand, [HL] (1)

Ligand was prepared by refluxing with stirring equimolar amounts of ethoxy-oxime [1:1] (10 gm, 0.062 mol) and p-aminophenol (6.85 gm, 0.062 mol) in ethanol (100 cm³) for 2 hrs. The black product obtained was filtered off, washed several times with ethanol and dried in vacuum over P₄O₁₀. Analytical data are given in Table 1.

Preparation of metal complexes (2)-(23)

A filtered ethanolic (50 cm³) of Cu(OAc)₂.H₂O was added to an ethanolic (50 cm³) of the ligand, (1) (3.99 gm, 0.02 mol) [1L:1M] complex (2), (1.99 gm, 0.01 mol) of Cu(OAc)₂.H₂O [2L:1M] complex (3), (7.98 gm, 0.04 mol) of Cu(OAc)₂.H₂O [1L:2M] complex (4), (3.19 gm, 0.02 mol) of CuSO₄ complex (5), (4.97 gm, 0.02 mol) of Ni(OAc)₂.4H₂O [1L:1M] complex (6), (9.94 gm, 0.04 mol) of Ni(OAc)₂.4H₂O [1L:2M] complex (7), (5.25 gm, 0.02 mol) of NiSO₄.6H₂O complex (8), (4.97 gm, 0.02 mol) of Co(OAc)₂.4H₂O [1L:1M] complex (9), (9.94 gm, 0.04 mol) of Co(OAc)₂.4H₂O [1L:2M] complex (10), (3.45 gm, 0.02 mol) of CoSO₄.H₂O complex (11), (4.89 gm, 0.02 mol) of Mn(OAc)₂.4H₂O [1L:1M] complex (12), (9.78 gm, 0.04 mol) of Mn(OAc)₂.4H₂O [1L:2M] complex (13), (3.37 gm, 0.02 mol) of MnSO₄.H₂O complex (14), (4.38 gm, 0.02 mol) of Zn(OAc)₂.2H₂O [1L:1M] complex (15), (8.77, 0.04 mol) of Zn(OAc)₂.2H₂O [1L:2M] complex (16), (5.74, 0.02 mol) of ZnSO₄.7H₂O complex (17), (6.37 g, 0.02 mol) of Hg(OAc)₂ [1L:1M] complex (18), (12.74 gm, 0.04 mol) of Hg(OAc)₂ [1L:2M] complex (19), (5.61 gm, 0.02 mol) of Hg(NO₃).H₂O complex (20), (4.96 gm, 0.02 mol) of Cd(OAc)₂.H₂O [1L:1M] complex (21), (9.92 gm, 0.04 mol) of Cd(OAc)₂.H₂O [1L:2M] complex (22), (4.16 gm, 0.02 mol) of CdSO₄ complex (23). All complexes were prepared in the presence of 3ml dimethylamine. The mixture was refluxed with stirring for 1-3hrs range, depending on the nature of metal salts. The coloured complex was filtered off, washed with ethanol and dried under vacuo over P₄O₁₀.

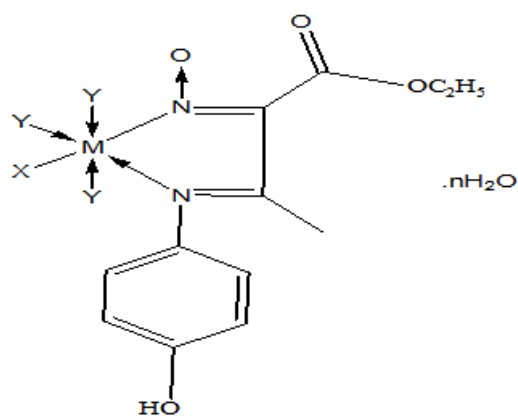
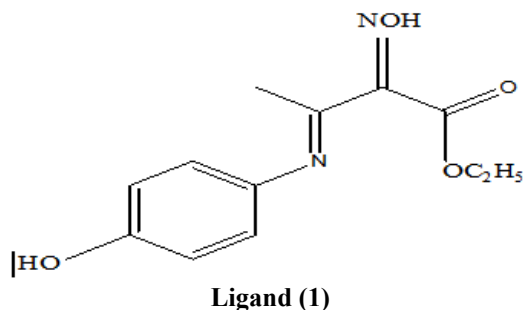
Antibacterial activity (In Vitro)

The ethoxy-oxime ligand and its metal complexes have been considered to exploring the antibacterial activities against two Gram-negative bacteria including *Escherichia coli* (RCMB 010052) and *Pseudomonas aeruginosa* (RCMB 010043) and two Gram-positive bacteria such as *Bacillus subtilis* (RCMB

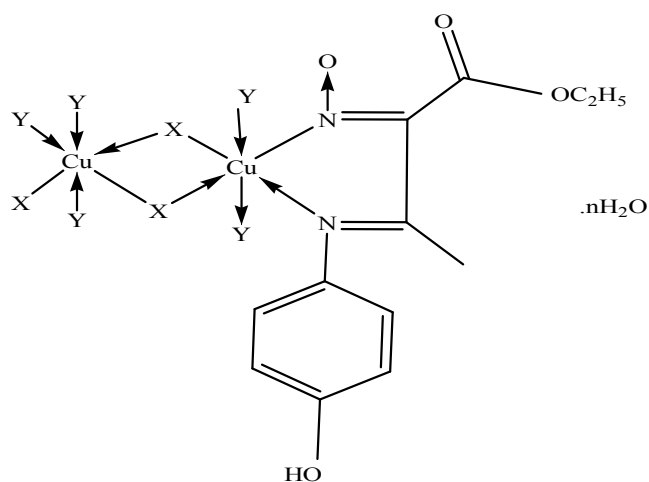
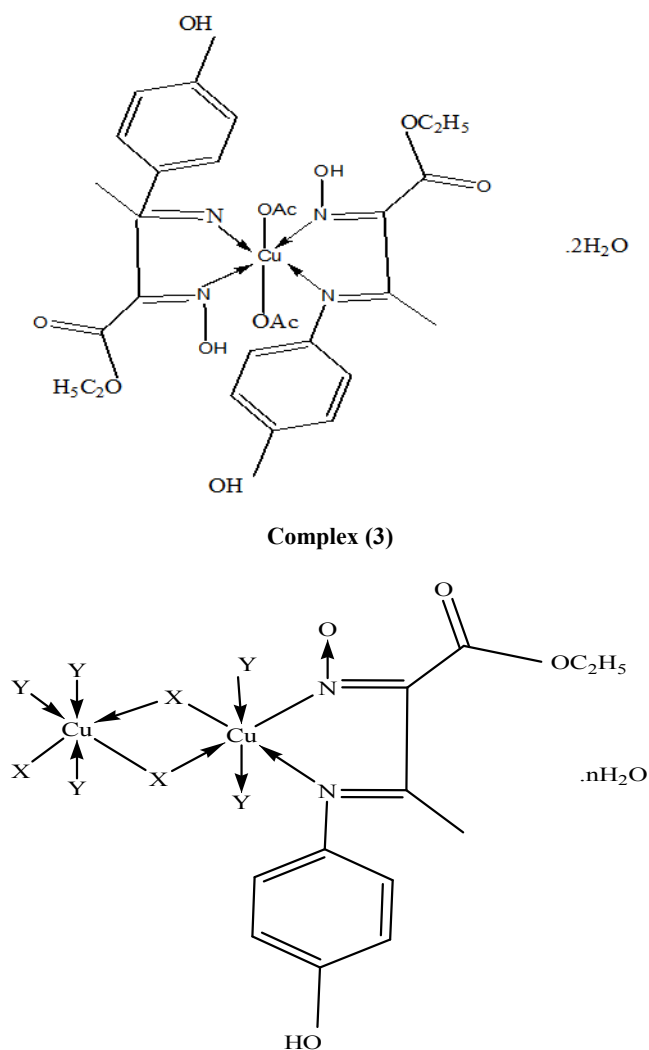
010067) and *Streptococcus pneumoniae* (RCMB 010010) by disc diffusion based on Muller-Hinton agar medium (Merck, Germany) (El-Tabl *et al.*, 2013). The sterile petri plates containing Muller Hinton agar medium are fertilized with 0.1 ml of the specific bacterium, which included nearly 0.5 x 10⁶ (CFU/ml) (equal to 0.5 McFarland standards) (Chohan, 2010). On the other hand, sterile disks (6 mm in diameter) have been soaked at samples with different concentrations (5, 2.5, 1.25 mg/disk in DMSO) and located on the agar plates. Entire plates were incubated at 37^o C for 24 hrs. After the sufficient time, inhibitory zone diameter (mm) of each complex was appeared measured and reported as the antibacterial activity. In accordance with some other reports in literature, DMSO exhibited no effect at the same biological environment (Chohan *et al.*, 2010 and Durai Anad *et al.*, 2008). Some commercial antibiotics such as *Gentamicin* and *Ampicillin* used as reference (positive controls).

Minimum inhibitory concentration

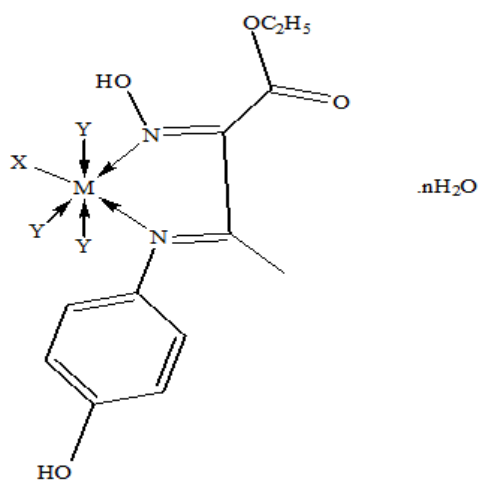
Beside the disk diffusion method, MIC has used as the next method to apprising antibacterial activities of our synthetic complexes. For this test, various concentrations of the complexes through serial dilution (1000 to 31.25 µg/ml) were prepared in sterile test tube and then 650 µl of sterile Muller-Hinton broth medium (Scharlab) and 100µl of the specific bacterium were added to them and finally entire ones incubated at 37^o C for 24 hrs. According to the observation of test tubes, the lowest concentration of each complex, which inhibited visible growth of bacteria, is reported as MIC of it¹⁵.



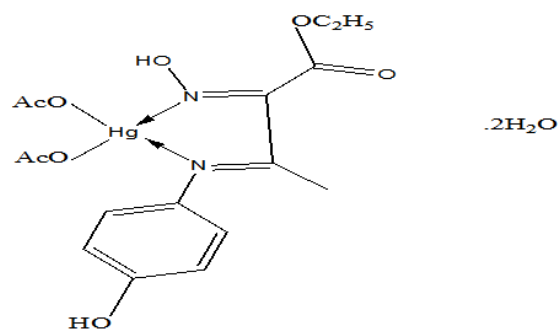
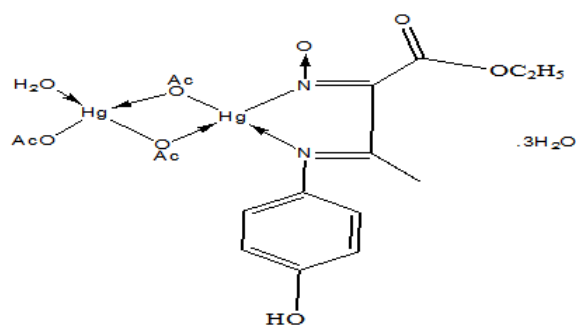
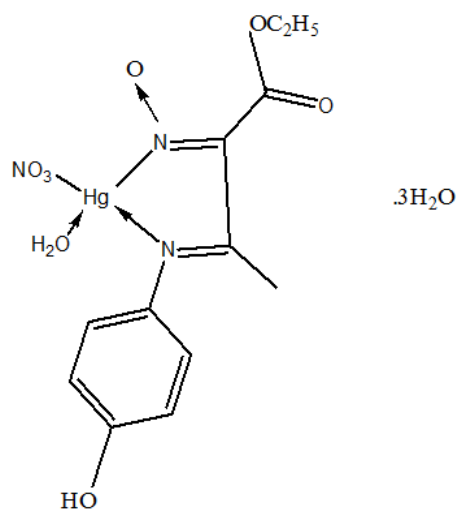
- M=Cu(II), X=OAc, Y=H₂O, n=2 (2)
 M=Ni(II), X=OAc, Y=H₂O, n=3 (6)
 M=Co(II), X=OAc, Y=H₂O, n=2 (9)
 M=Mn(II), X=OAc, Y=H₂O, n=1 (12)
 M=Zn(II), X=OAc, Y=H₂O, n=3 (15)
 M=Cd(II), X=OAc, Y=H₂O, n=2 (21)



- M=Cu(II), X=OAc, Y=H₂O, n=3 (4)
 M=Ni(II), X=OAc, Y=H₂O, n=3 (7)
 M=Co(II), X=OAc, Y=H₂O, n=3 (10)
 M=Mn(II), X=OAc, Y=H₂O, n=3 (13)
 M=Zn(II), X=OAc, Y=H₂O, n=3 (16)
 M=Cd(II), X=OAc, Y=H₂O, n=3 (22)



- M=Cu(II), X=SO₄, Y=H₂O, n=5 (5)
 M=Ni(II), X=SO₄, Y=H₂O, n=5 (8)
 M=Co(II), X=SO₄, Y=H₂O, n=2 (11)
 M=Mn(II), X=SO₄, Y=H₂O, n=5 (14)
 M=Zn(II), X=SO₄, Y=H₂O, n=5 (17)
 M=Cd(II), X=SO₄, Y=H₂O, n=2 (23)

**Complex (18)****Complex (19)****Complex (20)****Figure 1.**

RESULTS AND DISCUSSION

All the complexes are stable at room temperature, non hygroscopic, insoluble in water and partially soluble in common organic solvents such as CHCl₃, but soluble in DMF and DMSO. The analytical and physical data of the ligand and its complexes are given in Table-1, spectral data, Tables-2-5, are compatible with the proposed structures, Figure 1. The molar conductances are in the (22-11) ohm⁻¹cm²mol⁻¹ range, Table-1, indicating a non-electrolytic nature (Geary *et al.*, 1971). The high value for some complexes suggests partial dissociation in DMF. Many attempts were made to grow a single crystal but unfortunately, they were failed. Reaction of (1) with metal salts using (1L:1M), (1L:2M) and (2L:1M) molar ratios in ethanol gives complexes (2)-(23).

Table-1 Analytical and physical data of the ligand, (1), [HL] and its metal complexes

No.	Ligands/Complexes	Color	FW	M.P (°C)	Yield (%)	Anal./ Calc. (Found) (%)				
						C	H	N	M	Molar conductance Λ_m ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$)
(1)	[HL] $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}_4$	Brown	250	240	70	57.6 (57.0)	5.6 (5.32)	11.2 (11.11)	–	–
(2)	[L(Cu)(OAc)(H ₂ O) ₃].2H ₂ O $\text{C}_{14}\text{H}_{26}\text{N}_2\text{O}_{11}\text{Cu}$	Black	462	>300	80	39.43 (39.9)	5.6 (5.9)	6.06 (6.1)	13.74 (13.0)	9.1
(3)	[(HL) ₂ Cu(OAc)].2H ₂ O $\text{C}_{26}\text{H}_{39}\text{N}_5\text{O}_{14}\text{Cu}$	Black	708.5	>300	67	44.03 (44.3)	5.5 (5.1)	9.6 (9.9)	8.96 (8.5)	9.8
(4)	[L(Cu) ₂ (OAc) ₃ (H ₂ O) ₅].3H ₂ O $\text{C}_{18}\text{H}_{38}\text{N}_2\text{O}_{18}\text{Cu}_2$	Black	697	>300	84	30.98 (30.53)	5.45 (5.0)	4.01 (4.32)	18.22 (18.3)	11.2
(5)	[(HL)Cu(SO ₄)(H ₂ O) ₃].5H ₂ O $\text{C}_8\text{H}_{31}\text{N}_2\text{O}_{16}\text{SCu}$	Black	506.5	>300	69	18.95 (18.9)	6.12 (6.41)	5.52 (5.41)	12.53 (12.4)	13.5
(6)	[LNi(OAc)(H ₂ O) ₃].3H ₂ O $\text{C}_{14}\text{H}_{28}\text{N}_2\text{O}_{12}\text{Ni}$	Yellowish brown	474.6	>300	71	35.39 (35.49)	5.89 (5.81)	5.89 (5.52)	12.34 (12.41)	8.9
(7)	[L(Ni) ₂ (OAc) ₃ (H ₂ O) ₅].3H ₂ O $\text{C}_{18}\text{H}_{38}\text{N}_2\text{O}_{18}\text{Ni}_2$	Yellowish brown	687.2	>300	80	31.43 (31.52)	5.52 (5.41)	4.07 (4.23)	17.05 (17.33)	10.1
(8)	[(HL)(Ni)(SO ₄)(H ₂ O) ₃].5H ₂ O $\text{C}_8\text{H}_{31}\text{N}_2\text{O}_{16}\text{SNi}$	Yellowish brown	549.6	>300	72	17.46 (17.3)	5.64 (5.5)	5.09 (5.26)	10.66 (10.53)	11.5
(9)	[L(Co)(OAc)(H ₂ O) ₃].2H ₂ O $\text{C}_{14}\text{H}_{26}\text{N}_2\text{O}_{11}\text{Co}$	Brown	456.9	>300	68	36.76 (36.31)	5.6 (5.81)	6.1 (6.4)	12.89 (12.6)	10.3
(10)	[L(Co) ₂ (OAc) ₃ (H ₂ O) ₅].3H ₂ O $\text{C}_{18}\text{H}_{38}\text{N}_2\text{O}_{18}\text{Co}_2$	Pale brown	687.8	>300	65	31.4 (31.5)	5.52 (5.88)	4.07 (4.34)	17.12 (17.41)	9.72
(11)	[(HL)(Co)(SO ₄)(H ₂ O) ₃].2H ₂ O $\text{C}_{12}\text{H}_{24}\text{N}_2\text{O}_{13}\text{SCo}$	Yellowish brown	494.9	>300	65	29.9 (29.7)	4.84 (4.77)	5.6 (5.31)	11.9 (11.6)	11.3
(12)	[L(Mn)(OAc)(H ₂ O) ₃].H ₂ O $\text{C}_{14}\text{H}_{25}\text{N}_2\text{O}_{10}\text{Mn}$	Black	435.9	>300	89	38.54 (38.44)	5.73 (5.95)	6.4 (6.1)	12.59 (12.9)	9.6
(13)	[L(Mn) ₂ (OAc) ₃ (H ₂ O) ₅].3H ₂ O $\text{C}_{18}\text{H}_{38}\text{N}_2\text{O}_{18}\text{Mn}_2$	Black	679.8	>300	55	31.77 (31.5)	5.58 (5.4)	4.11 (4.22)	8.07 (8.1)	8.8
(14)	[(HL)(Mn)(SO ₄)(H ₂ O) ₃].5H ₂ O $\text{C}_8\text{H}_{31}\text{N}_2\text{O}_{16}\text{SMn}$	Black	497.9	>300	82	19.28 (19.22)	6.22 (6.3)	5.62 (5.51)	11.02 (11.15)	11.8
(15)	[L(Zn)(OAc)(H ₂ O) ₃].3H ₂ O $\text{C}_{14}\text{H}_{28}\text{N}_2\text{O}_{12}\text{Zn}$	Black	481.39	>300	74	34.89 (34.6)	5.81 (5.7)	5.81 (5.7)	13.58 (13.4)	7.8
(16)	[L(Zn) ₂ (OAc) ₃ (H ₂ O) ₅].3H ₂ O $\text{C}_{18}\text{H}_{38}\text{N}_2\text{O}_{18}\text{Zn}_2$	Black	700.78	>300	66	30.82 (30.23)	5.4 (5.8)	3.99 (3.23)	18.66 (18.82)	8.2
(17)	[(HL)(Zn)(SO ₄)(H ₂ O) ₃].5H ₂ O $\text{C}_8\text{H}_{31}\text{N}_2\text{O}_{16}\text{SZn}$	Black	508.39	>300	73	18.88 (18.87)	6.09 (6.41)	5.5 (5.1)	12.86 (12.2)	11.5
(18)	[(HL)(Hg)(OAc) ₂].2H ₂ O $\text{C}_{16}\text{H}_{24}\text{N}_2\text{O}_{10}\text{Hg}$	Black	604.59	>300	76	31.75 (31.1)	3.96 (3.52)	4.63 (4.1)	33.16 (33.8)	7.0

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(19)	[L(Hg) ₂ (OAc) ₃ (H ₂ O)].3H ₂ O C ₁₈ H ₃₀ N ₂ O ₁₄ Hg ₂	Black	899.18	>300	70	24.02 (24.32)	3.33 (3.11)	3.11 (3.2)	44.59 (44.2)	7.6
(20)	[L(Hg)(NO ₃)(H ₂ O)].3H ₂ O C ₁₂ H ₂₁ N ₄ O ₁₃ Hg	Black	629.59	>300	60	22.87 (22.42)	3.33 (3.48)	8.89 (9.1)	31.84 (31.72)	7.9
(21)	[L(Cd)(OAc)(H ₂ O) ₃].2H ₂ O C ₁₄ H ₂₆ N ₂ O ₁₁ Cd	Black	510.41	>300	56	32.91 (32.32)	5.09 (5.1)	5.48 (5.3)	22.02 (22.2)	7.6
(22)	[L(Cd) ₂ (OAc) ₃ (H ₂ O) ₅].3H ₂ O C ₁₈ H ₃₈ N ₂ O ₁₈ Cd ₂	Black	814.82	>300	77	26.5 (26.88)	4.66 (4.23)	3.43 (3.6)	27.58 (27.68)	8.1
(23)	[(HL)(Cd)(SO ₄)(H ₂ O) ₃].2H ₂ O C ₁₂ H ₂₄ N ₂ O ₁₃ SCd	Black	548.41	>300	76	26.25 (26.21)	4.37 (4.19)	5.1 (5.2)	20.49 (20.31)	10.7

Table 2. IR frequencies of the bands (cm⁻¹) of ligand [HL] and its metal complexes and their assignments

No.	((OH)/H ₂ O)	ν (H-bonding)	ν (OC ₂ H ₅)	ν (C=O)	ν (C=N)	ν (C=NO)	ν (Ar)	ν (NO)/NOH	ν (OAc)/SO ₄ /[NO ₃]	ν (M-O)	ν (M-N)	ν (M-Cl)
(1)	3455, 3400	3550-3220 3200-2585	3355	1687	1637	1605	1595, 851	1207, 1127, 1003, 938	-	-	-	-
(2)	3450 3395-3260 3250-3180	3600-3280 3270-2400	3260	1675	1622	1600	1580, 878	1195,1145, 1115, 1060 1060	(1500,1350)	621	562	-
(3)	3450-3385 3385-3350 3340-3160	3620-3350 3330-2650	3260	1675, 1665	1600, 1590	1598, 1590	1580, 835	1195, 1115, 1025, 996	(1472, 1345)	619	550	-
(4)	4445 3395-3310 3300-3190	3640-3280 3284-2850	3229	1665	1619	1596	1582, 850	1165,1110, 1025, 995	(1556,1470,1485,1385)	612	560	-
(5)	3450 3390-3335 3290-3165	3675-3215 3200-2860	3250	1665	1615	1595	1585, 850	1200, 1165, 1109, 1024, 985 955	1264, 1110, 1035, 649	616	515	-
(6)	3452 3385-3250 3245-3155	3640-3275 3270-2560	3255	1674	1616	1595	1583, 835	1189,1115, 1025, 950	(1510, 1385)	625	535	-
(7)	3450 3390-3310 3300-3160	3640-3280 3270-2870	3265, 3229	1675	1610	1594	1585, 830	1165,1107, 1023, 980	(1546, 1490, 1480, 1360)	630	585	-
(8)	3450 3380-3345 3285-3160	3670-3210 3190-2860	3265	1670	1615	1590	1590, 810	1201, 1160,1110, 1020, 950	1235, 1108, 1035, 649	640, 635	580	-
(9)	3552 33850-3310 3300-3140	3650-3240 3230-2740	3260	1665	1620	1595	1580, 835	1160,1120, 1025, 980 980	(1530, 1420)	610	560	-

Continue.....

(10)	3448 3390-3210 3200-3135	3640-3240 3210-2850	3245	1665	1615	1590	1580, 830	1165,1107, 1022, 980	(1572, 1465, 1483, 1382)	590	545	-
(11)	3450 3395-3340 3220-3150	3650-3210 3185-2770	3255	1665	1616	1592	1580, 840	1185,990, 1138, 1025, 975 975	1225, 1165, 1105, 690	630	535	-
(12)	3452 3560-3350 3330-3170	3680-3250 3240-2740	3245	1676	1615	1595	1585, 850	1203, 1180, 1120,1070, 980	(1530, 1370)	570	525	-
(13)	3450 3385-3315 3300-3176	3640-3280 3270-2860	3254	1676	1618	1595	1585, 835	1165,1107, 1021, 980	(1570,1482, 1445, 1350)	592	520	-
(14)	3452 3390-3335 3280-3165	3675-3215 3240-2866	3250	1670	1615	1590	1590, 830	1200, 1164,1105, 1024, 955	1225, 1105, 1035. 645	580	510	-
(15)	3447 3385-3250 3240-3160	3600-3240 3225-2575	3250	1665	1616	1590	1590, 840	1145, 1117, 1020, 975	(1460, 1335)	635	515	-
(16)	3450 3390-3200 3280-3112	3550-3290 3280-2760	3246	1675	1615	1595	1580, 850	1156, 1128, 1013, 980	(1576, 1453, 1472, 1372)	587	517	-
(17)	3448 3385-3330 3280-3170	3670-3210 3190-2860	3260	1670	1615	1596	1590, 830	1198, 1165,1108, 1023, 980	1210, 1133, 1035, 685	580	500	-
(18)	3450 3380-3335 3230-3160	3650-3164 3125-2640	3255	1665	1610	1590	1580, 850	1200, 1180, 1132, 1110, 1025 935	(1470, 1355)	565	505	-
(19)	3450 3380-3305 3300-3180	3650-3280 3260-2850	3256	1670	1615	1590	1580, 835	1165, 1130, 1104, 1021, 975	(1519, 1405, 1472,1381)	575	510	-
(20)	3450 3375-3310 3300-2150	3642-3220 3164-2600	3255	1675	1615	1592	1585, 848	1175, 1135, 1020, 1105, 980	[1364, 1285, 820]	575	520	-
(21)	3452 3385-3340 3330-3185	3650-3140 3130-2610	3250	1665	1618	1595	1590, 830	1180, 1110, 1025, 980	(1510, 1310)	580	515	
(22)	3450 3380-3300 3290-3160	3640-3280 3270-2850	3245	1676	1617	1595	1585, 840	1165, 1135, 1130, 1106, 1023	(1573, 1472, 1470, 1381)	580	505	
(23)	3450, 3390 3650-3330 3320-3180	3640-3200 3195-2640	3245	1670	1616	1590	1580, 840	1204, 1185, 1135, 1064, 995	1231, 1135, 1030, 610	560	510	

Table 3. The electronic absorption spectral bands (nm) and magnetic moments (B.M.) for the ligand [HL], (1) and its metal complexes

No.	λ_{\max} (nm)	μ_{eff} in B.M.	V_2/V_1
(1)	295 nm (log ϵ = 4.05), 315 nm (log ϵ = 4.16), 325 nm (log ϵ = 4.30)	-	-
(2)	290, 305, 315, 495, 585, 630	1.71	-
(3)	285, 300, 370, 485, 550, 615	1.6	-
(4)	295, 305, 365, 465, 560, 625	1.63	-
(5)	290, 303, 445, 550, 635	1.7	-
(6)	285, 302, 315, 490, 580, 610, 725	2.83	1.19
(7)	292, 305, 360, 485, 575, 620, 735	2.3	1.19
(8)	290, 300, 365, 475, 565, 615, 725	3.01	1.18
(9)	285, 305, 310, 485, 550, 630	4.65	-
(10)	290, 302, 365, 470, 580, 625	3.35	-
(11)	292, 305, 375, 480, 575, 620	4.72	-
(12)	295, 305, 310, 475, 570, 630	5.61	-

Table 4. ESR data for the metal(II) complexes

No.	g_{\parallel}	g_{\perp}	g_{iso}^a	A_{\parallel} (G)	A_{\perp} (G)	A_{iso}^b (G)	G^c	ΔE_{xy}	ΔE_{xz}	K_{\perp}^2	K_{\parallel}^2	K	K^2	$g_{\parallel}/A_{\parallel}$	α^2	β^2	β_1^2	-2 B	a_d^2 (%)
(2)	2.22	2.06	2.11	225	45	105	3.66	17094	20202	0.70	0.56	0.8	0.65	170.7	0.61	1.15	0.92	193.5	82.36
(3)	2.23	2.04	2.10	135	15	55	5.75	18181	20833	0.48	0.63	0.73	0.53	159.3	0.67	0.72	0.94	173	73.5
(4)	Broad	signal	in	the	low	and	high	region											
(5)	2.25	2.07	2.13	215	35	95	3.57	18181	20202	0.82	0.68	0.88	0.77	173.1	0.68	1.2	1.0	139.5	59.3
(9)			2.1																
(11)			2.13																
(12)			2.008																
(14)			2.01																

a) $g_{\text{iso}} = (2g_{\perp} + g_{\parallel})/3$, b) $A_{\text{iso}} = (2A_{\perp} + A_{\parallel})/3$, c) $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$

Table 5. Thermal data for the metal complexes

No.	Temp. (°C)	DTA (Peak)	TGA (wt. loss%)		Assignments
			Calc.	Found	
(4)	55	Endo	7.74	7.41	Loss of three hydrated water
	85	Endo	9.17	9.25	Loss of one terminal coordinated water
	185	Endo	12.32	12.47	Loss of four axial coordinated water
	245	Endo	11.52	11.58	Loss of one terminal coordinated acetate
	290	Endo	26.04	26.18	Loss of two bridged coordinated acetate
	370	Endo	-	-	Melting point
	470, 510, 620, 650	Exo	47.46	47.77	Decomposition with formation 2CuO
(5)	60	Endo	17.76	17.5	Loss of five hydrated water
	85	Endo	4.32	4.4	Loss of one terminal coordinated water
	180	Endo	9.03	9.1	Loss of two axial coordinated water
	310	Endo	26.48	26.52	Loss of one terminal coordinated sulphate
	360	-	-	-	Melting point
450, 520, 630, 670	Exo	29.83	29.79	Decomposition with formation of CuO	
(7)	64	Endo	7.85	7.7	Loss of three hydrated water
	120	Endo	2.84	2.71	Loss of one terminal coordinated water
	150	Endo	11.7	11.6	Loss of four of axial coordinated water
	275	Endo	10.86	10.81	Loss of one terminal coordinated acetate
	330	Endo	24.37	24.31	Loss of two bridged coordinated acetate
	380	-	-	-	Melting point
	420, 560, 620	Exo	40.74	40.6	Decomposition with formation of 2 NiO

complex	<i>Escherichia coli</i> (RCMB 010052)	<i>Pseudomonas aeruginosa</i> (RCMB 010043)	<i>Streptococcus pneumoniae</i> (RCMB 010010)	<i>Bacillus subtilis</i> (RCMB 010067)
standard	19.9	17.3	23.8	32.4
Ligand	9	9.2	7.2	7.2
Complex (2)	23.5	22.1	18.3	18.7
Complex (6)	10.3	12.3	11.2	11.6
Complex(9)	9.8	11.5	9.3	9.2
Complex (12)	21.2	19.5	22.8	20.3
complex (15)	18.4	15.4	14.2	15.6
complex (18)	19.7	16.5	12.9	15.8
complex (21)	8.2	10.3	8.9	13.2
DMSO	0	0	0	0

The composition of the complexes formed depends on metal salts, the medium of the reaction and the molar ratios.

¹H-NMR spectra

The ¹H-NMR spectra of the ligand and its Zn(II) complex (15) in deuterated DMSO show signals consistent with the proposed structure, Figure 1. Ligand shows singlet peak at 10.54 ppm, assigned to proton of OH group (El-Tabl *et al.*, 2007 and Kantekin *et al.*, 2004 and Plass *et al.*, 2009). The signal of oxime group is observed at 9.6 ppm as singlet peak (Plass *et al.*, 2009; Gup *et al.*, 2009 and Gup *et al.*, 2005). The lower the value, may be due to hydrogen bonding of the oxime group. Resonances appeared at 3.7, 3.1 and 2.88 ppm are due to methyl (singlet) protons attach to imino group, ethoxy group (tetraplet) and methyl (triplet) ¹⁷, ¹⁹, ²². Also, the spectrum showed a set of peaks as multiples at 6.65-8.33 ppm range which are assigned to the protons of aromatic ring (El-Tabl *et al.*, 2010). However, for complex (15), the signal due to the oxime proton is disappeared, indicating coordination to the Zn(II) ion. The singlet observed at 10.41 ppm is assigned to OH proton (El-Tabl *et al.*, 2010). Ethoxy and methyl protons appear at 3.0 and 2.8 ppm (El-Tabl *et al.*, 2010). A set of peaks appeared as multiples at 6.25-8.28 ppm range are corresponding to protons of aromatic ring (El-Tabl *et al.*, 2010). The appearance of new signal at 1.88 ppm is due to protons of coordinated acetate group as singlet peak (Baligar *et al.*, 2006 and El-Tabl *et al.*, 2009).

Mass spectra

The mass spectra of the ligand and its Zn(II) complex (15) confirmed their proposed formulations. The spectrum of ligand reveals the molecular ion peaks (m/z) at 250 amu consistent with the molecular weight of the ligand (250). Furthermore, the fragments observed at m/z = 45, 73, 116, 143, 157 and 233 amu correspond to C₂H₅O, C₃H₅O₂, C₄H₆NO₃, C₆H₉NO₃, C₆H₉N₂O₃ and C₁₂H₁₃N₂O₃ moieties respectively. However, the Zn(II) complex (15) shows peak (m/z) at 428.4 amu. Additionally, the peaks observed at 73, 113, 157, 222.4, 258.4, 335.4 and 411.4 are due to C₃H₅O₂, C₆H₆O₂, C₆H₆N₂O₃, C₆H₉N₂O₃Zn, C₆H₁₃N₂O₅Zn, C₈H₁₈N₂O₈Zn and C₁₄H₂₂N₂O₈Zn moieties respectively.

IR spectra

The IR spectra of the ligand and its complexes (2)-(23) are given in Table-2. The spectrum of (1) showed ν(OH) band of the phenolic and oxime groups at 3455 and 3400 cm⁻¹, the appearance of two broad bands in the 3350-3220 and 3200-2585 cm⁻¹ ranges, commensurate the presence of two types of intra-and intermolecular hydrogen-bonded phenolic and oxime

groups (El-Tabl *et al.*, 1997 and Dongli *et al.*, 1994). Thus, the higher frequency band is associated with a weaker hydrogen bond and the lower frequency band with a strong hydrogen bond. Also, the spectrum shows bands at 1687, 1637 and 1605 cm⁻¹, assigned to ν(C=O), ν(C=N)_{imine} and ν(C=N)_{oxime} respectively (Tas *et al.*, 2005; Tas *et al.*, 1999 and El-Behry *et al.*, 2007). Medium bands at 1207, 1127, 1003 and 938 cm⁻¹ are assigned to ν(NO) vibration (Tas *et al.*, 2008; Plass *et al.*, 2009; Brezina *et al.*, 1996). P-substituted aromatic ring appears at 1595 and 851 cm⁻¹ (Nakatamato *et al.*, 1967). The IR spectra of the complexes show, the ν(C=N)_{imine} stretching frequency undergoes a shift to lower frequency by 38-15 cm⁻¹. This is indicative of nitrogen coordination of the azomethine to the metal ion (El-Tabl *et al.*, 2002 and Mahapatra *et al.*, 1997). The ν(C=O) of amide group appears in the 1676-1665 cm⁻¹, range. This vibration is located in the region of non-coordinated carbonyl group attached to a five-membered chelate ring (El-Tabl *et al.*, 2002 and El-Tabl *et al.*, 1993). The ν(OC₂H₅) appears in the 3265-3229 cm⁻¹ range (El-Tabl *et al.*, 2007 and Pouralimardan *et al.*, 2007).

The bands observed in the 1600-1590 and 1595-1580 and 878-810 cm⁻¹ ranges are due to ν(C=N)_{oxime} and aromatic groups (El-Tabl *et al.*, 1997; Nakatamato *et al.*, 1967 and El-Tabl *et al.*, 2002). The complexes show strong bands in the 1195-1145 range, indicating N-coordination of the oximato group (El-Tabl *et al.*, 1997; El-Tabl *et al.*, 2002 and Aly *et al.*, 1985). Complexes (3), (5), (8), (11), (14), (17), (18) and (23) show band in the 1204-1198 range Table (2) corresponding to ν(NOH) (El-Tabl *et al.*, 2002 and 1997). However, complexes (2), (4), (5), (6), (7), (8), (9), (10), (11), (12), (13), (14), (15), (16), (17), (18), (19), (20), (21) and (22) show medium band in the 3452-3447 cm⁻¹ range is due to ν(OH) group (El-Tabl *et al.*, 1997 Nakatamato, 1967). Complexes show broad bands in the 3680-3125 and 3350-2400 cm⁻¹, ranges, corresponding to intra-and intermolecular hydrogen bondings (El-Tabl *et al.*, 1997 and El-Tabl *et al.*, 1994), however, the hydrated and coordinated water molecules appear in the 3395-3200 and 3350-3100 cm⁻¹ ranges (El-Tabl *et al.*, 2007; El-Tabl *et al.*, 2003 and Hegazy *et al.*, 2001). Extensive IR spectral studies reported on metal acetate complexes (El-Tabl, 2002) indicate that, the acetate ligand coordinates in either a monodentate, bidentate or bridging manner.

In monodentate, the coordination of ν(C=O) is observed at higher energy than ν_a(CO₂) and ν_s(C-O) is appeared at lower than ν_s(CO₂). As a result, the separation between (CO) bands is much larger in monodentate complexes. In complexes (2), (3), (4), (6), (7), (9), (10), (12), (13), (15), (16), (18), (19) and (22), the band is due to ν_a(CO₂) appears in the 1530-1460 cm⁻¹ and the ν_s(CO₂) observed in the 1420-1310 cm⁻¹ ranges. The difference between these two bands is in the 110-150 cm⁻¹

range, suggesting that, the acetate group coordinates in unidentate manner with the metal ion (Nakatamoto *et al.*, 1967; El-Tabl, 2002 and Fouda *et al.*, 2008). However, bridging acetate with both oxygen atoms coordinated have $\nu(\text{CO})$ bands close to the free ion values^{33, 42, 43} as found for complexes (4), (7), (10), (13), (16) and (22), $\nu_a(\text{CO}_2) = 1556, 1546, 1572, 1570, 1576$ and 1573 cm^{-1} respectively and $\nu_s(\text{CO}_2) = 1485, 1480, 1483, 1445, 1453$ and 1470 cm^{-1} respectively. Complexes (5), (8), (11), (14), (17) and (23) show bands at 1264-1210, 1135-1105 and 690-610 cm^{-1} ranges respectively are corresponding to monodentate coordinate sulphate group (Kuska *et al.*, 1971). Complex (20) showed bands in the 1364, 1285 and 820 cm^{-1} , assigned to coordinated nitrate group (El-Tabl *et al.*, 2004 and Nakamoto *et al.*, 1977).

Magnetic moments

The magnetic moments of the complexes (2)-(23) are shown in Table-3. Copper(II) complexes (2)-(5) show values 1.63-1.71 B.M range, corresponding to one unpaired electron in an octahedral structure (El-Tabl *et al.*, 2004 and El-Tabl *et al.*, 2002), complex (3) shows value 1.68 B.M. which is well below the spin only value (1.73 B.M), indicating that, spin-exchange interactions takeplace between the copper(II) ions through hydrogen bondings in an octahedral geometry (Gudasi *et al.*, 2006). Nickel(II) complexes (6)-(8) show value 2.83-3.01 B.M., indicating an octahedral geometry around Ni(II) ion (Motaleb *et al.*, 1997).

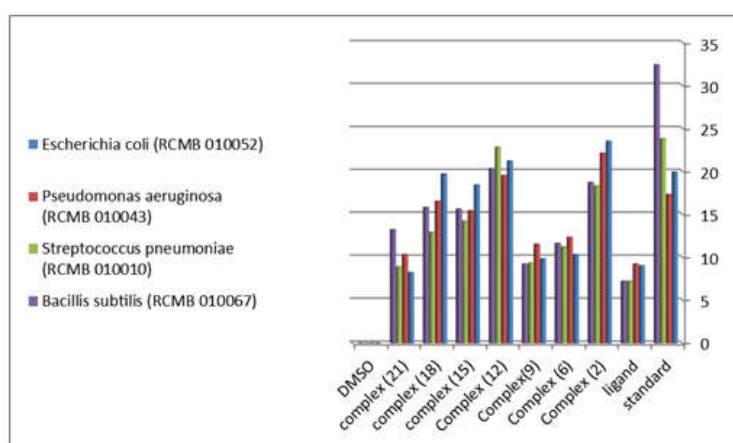


Figure 2. Antibacterial screening disc diffusion assay of ligand and metal complexes (2), (6), (9), (12), (15), (18) and (21) using (5 mg/ml)

complex	<i>Escherichia coli</i> (RCMB 010052)	<i>Pseudomonas aeruginosa</i> (RCMB 010043)	<i>Streptococcus pneumoniae</i> (RCMB 010010)	<i>Bacillus subtilis</i> (RCMB 010067)
standard	19.9	17.3	23.8	32.4
Ligand	9	9.2	7.2	7.2
Complex (2)	23.5	22.1	18.3	18.7
Complex (6)	10.3	12.3	11.2	11.6
Complex(9)	9.8	11.5	9.3	9.2
Complex (12)	21.2	19.5	22.8	20.3
complex (15)	18.4	15.4	14.2	15.6
complex (18)	19.7	16.5	12.9	15.8
complex (21)	8.2	10.3	8.9	13.2
DMSO	0	0	0	0

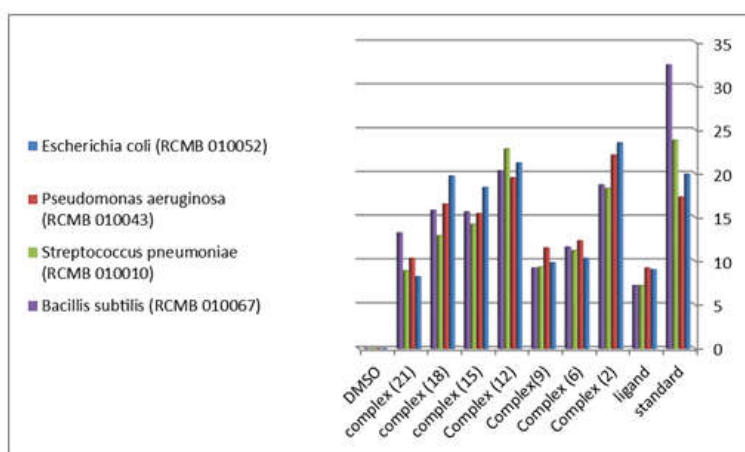


Figure 2. Antibacterial screening disc diffusion assay of ligand and metal complexes (2), (6), (9), (12), (15), (18) and (21) using (5 mg/ml)

Cobalt(II) complexes (9)-(11) show 4.45-4.72 B.M. range, indicating high spin octahedral cobalt(II) complexes (El-Tabl *et al.*, 1993 and Al-Hakimi *et al.*, 2011). Manganese(II) complexes (12)-(14) show 5.61-5.78 B.M. range, suggesting high spin octahedral geometry around the Mn(II) ion (El-Tabl *et al.*, 1993 and Al-Hakimi *et al.*, 2011). Zinc(II), complexes (15)-(17), mercury(II) complexes (18)-(20) and cadmium(II) complexes (21)-(23) show diamagnetic property (El-Tabl *et al.*, 1997).

Electronic spectra

The electronic spectral data for the ligand and its complexes in DMSO solution are summarized in Table-3. Ligand in DMSO solution shows three bands at 325 nm ($\log\epsilon=4.3$), 315 nm ($\log\epsilon=4.16$) and 295 nm ($\log\epsilon=4.05$), which may be assigned to the $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions respectively (Gudasi *et al.*, 2006). Copper(II) complexes (2)-(5) show bands in the 285-295 and 300-315 nm ranges, these bands are due to intraligand transitions, however, the bands appear in the 445-495, 550-585 and 615-635 nm ranges are assigned to $O\rightarrow Cu$ charge transfer, ${}^2B_1\rightarrow{}^2E$ and ${}^2B_1\rightarrow{}^2B_2$ transitions, indicating a distorted tetragonal octahedral structure (El-Tabl *et al.*, 2004; Ainscough *et al.*, 1998 and Sallam *et al.*, 2002). Nickel(II) complexes (6)-(8) show bands 285-290, 302-305, 315-365, 475-490, 565-580, 610-620 and 725-735 nm ranges respectively, the first three bands are within the ligand and the other three bands are attributable to ${}^3A_{2g}(F)\rightarrow{}^3T_{1g}(P)(\nu_3)$, ${}^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)(\nu_2)$ and ${}^3A_{2g}(F)\rightarrow{}^3T_{2g}(F)(\nu_1)$ transitions respectively, indicating an octahedral Ni(II) complex^{52, 55}. The ν_2/ν_1 ratio for the nickel(II) complex (6)-(8) is 1.18-1.19 range, which is less than the usual range of 1.5-1.75, indicating a distorted octahedral Ni(II) complex (El-Tabl *et al.*, 2004 and Chinvmia *et al.*, 1995).

Cobalt(II) complexes (9)-(11) show bands at 285-292, 302-305, 310-375, 470-485, 550-580 and 620-630 nm ranges, the first three bands are within the ligand and the other bands are assigned to ${}^4T_{1g}(F)\rightarrow{}^4A_{2g}$ and ${}^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)$ transitions respectively, corresponding to high spin Co(II) octahedral complexes⁵⁸. Manganese(II) complexes (12)-(14) show bands at 293-295, 302-305, 310-370, 475-480, 570-580 and 625-630 nm ranges, respectively, the first three bands are within the ligand, however, the other bands are corresponding to ${}^6A_{1g}\rightarrow{}^4E_g$, ${}^6A_{1g}\rightarrow{}^4T_{2g}$ and ${}^6A_{1g}\rightarrow{}^4T_{1g}$ transitions which are compatible to an octahedral geometry around the Mn(II) ion (Parihari *et al.*, 2000). Zinc(II) complexes (15)-(17), mercury(II) complexes (18)-(20) and cadmium(II) complexes (21)-(23) show three bands in the 290-295, 305-315 and 375-385 nm ranges, which are assigned to intraligand transitions.

Electron spin resonance (ESR)

The ESR spectral data for complexes (2), (3), (4), (5), (9), (11), (12) and (14) are presented in Table-4. The spectra of copper(II) complexes (2), (3), (4) and (5) are characteristic of species, d^9 configuration and having axial type of a $d_{(x^2-y^2)}$ ground state which is the most common for copper(II) complexes (El-Tabl *et al.*, 2002 and El-Tabl *et al.*, 2011). The complexes show $g_{\parallel} > g_{\perp} > 2.0023$, indicating octahedral geometry around copper(II) ion^{61, 62}. The g-values are related by the expression^{45, 61}, $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$, if $G > 4.0$, then, local tetragonal axes are aligned parallel or only slightly misaligned, if $G < 4.0$, the significant exchange coupling is present. Complexes (2), (3) and (5) show values 3.66, 5.75 and 3.57 indicating spin-exchange interactions takeplace between copper(II) ions through (2) or (3) or (5).

Complex	<i>Escherichia coli</i> (RCMB 010052)	<i>Pseudomonas aeruginosa</i> (RCMB 010043)	<i>Streptococcus pneumoniae</i> (RCMB 010010)	<i>Bacillus subtilis</i> (RCMB 010067)
Standard	19.9	17.3	23.8	32.4
Ligand	8.2	8.5	6.3	6.1
Complex (2)	22.8	21.5	17.2	17.8
Complex (6)	9.4	11.4	10.3	10.3
Complex(9)	8.5	10.1	8.4	8.7
Complex (12)	20.9	18.8	21.2	19.6
complex (15)	17.2	14.3	13.8	14.1
complex (18)	18.3	15.3	11.5	14.7
complex (21)	6.9	9.4	7.3	12.1
DMSO	0	0	0	0

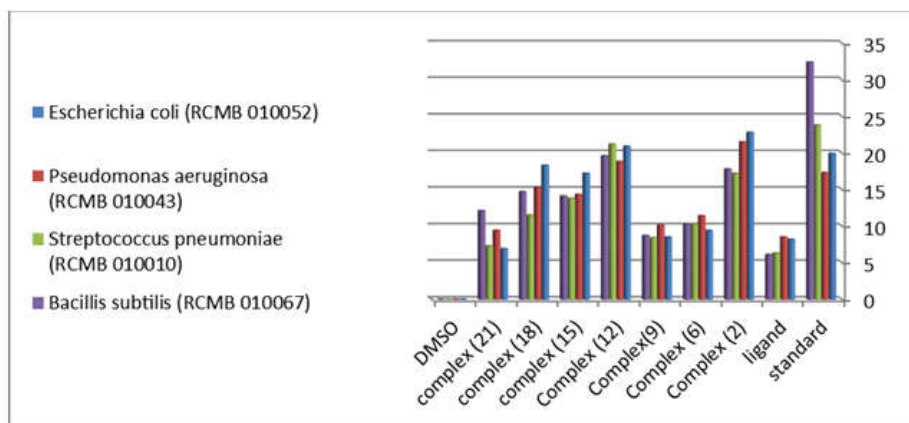


Figure 3. Antibacterial screening disc diffusion assay of ligand and metal complexes (2), (6), (9), (12), (15), (18) and (21) using (2.5 mg/ml)

This phenomenon is further confirmed by magnetic moments (1.71, 1.68 and 1.7 B.M. respectively). K Table-4, for the copper(II) complexes (2), (3) and (5), indicating covalent bond character (Ray *et al.*, 1990 and El-Tabl *et al.*, 2004). The g-values reported here Table (4) show considerable covalent bond character (Gudasi *et al.*, 2006; Procter, 1965). Also, the in-plane σ - covalency parameter, $\alpha^2(\text{Cu})$, Table-4, suggests a covalent bonding (Kuska *et al.*, 1971 and El-Tabl *et al.*, 2004). The complexes show β_1^2 values 0.92, 0.94 and 1.0 indicating a covalency in the in-plane π - bonding (Motaleb *et al.*, 1997; El-Boraey *et al.*, 2003 El-Tabl *et al.*, 2004). While β^2 for complexes (2), (3) and (5) are 1.15, 0.72 and 1.2 respectively, indicating covalent bonding character out of-plane π - bonding. The calculated orbital populations (a^2_d) for the copper(II) complexes (2), (3) and (5), Table 4, indicate a $d_{x^2-y^2}$ ground state (Al-Hakimi *et al.*, 2011; El-Tabl *et al.*, 2002). Co(II) complexes (9) and (11), Mn(II) complexes (12), (14) show g_{iso} values 2.10, 2.13, 2.008 and 2.01 respectively.

Thermal analyses (DTA and TGA)

The thermal curves in the temperature 27-800 °C range for metal complexes Cu(II) complexes (4), (5) and Ni(II) complex (7) indicate that the metal complexes are thermally stable up to 50 °C. The weight loss recorded in the 60-80 °C range is due to elimination of hydrated water (El-Tabl *et al.*, 1997 and Gaber *et al.*, 1991). Cu(II) complex (4) showed an endothermic peak at 55 °C, with 7.41% weight loss (Calc. 7.74%) corresponding to loss of three hydrated water. Another endothermic peak was observed at 85 °C, with 9.25% weight loss (Calc. 9.17%) corresponding to loss of one terminal coordinated water. Endothermic peak was observed at 185 °C with 12.47% weight loss (Calc. 12.32%) corresponding to loss of four axial coordinated water molecules.

Endothermic peak was observed at 245 °C with 11.58% weight loss (Calc. 11.52%) corresponding to loss of one terminal coordinated acetate group. An endothermic peak was observed at 290 °C with 26.18% weight loss (Calc. 26.04%) which is assigned to loss of two bridged coordinated acetate group. The endothermic peak observed at 370 °C is assigned to its melting point. Finally, the complex showed exothermic peaks at 470, 510, 620 and 650 °C, with weight loss 47.77% (Calc. 47.46%), corresponding to thermal decomposition with formation of two CuO molecules (El-Tabl *et al.*, 1997). Cu(II) complex (5) showed an endothermic peak at 60 °C, with 17.5% weight loss (Calc. 17.76%) corresponding to the loss of five hydrated water. The endothermic peak observed at 85 °C, with 4.4% weight loss (Calc. 4.32%) is assigned to loss of one terminal coordinated water molecule. Another endothermic peak was observed at 180 °C, with 9.1% weight loss (Calc. 9.03%) which is assigned to loss of two axial coordinated water molecules. The endothermic peak observed at 310 °C, with 26.52% weight loss (Calc. 26.48%) is assigned to loss of one terminal coordinated sulphate. The endothermic peak observed at 360 °C, is corresponding to melting point. Finally, the complex showed multiple exothermic peaks at 450, 520, 630 and 670 °C, 29.79% with weight loss (Calc. 29.83%), corresponding to thermal decomposition with formation of one CuO. Ni(II) complex (7) showed an endothermic peak at 64 °C, with 7.7% weight loss (Calc. 7.85%) corresponding to the loss of three hydrated water molecules.

Another endothermic peak observed at 120 °C, with 2.71% weight loss (Calc. 2.84%) due loss of one terminal coordinated water molecule. Another endothermic peak was observed at 150 °C, with 11.6% weight loss (Calc. 11.7%) which is assigned to loss of four axial coordinated water molecules.

Complex	<i>Escherichia coli</i> (RCMB 010052)	<i>Pseudomonas aeruginosa</i> (RCMB 010043)	<i>Streptococcus pneumoniae</i> (RCMB 010010)	<i>Bacillus subtilis</i> (RCMB 010067)
Standard	19.9	17.3	23.8	32.4
Ligand	6.2	7.8	5.1	5.3
Complex (2)	21.7	20.7	16.5	16.7
Complex (6)	8.1	10.1	9.8	9.9
Complex(9)	7.8	9.3	7.5	7.2
Complex (12)	20.2	18.1	20.5	18.4
complex (15)	15.8	13.5	12.2	12.9
complex (18)	17.7	14.2	10.3	13.2
complex (21)	5.3	8.1	6.5	10.9
DMSO	0	0	0	0

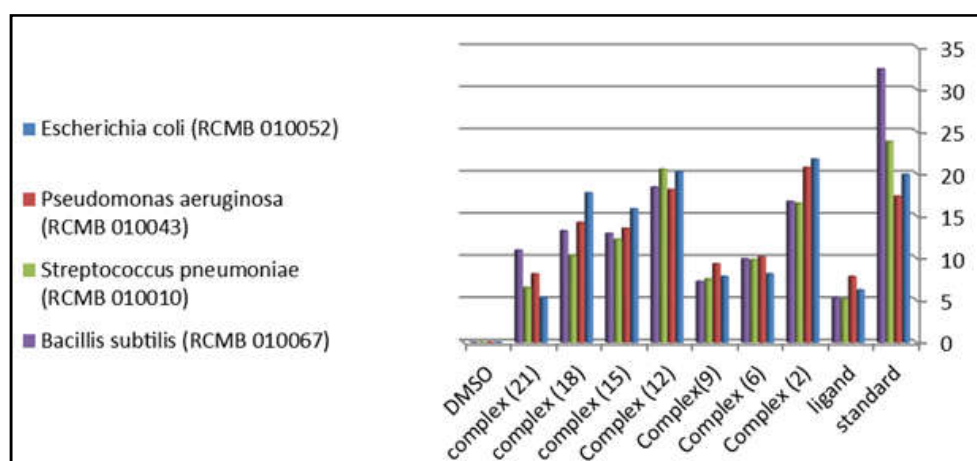


Figure 4 Antibacterial screening disc diffusion assay of ligand and metal complexes (2), (6), (9), (12), (15), (18) and (21) using (1.25 mg/ml)

Complex	Escherichia coli (RCMB 010052)	Pseudomonas aeruginosa (RCMB 010043)	Streptococcus pneumoniae (RCMB 010010)	Bacillis subtilis (RCMB 010067)
Ligand	N.D	N.D	1000	125
Complex (2)	62.5	31.25	125	62.5
Complex (6)	N.D	500	250	62.5
Complex(9)	500	125	250	125
Complex (12)	31.25	62.5	62.5	125
complex (15)	N.D	N.D	500	500
complex (18)	500	N.D	125	N.D
complex (21)	N.D	500	500	N.D

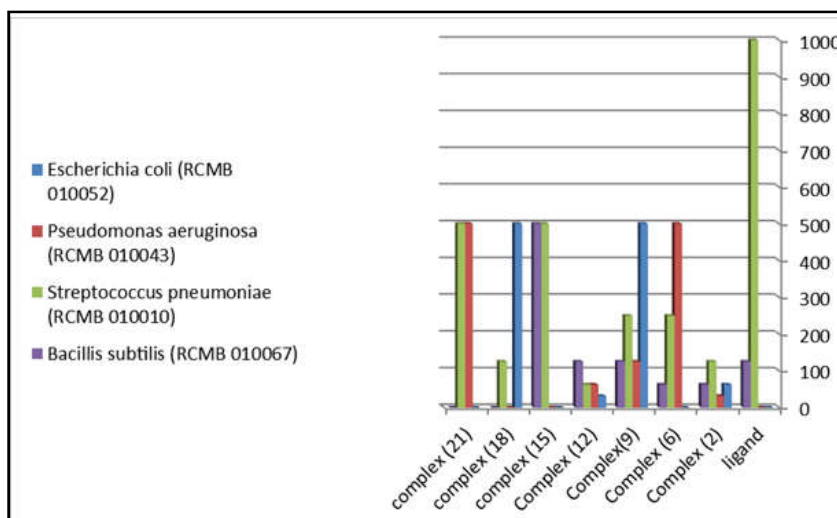


Figure 5. MIC of ligand and its metal complexes (2), (6), (9), (12), (15), (18) and (21) for inhibition of the growth (µg/ml)

Another endothermic peak observed at 275 °C, with 10.81% weight loss (Calc. 10.86%) corresponding to loss of one terminal coordinated acetate group. An endothermic peak was observed at 330 °C with 24.31% weight loss (Calc. 24.37%) corresponding to loss of two bridged coordinated acetate groups. The endothermic peak observed at 380 °C, is corresponding to the melting point. Finally, the complex shows multiple exothermic peaks at 420, 560 and 620 °C, 40.6% with weight loss (Calc. 40.74%), corresponding to thermal decomposition with formation of two NiO⁶⁸. The thermal data are presented in Table 5.

Antibacterial bioassay (In Vitro)

Offering novel and wide application by oxime in various field conducted us for testing the antibacterial activities of the oxime ligand and its metal complexes. Exams reply acceptable in vitro activities against specified bacteria that includes two Gram-negative bacteria including *Escherichia coli* and *Pseudomonas aeruginosa* and two Gram-positive bacteria such as *Bacillus subtilis* and *Streptococcus pneumoniae*. A comparison between oxime ligand and its metal complexes with standard antibiotics (*Gentamicin* and *Ampicillin*) in the same condition confirmed the capability of our complexes but standard antibiotics were more effective than the ligand and its metal complexes against entire bacterial strains except *Escherichia coli* and *Pseudomonas aeruginosa*, for which antibiotics had no growth inhibitory effect. According to obtained results of disk diffusion method, the ligand was found as the complex with the lowest activity. Cu(II) complex (2) and Mn(II) complex (12) were the effective complexes against *Escherichia coli* with 21.7 mm and 20.2 mm inhibitory diameter of zone respectively.

Effective complexes in other cases were complex (2) and (12) with value of 20.7 mm and 18.1 mm against *Pseudomonas aeruginosa*. Based on the zone of inhibition of the growth it seems that the complexes are more smoothly effective against Gram-negative than Gram-positive bacterial strains, this perhaps due to the change in structure as a result of coordination, as chelating tends to make metal complexes act as more powerful and potent bacteriostatic agent, thus, inhibiting the growth of the microorganisms (Chohan *et al.*, 2006 and 2003).

MIC as alternative method in this work reported in µg/ml. Because of turbidity and or intense color of complexes solutions MIC was tested for antibacterial investigations. The minimum of MIC value against *Escherichia coli* was related to complex (12) (31.25 µg/ml) and in the case of *Pseudomonas aeruginosa*, complex (2) had minimum value equal (31.25 µg/ml) as shown in Figures 2-5.

Conclusion

Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes of ethoxy-oxime ligand have been prepared and spectrally characterized. The IR data show that, the ligand behaves as monobasic bidentate or neutral bidentate. Molar conductances in DMSO indicate that, the complexes are non-electrolytes. ESR spectra of solid Cu(II) complexes at room temperature show axial type ($d_{x^2-y^2}$) with covalent bond character in an octahedral environment. Antibacterial investigation demonstrated that, these complexes have antibacterial activities and in all observations, the ligand exhibited weak antibacterial activities in compared to its metal complexes.

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