Synthesis and Antibacterial Investigation of Mn(II) and Co(II) Complexes of Schiffs Base Ligand

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Complexes of chlorides and acetates of Mn(II) and Co(II) with ligand, 3-[mercapto-[1,3,4]thiadiazol-2-ylimino)-methyl]-benzene-1,2-diol has been synthesized and characterized. The metal complexes so formed were characterized by molar conductance, elemental analysis, mass, EPR, IR and electronic spectral studies. Geometry of the ligand and its metal complexes was optimized by (B3LYP) functional with 6-31G (d,p) basis sets method of the Gaussian 09 W. All the metal complexes were found to be non-electrolytes. Metal complexes are represented as $[M(L)_2X_2]$ [where L = Schiffs base ligand, M = Mn(II), Co(II) and X = Cl$^-$, CH$_3$COO$^-$]. Octahedral geometry for Mn(II) and Co(II) complexes was determined by means of spectral studies and molecular modelling. Ligand and its metal complexes were screened against three bacteria- *P. aeruginosa, S. pyogens* and *B. subtilis* using well diffusion method. Complexes are found to be more potent as compare to the ligand.

Keywords: Metal complexes, Spectral studies, Antibacterial screening, Molecular modelling.
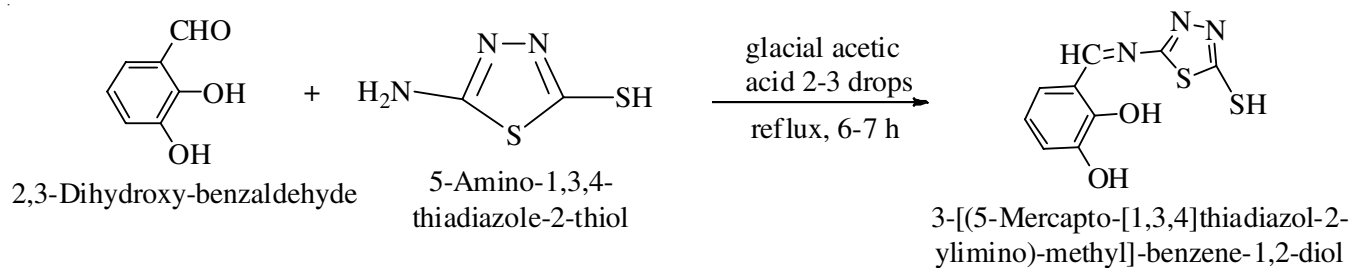
INTRODUCTION

The metal complexes of transition element derived from Schiffs base ligand widely studied as they are easily prepared, available, low cost materials, have tendency of complexation [1]. The Schiffs base compounds contains the >C=N– linkage which is generally formed by condensation reaction between amine and ketone or aldehyde [2]. From last decades, various applications like antifungal, anticancer, antioxidant, antiviral, antimalarial, anti-inflammotry and antibacterial activities were reported [3]. Schiffs bases generally used as the ligands, have strong tendency to coordinate with the main group metals and transition metals [4]. Metal complexes of Schiffs base stimulated a vigorous interest for the contributions as material [5-9], as they have various applications in the fundamental and the applied sciences [10-12] widely in coordination chemistry [13,14]. Synthesis of new ligand which have different properties and the novel reactivity was perhaps the most important step as the ligands have electron donor and electron acceptor properties, different structural functional groups [15]. Position of ligand in coordination sphere is a major factor of the different studies [16]. Complexes of the multi-donor ligands widely used as they are biological active substances [17]. Thiadiazole derivatives

as ligands are widely used for complexation as they provide many potential binding sites [18]. 5-Amino-1,3,4-thiadiazole-2-thiol has been claimed for having biological properties likewise antituberculosis, anti-inflammotry, antiviral, antioxidant, anticancer [19], antimicrobial [20]. Here we present the synthesis, characterization, examination of biological activity of the ligand and its transition metal complexes of Mn(II) and Co(II). General composition is represented as $[ML_2X_2]$, where X= Cl$^-$, CH$_3$COO$^-$.

EXPERIMENTAL

All the chemicals were used as supplied and were of Anala R grade. 2,3-Dihydroxy benzaldehyde and 5-amino-1,3,4-thiadiazole-2-thiol purchased from Sigma-Aldrich and Alfa Aser. Metal salts and solvents were purchased from E. Merck.

Synthesis of ligand: First of all (0.001 mol, 0.138 g) of 2,3-dihydroxybenzaldehyde was added to about 20-25 mL ethanol and warm until a clear solution is obtained. This solution was added to hot ethanolic solution of 5-amino-1,3,4-thiadiazole-2-thiol (0.001 mol, 0.133 g). This mixture was refluxed for about 8-9 h at 70-75 °C. The reaction was adjusted at 3-4 pH by adding 1-2 drops of glacial acetic acid. A light yellow

2,3-Dihydroxy-benzaldehyde   5-Amino-1,3,4-thiadiazole-2-thiol   glacial acetic acid 2-3 drops / reflux, 6-7 h   3-[(5-Mercapto-[1,3,4]thiadiazol-2-ylimino)-methyl]-benzene-1,2-diol

Scheme-I: Synthesis of Schiffs base ligand

coloured precipitate was obtained after refluxing. It was cooled, filtered and dried over P_4O_{10} (**Scheme-I**).

Synthesis of Mn(II) and Co(II) complexes: Hot ethanolic solution of chloride and acetate salts of Mn(II) and Co(II) were added to hot ethanolic solution of ligand in 1:2 mole ratio. This solution was refluxed at 70-75 °C for about 10-11 h. On completion of refluxing, the mixture was cooled by keeping overnight in refrigerator. Different colour precipitates were separated out, washed with diethylether and dried over P_4O_{10}.

Physical measurement: Elemental analysis (C, H and N) of ligand and its metal complexes was done on EA1106 elemental analyzer in USIC (University of Delhi). For evaluating molar conductances, ELICO (type CM82T) conductivity bridge was used. IR spectra were recorded in range of 4000-400 cm^{-1} on the IR spectrophotometer in KBr pellet in USIC (University of Delhi). Shimadzu UV-visible mini-1240 spectrophotometer was used for recording electronic spectra in DMSO as solvent. ^{1}H NMR was recorded on Bruker Advanced DPX-300 spectrometer by using DMSO-d_6 as solvent in University of Delhi. In JNU LC-ESI-MS based analysis was done for calculating electronic impact mass spectrum. In IIT Bombay EPR spectrum of metal complexes as polycrystalline samples was recorded by using DPPH as g marker. Gaussian 09 W was used for molecular modelling of ligand and its metal complexes.

RESULTS AND DISCUSSION

Conventional condensation method was used for synthesis of ligand and its Mn(II) and Co(II) complexes. The analytical and spectral data suggest the general composition [ML_2X_2], where X= Cl$^-$, CH$_3$COO$^-$. Molar conductance studies suggested the non-electrolytic nature of all the metal complexes. Analytical and physical data of bidentate and its metal complexes is given in Table-1. Coordination of the ligands to metal ion through nitrogen and oxygen confirm by the IR spectroscopic studies.

Octahedral geometry for Mn(II) and Co(II) complexes suggested on the basis of spectral studies (Fig. 1).
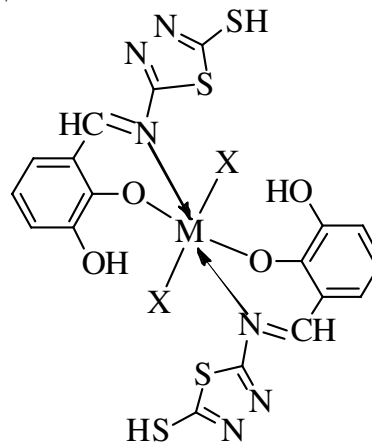

Fig. 1.   Proposed chemical structure of synthesized complexes; where, [M = Mn(II), Co(II)] and [X = Cl$^-$ or CH$_3$COO$^-$]

^{1}H NMR spectrum of the ligand: ^{1}H NMR spectrum of the ligand shows different signals which confirms the presence of different types of the protons. ^{1}H-NMR spectrum of the ligand 3-[(5-Mercapto-[1,3,4]thiadiazol-2-ylimino)-methyl]-benzene-1,2-diol, in DMSO-d_6 shows following signals: 8.1 ppm (1H, s, >C=NH), 3.3 ppm (1H, s, -SH), 6.6 -7.0 ppm (3H, m, Ar-H), 10.11 ppm (2H, s, -OH).

Mass spectrum: Molecular ion peak has been observed at *m/z* 254.01, in the electronic mass spectrum (Fig. 2) of the Schiffs base ligand which confirm the proposed formula [$C_9H_8N_3O_2S_2$]$^+$. The spectrum also shows other peaks observed at 133.90, 153.03, 162.02, 219.99, 228.07 corresponding to various fragments. Intensities of the peaks make an idea of the stabilities of fragments.

TABLE-1
PHYSICAL DATA AND ANALYTICAL DATA OF LIGAND AND ITS Mn(II) AND Co(II) COMPLEXES

| Compound	m.w.	Molar conductance (Ω^{-1} cm^2 mol^{-1})	Colour	Yield (%)	m.p. (°C)	Elemental analysis (%): Found (calcd.)			
						M	C	H	N
[Ligand (L) C$_9$H$_7$N$_3$O$_2$S$_2$	253	–	Light yellow	54	187	–	42.68 (42.69)	2.79 (2.75)	16.59 (16.32)
[Mn(L)$_2$Cl$_2$] C$_{18}$H$_{12}$N$_6$O$_4$S$_4$Cl$_2$Mn	630	4	Cream	63	> 300	8.71	34.29 (34.33)	1.92 (1.93)	13.33 (13.41)
[Mn(L)$_2$(CH$_3$COO)$_2$] C$_{20}$H$_{12}$N$_6$O$_{10}$S$_4$Mn	679	5	Pink	65	> 300	8.08	35.35 (35.41)	1.78 (1.79)	12.37 (12.35)
[Co(L)$_2$Cl$_2$] C$_{18}$H$_{12}$N$_6$O$_4$S$_4$Cl$_2$Co	633	5	Light brown	69	> 300	9.29	34.08 (34.06)	1.91 (1.94)	13.25 (13.19)
[Co(L)$_2$(CH$_3$COO)$_2$] C$_{20}$H$_{12}$N$_6$O$_{10}$S$_4$Co	683	6	Brown	70	> 300	8.62	35.14 (35.65)	1.77 (1.82)	12.29 (12.31)
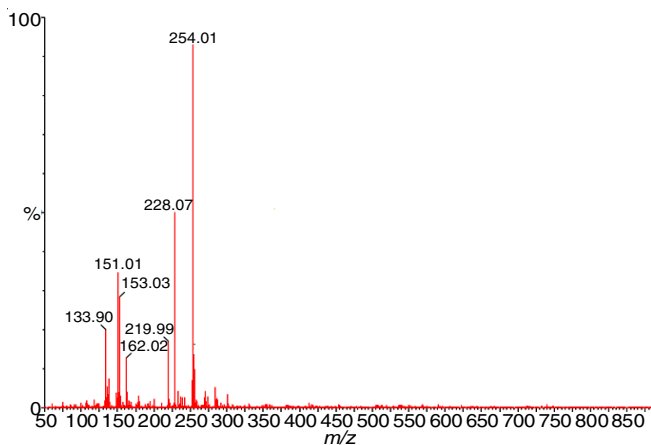
Fig. 2. Mass spectrum of the ligand

Infrared spectra: Important IR bands for ligand and its metal complexes are given in Table-2. The IR value for ligand and metal complexes give an idea of mode of binding. The value of IR peaks located at 1630 cm^{-1} assigned to the >C=N-linkage. In the metal complexes formation this value is shifted to the lower value 1611-1593 cm^{-1} [21]. The band corresponding to carbonyl and free amino group was disappear indicating complete condensation of amino group with keto group.

Band corresponding to –OH group observed in the range of 3438-3398 cm^{-1} [22]. In case of ligand band corresponding to –SH group observed at 2765 cm^{-1} and at 870-798 cm^{-1} give an idea of -C-S-C- linkage [23]. In complexes the value corresponding to –SH have not change indicating that –SH not coordinated to the metal atom in complex formation. Band observed at 576-531 cm^{-1} corresponding to M-O linkage and 464-421 cm^{-1} corresponding to M-N linkage. It indicates the coordination take place through the nitrogen atom of the azomethine group, oxygen atom of –OH group.

Molar conductance: Molar conductance for Mn(II) complexes lies in the range of 4-5 (Ω^{-1} cm^2 mol^{-1}) and for Co(II) complexes lies in the range of 5-6 (Ω^{-1} cm^2 mol^{-1}) in DMSO, indicate the non-electrolytic character of the metal complexes [24].

Magnetic moment: Manganese(II) complexes show magnetic moment in the range of 5.96-5.98 B.M. corresponding to the five unpaired electrons. Cobalt(II) complexes show magnetic moment in the range of 4.73-4.99 B.M. corresponding to the three unpaired electrons and paramagnetic behaviour. The complexes are supposed to six coordinated and to have octahedral geometry [25].

Electronic spectra: DMSO solution is used for recording electronic spectra of Mn(II) and Co(II) complexes. Four absorption bands for Mn(II) complexes are observed in the range of 17543-18567, 19315-20527, 23545-24522 and 33543-37865 cm^{-1} corresponding to the $^6A_{1g}\rightarrow{}^4T_{2g}$ (^{4}G), $^6A_{1g}\rightarrow{}^4E_g$, $^4A_{1g}$ (^{4}G), $^6A_{1g}\rightarrow{}^4E_g$ (^{4}D) and $^6A_{1g}\rightarrow{}^4T_{2g}$ (^{4}P) transitions respectively, the position of electronic spectral bands suggest octahedral geometry for Mn(II) complexes [26].

Electronic spectra for Co(II) complexes display electronic spectral bands in the range of 9754-98756, 12569-12787 and 18654-19543 cm^{-1}. These may assigned to the $^4T_{1g}\rightarrow{}^4T_{2g}$ (F), $^4T_{1g}\rightarrow{}^4A_{2g}$ (F), $^4T_{1g}\rightarrow{}^4T_{1g}$ (P) transitions respectively [27].

Depending on the position of the bands an octahedral geometry was suggested for Co(II) complexes [28]. Electronic spectral bands for Mn(II) and Co(II) complexes shown in Table-2.

Electron paramagnetic resonance spectra: EPR spectra for Mn(II) and Co(II) complexes were recorded at LNT in polycrystalline form at a frequency of 9.1 GHz and of 3000 G magnetic field strength. The value of g_{iso} were calculated by making an average of the observed lines. The value of g_{iso} *i.e.* electron spin-nuclear spin hyperfine coupling constant is calculated as 1.97-2.04 for Mn(II) complexes and 2.10-2.88 for Co(II) complexes.

In case of Co(II) complexes at higher temperature rapid spin lattice relaxation broadens lines [29]. The value for $g_\parallel$, $g_\perp$ and g_{iso} are summarized in Table-2. The structure (Fig. 1) can be proposed for the synthesized complexes on the basis of the above discussion.

Molecular modelling analysis: In order to find out general structural information about the ligand and its metal complexes geometric optimization was carried out. (B3LYP) functional with 6-31G(d,p) basis sets method of the Gaussian 09 W package in the gas phase is used for the optimization of the ligand and complexes. Molecular modelling analysis is used for evaluation of the bond angles and bond lengths [30].

Structure of optimized ligand, [Mn(L)$_2$(CH$_3$COO)$_2$] and [Co(L)$_2$(CH$_3$COO)$_2$] complexes are shown in Fig. 3. Both [Mn(L)$_2$(CH$_3$COO)$_2$] and [Co(L)$_2$(CH$_3$COO)$_2$] complexes have octahedral geometry. The bond length for C=N is observed as 1.31 Å, C-S is 1.73 Å, N-N is 1.45 Å and bond angle for C=N-C is 120°, S-C-S is 125 degree in case of ligand. In [Mn(L)$_2$(CH$_3$COO)$_2$] two equatorial Mn-N distances were 2.13 Å, 2.11 Å and the two axial Mn-O distances were 1.96 Å, 1.94 Å. In [Co(L)$_2$(CH$_3$COO)$_2$] two equatorial Co-N distances were 2.16 Å, 2.19 Å and the two axial Co-O distances were 1.86 Å, 1.79 Å. In Table-3 other bond lengths and bond angles are summarized.

Antibacterial activity: Antibacterial activity for ligand and its metal complexes has been examined by using well diffusion method. Activity was checked against three bacteria, *P. aeruginosa*, *S. pyogens* and *B. subtilis*. DMSO was used to

TABLE-2
IR, MAGNETIC MOMENT, ELECTRONIC SPECTRAL AND EPR DATA OF LIGANDS AND THEIR METAL COMPLEXES

Compound	IR (cm^{-1})						μ_{eff} (B.M.)	Electronic data	EPR parameters		
	>C=N-	-OH	-SH	M-O	M-N	-C-S-C-		λ_{max} (cm^{-1})	$g_\parallel$	$g_\perp$	g_{iso}
[Ligand (L)	1630	3438	2765	–	–	870	–	–	–	–	–
[Mn(L)$_2$Cl$_2$]	1611	3407	2764	576	443	868	5.96	17543, 19315, 23545, 33543	–	–	2.09
[Mn(L)$_2$(CH$_3$COO)$_2$]	1598	3428	2702	573	421	801	5.98	18567, 20527, 24522, 37865	–	–	2.07
[Co(L)$_2$Cl$_2$]	1601	3411	2765	542	426	798	4.83	9754, 12569, 18654	2.30	2.01	2.10
[Co(L)$_2$(CH$_3$COO)$_2$]	1593	3398	2764	531	464	861	4.99	98756, 12787, 19543	2.27	1.75	2.88
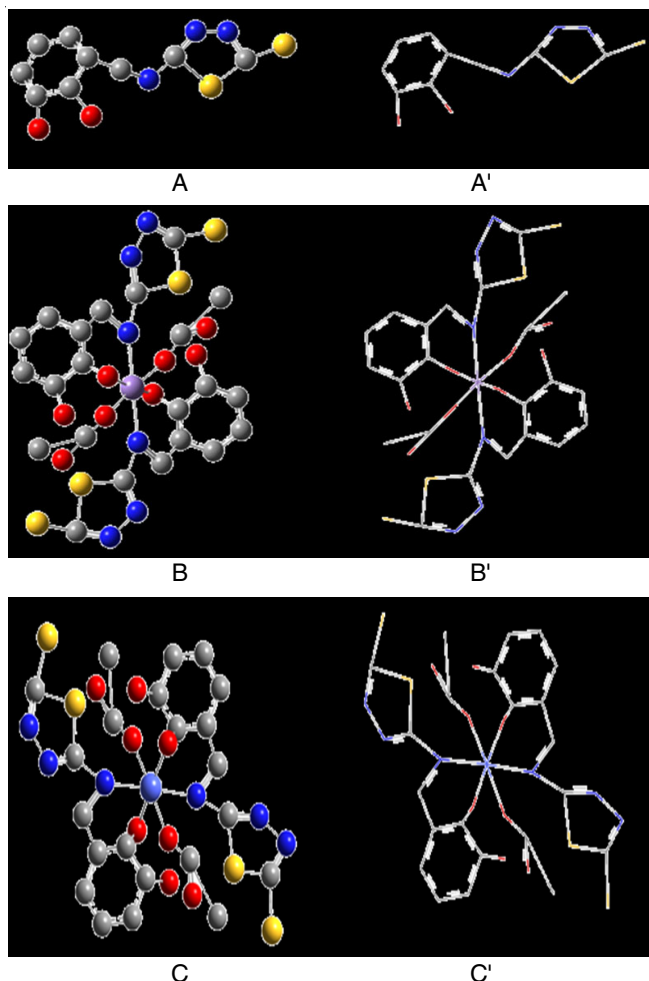
Fig. 3.　Geometry optimized structure of ligand and metal complexes; (A) Ligand, (B) [Mn(L)$_2$(CH$_3$COO)$_2$] and (C) [Co(L)$_2$(CH$_3$COO)$_2$]; [Colour code: C-grey, N-blue, O-red, S-yellow, Mn-purple, Co-sky blue]

get the different concentrations *i.e.* 1000, 750 and 500 ppm of tested compounds. Streptomycin was used as standard drug and DMSO is served as control. The activity was checked by measuring growth inhibition zone. Antibacterial screening data

indicates the antibacterial properties of both the ligand as well as its metal complexes. After study metal complexes was found more potent against bacteria as compare to the parent ligand.

The reason for it, may be the greater lipophilicity of complex as lipophilicity controls the activity of compounds. Chelation increases lipophilicity of the metal atom and favours penetration of complexes in lipid membranes of the microorganism [31]. Every compound show different activity due to impermeablity of cell [32]. On increasing concentration degree of inhibition increases, activity also increaes.

Antibacterial zone of inhibition (mm) of compounds given in the Table-4. The order of antibacterial activity against *P. aeruginosa*, is found to be as: standard drug > [Co(L)$_2$(OAc)] > [Co(L)$_2$Cl$_2$] > [Mn(L)$_2$(OAc$_2$)] > [Mn(L)$_2$Cl$_2$] > L. The order of antibacterial activity against *S. pyogens* is found to be as: standard drug > [Co(L)$_2$ (OAc$_2$)] > [Mn(L)$_2$(OAc$_2$)] > [Co(L)$_2$Cl$_2$] > [Mn(L)$_2$Cl$_2$] > L. The order of antibacterial activity against *B. subtilis* is found to be as: standard drug > [Co(L)$_2$(OAc)$_2$] > [Co(L)$_2$Cl$_2$] > [Mn(L)$_2$Cl$_2$] > [Mn(L)$_2$(OAc)$_2$] > L.

Conclusion

Complexes of chlorides and acetates of metal Mn(II) and Co(II) with ligand, 3-[mercapto-[1,3,4]thiadiazol-2-ylimino)-methyl]-benzene-1,2-diol is synthesized and characterized. The structure is confirmed by spectral, magnetic, analytical and molecular modelling. Potential activity towards microbial strains was shown by Schiffs base ligand and its metal complexes. All the complexes have octahedral geometry.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

TABLE-3
OPTIMIZED GEOMETRY STRUCTURES OF SCHIFF BASE LIGAND AND
METAL COMPLEXES (BOND LENGTHS, Å AND BOND ANGLE, °)

	Bond lengths (Å)				Bond angle (°)		
Atoms	Ligand	[Mn(L)$_2$(CH$_3$COO)$_2$]	[Co(L)$_2$(CH$_3$COO)$_2$]	Atoms	Ligand	[Mn(L)$_2$(CH$_3$COO)$_2$]	[Co(L)$_2$(CH$_3$COO)$_2$]
C$_9$-N$_{10}$	1.31	1.29	1.28	C$_1$-C$_9$-N$_{10}$	120	119	119
C$_{11}$-S$_{16}$	1.73	1.65	1.69	S$_{16}$-C$_{14}$-S$_{15}$	125	124	123
C$_{11}$-N$_{12}$	1.32	1.30	1.29	N$_{10}$-C$_{11}$-S$_{16}$	126	125	123
N$_{12}$-N$_{13}$	1.45	1.41	1.41	C$_2$-C$_3$-C$_4$	119	117	118
N$_{13}$-C$_{14}$	1.32	1.30	1.30	C$_4$-C$_5$-C$_7$	121	120	120
C$_{14}$-S$_{15}$	1.78	1.69	1.67	C$_4$-C$_5$-O$_6$	120	119	118
C$_{14}$-S$_{16}$	1.73	1.68	1.68	C$_5$-C$_7$-O$_8$	121	118	119
C$_7$-O$_8$	1.43	1.41	1.40	C$_9$-N$_{10}$-C$_{11}$	120	117	121
C$_5$-O$_6$	1.42	1.39	1.41	N$_{10}$-Mn$_{17}$-O$_{35}$	–	98.5	–
C$_2$-C$_3$	1.39	1.37	1.38	N$_{10}$-Co$_{17}$-O$_{35}$	–	–	89.5
O$_{35}$-Co$_{17}$	–	–	1.86	O$_{18}$-Mn$_{17}$-N$_{27}$	–	58.9	–
O$_{34}$-Co$_{17}$	–	–	1.79	O$_{18}$-Co$_{17}$-N$_{27}$	–	–	61.2
O$_{35}$-Mn$_{17}$	–	1.96	–	O$_{34}$-Mn$_{17}$-O$_{35}$	–	149	–
O$_{34}$-Mn$_{17}$	–	1.94	–	O$_{34}$-Co$_{17}$-O$_{35}$	–	–	148

TABLE-4
ANTIBACTERIAL ACTIVITIES DATA OF LIGAND (L) AND THEIR METAL COMPLEXES

Compounds	Antibacterial zone of inhibition (mm)								
	P. aeruginosa			*S. pyogens*			*B. subtilis*		
	1000	750	500	1000	750	500	1000	750	500
L	8	7	6	11	10	9	13	12	11
[Mn(L)$_2$Cl$_2$]	18	15	14	19	17	15	15	14	13
[Mn(L)$_2$(OAc$_2$)]	21	19	15	24	21	20	14	13	12
[Co(L)$_2$Cl$_2$]	25	23	21	22	20	19	17	16	14
[Co(L)$_2$ (OAc$_2$)]	34	31	29	33	31	29	22	20	19
Standard drug	36	34	30	34	33	29	29	27	26

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