

Study of Coordination Mode of Bidentate Ligands Derivative of 2-Benzoylpyridine Thiosemicarbazone, 2-Benzoylpyridine semicarbazone, and 2-Benzoyl thiophene thiosemicarbazone and their Co(II) complexes: Synthesis, Characterization, and their Biological Activity

Meenakshi Gupta^{1*}, Bhupendra Kumar Sarma¹, S. Chandra², Sangeeta Gupta³, Sanjay Singhal³

¹Department of Chemistry, Mewar University, Gangrar, Rajasthan, India, ²Department of Chemistry, Zakir Hussain Delhi College, University of Delhi, JLN Marg, New Delhi, India, ³Department of Microbiology, ESI Hospital, Basai, Darapur, New Delhi, India

ABSTRACT

Objective: The objective is to study the synthesis, characterization and biological activity of Co(II) complexes.

Materials and Methods: All the complexes and ligands were prepared by reflux for 7–8 h. Ethyl alcohol was used as solvent and pH was adjusted in the range of 3–4 in case of 1,3 ligands. Round bottom flask, heating mantle, glass rod, and condenser were used for the experiment.

Result: Co(II) complexes of general composition $(Co[L^2]X)_2$ have been synthesized (from Schiff base ligands of thiosemicarbazone, semicarbazone and 2-benzoylpyridine, and 2-benzoylthiophene) where L = 2-benzoylpyridinethiosemicarbazone ligand (L^1), 2-benzoylpyridine and semicarbazone ligand (L^2), and 2-benzoyl thiophene thiosemicarbazone ligand (L^3) and $X = NO_3^-$, $\frac{1}{2}SO_4^{2-}$, OAc^- , and Cl^- . All the complexes and ligands under study were characterized by infrared, nuclear magnetic resonance, elemental analysis, mass spectroscopy, electron paramagnetic resonance and ultraviolet spectroscopy, and magnetic susceptibility. The various physicochemical technique suggests octahedral geometry for chloro, acetato, and nitrate complexes and five coordinated trigonal bipyramidal geometry for sulfato complexes. The magnetic moment values suggest three unpaired electrons and high spin type complexes. The complexes under the study were screened against bacteria and pathogenic fungi *in vitro*.

Conclusion: The synthesized ligands were bidentate and complexes were found more active toward antimicrobial activity than ligands.

Key words: Electron paramagnetic resonance, infrared, mass, nuclear magnetic resonance, semicarbazone, thiosemicarbazide

INTRODUCTION

Thiosemicarbazones and semicarbazone Schiff's base ligands fascinate the attention of chemists for their pharmacological activities.^[1] Their metal complexes exhibit more activity in comparison with free ligands^[2,3] and have a wide range of biological activities including antibacterial,^[4,5] anti-inflammatory,^[6] and analgesic.^[7] Due to the presence of both hard nitrogen or oxygen and soft sulfur donor atoms in the backbone of these ligands, they readily coordinate with a large range of transition metal ions producing intensely colored and stable metal complexes, some of which has known to exhibit interesting physical and chemical properties^[8] and potentially useful biological activities.^[9] Some Schiff's base complexes are also used as model molecules for biological oxygen carrier systems^[10] and having applications in analytical fields.^[11]

Experimental Section

All reagents were commercially available and used without further purification purchased from Sigma Aldrich and metal salts were purchased from E. Merck. Solvents were spectroscopic pure from SRL/BDH or purified by conventional methods.

Preparation of Ligand (L^1)

Thiosemicarbazide (0.091 g, 0.01 mol) was dissolved in minimum quantity of ethanol. To this hot ethanolic solution, 0.18 g, 0.01M 2-benzoylpyridine was added very slowly with constant stirring. The resulting solution was refluxed at 78–80°C for 8 h and the pH was adjusted to approximately 4–5 using acetic acid (according to Scheme 1). On cooling, bright yellow-colored crystals were separated out. These crystals were washed out several times with cold ethanol. The ligand is highly soluble in water.

Preparation of Ligand (L^2)

Semicarbazide (0.11 g, 0.01 mol) and sodium acetate (0.11 g, 0.01 mol) were dissolved in a little amount of

*Corresponding author:

Email: meenakshigupta294@gmail.com

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distilled water and added to alcoholic solution of 0.36 g, 0.02 mol 2-benzoylpyridine with constant stirring and refluxed for 7–8 h at 78–80°C according to [Scheme 2]. The resultant solution was cooled for 24 h. On cooling, white shiny crystals were separated out which were washed with ethanol and ether several times to remove excessive reactant and dried over P_4O_{10} .

Preparation of Ligand (L³)

Thiosemicarbazide (0.91 g, 0.01 mol) was dissolved in minimum quantity of ethanol. To this solution, hot ethanolic solution of 2-benzoylthiophene (0.01 mol) was added very slowly with constant stirring. The resulting solution was refluxed at 78–80°C for 6 h, and the pH was adjusted to 4–5 using acetic acid (according to Scheme 3). On cooling, bright light yellow-colored crystals were separate out. These crystals were washed out several times with cold ethanol and dry ether several times to remove excessive reactant and dried over P_4O_{10} .

Characterization of Ligands

The ligand was characterized using analytical and spectroscopy technique such as elemental analysis infrared (IR), ¹H nuclear magnetic resonance (NMR), and mass spectrum.

IR Spectrum

In IR spectrum of ligand (L¹), Figure 1 shows several bands between 3125 and 3294 cm^{-1} corresponding to ν N-H stretching vibrations. The most significant bands of ligand (L¹) in KBr are 1618 cm^{-1} ν (C=N), 781 cm^{-1} ν (C=S), and 955 cm^{-1} ν (N-N) vibrations.^[12]

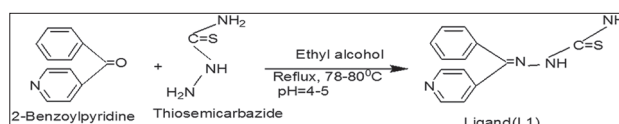
IR Spectrum

The IR spectra of ligand (L²) show a band at 3200 cm^{-1} corresponding to ν N-H stretching vibrations. The bands appeared at 1660 cm^{-1} , 1577 (cm^{-1}), and 931 cm^{-1} correspond to ν (C=N)_{azomethine}, ν (C=O) group, and ν N-N stretching vibrations.^[13]

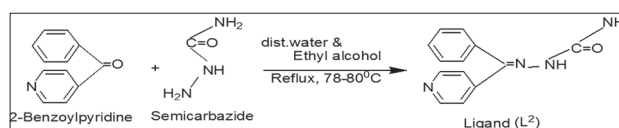
In IR spectra of ligand, several bands at 1598 cm^{-1} , 3162 cm^{-1} , and 921 cm^{-1} correspond to ν (C=N)_{azomethine} group, ν N-H, and ν N-N stretching vibrations.^[14] A band appeared at 837 (cm^{-1}) is due to ν (C=S) group.

¹H NMR Spectrum

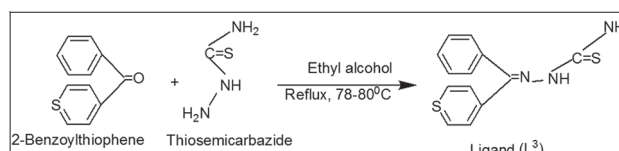
¹H NMR of ligands [Figure 2] was done in d^6 -dimethylsulfoxide (DMSO) on 44–300 MHz frequency. The aromatic proton appears as a set of singlet, doublet, and multiplet in the range δ 7.40–8.78 ppm.^[15] The singlet for NH proton appears at δ 9.32 ppm, while two NH_2



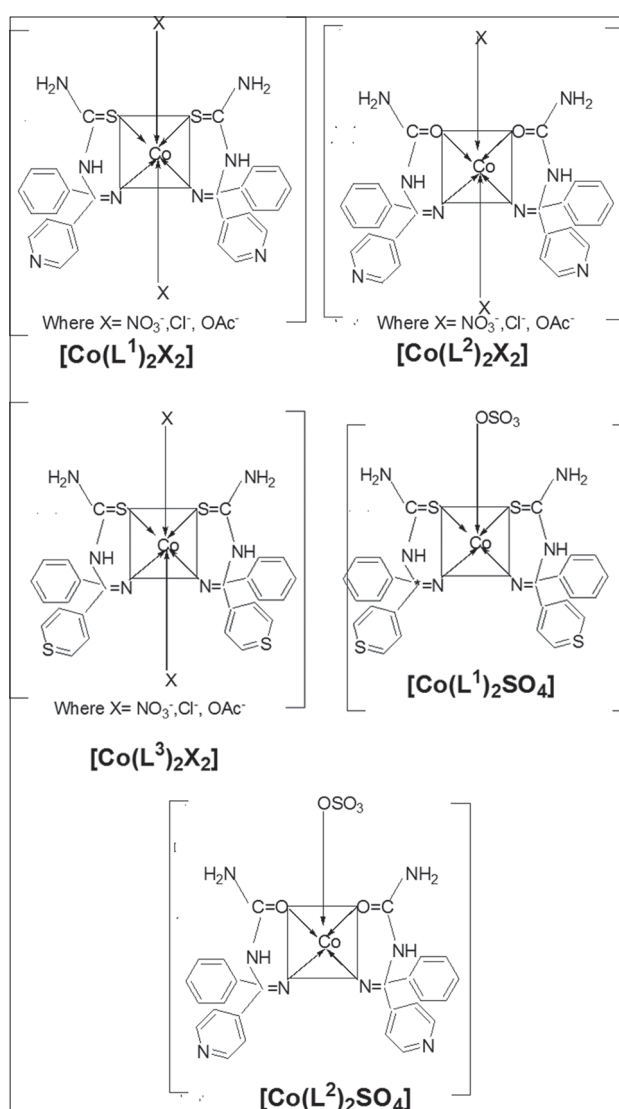
Scheme 1: Synthesis of ligand 1 (L¹)



Scheme 2: Synthesis of ligand 2 (L²)



Scheme 3: Synthesis of ligand 3 (L³)



Scheme 4: Proposed geometry of complexes under study

protons resonate as a multiplet at δ 7.34–7.38 ppm. The ν C=N peak was appeared at δ 8.212 ppm, and aromatic hydrogen peak was appeared at δ 7.62 ppm.

Mass Spectrum

Mass spectrum represented the important peaks regarding the proposed formula of the synthesized ligand (L^1). Mass spectrum of ligand shows a molecular ion peak at $m/z = 255$ amu corresponding to species $(C_{13}H_{11}N_4S)^+$. The peak at $m/z = 255$ amu indicates M+1 peak. This value favors the proposed formula of the ligand.

Mass spectrum of ligand (L^2) under study provides the important information regarding the proposed formula of the synthesized ligand. Mass spectrum of ligand shows a molecular ion peak at $m/z = 239$ amu corresponding to species $(C_{13}H_{11}N_4O)^+$. The peak at $m/z = 239$ amu indicates M+1 peak. This value is in agreement with the proposed formula of the ligand.

Mass spectrum of the ligands (L^3) [Figure 3] gives the information regarding the proposed formula of the ligand (L^3) under study. Mass spectra of ligands L^3 show a molecular ion peak at $m/z = 273$ amu corresponding to species $(C_{13}H_{12}N_3S)^+$ respectively. The peak at $m/z = 273$ amu indicates M+1 peak. This value favors the proposed formulae of the ligand.

Synthesis of Cobalt(II) Complexes

The complexes of cobalt(II) were synthesized from their respective ligands by condensation reaction between

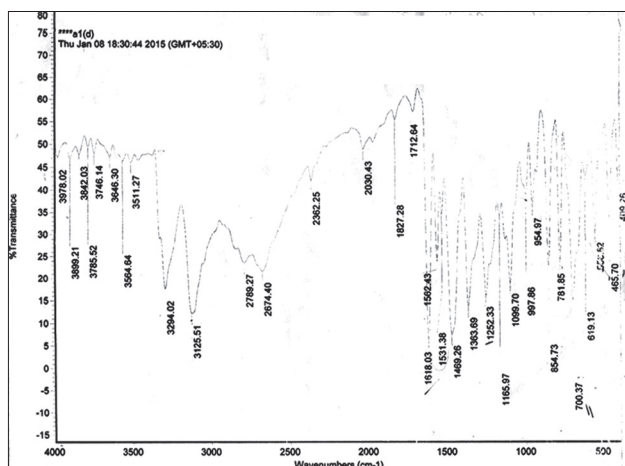


Figure 1: Infrared spectrum of ligand 1

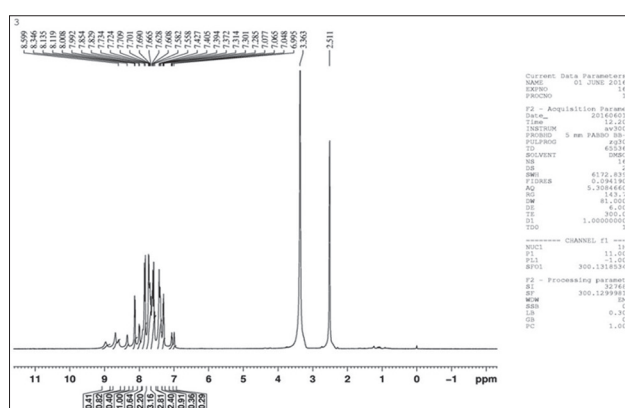


Figure 2: Nuclear magnetic resonance spectrum of ligand 3

ligand and corresponding metal salts in 1:2 ratio at pH range approximately 6–7.

Co(II) complexes with ligand L^2 and L^3

A warm ethanolic solution of ligand (0.002 mol) was added to a warm ethanolic solution of corresponding metal salts with constant stirring. The mixture was heated under reflux with constant stirring for 6 h. On cooling, a colored complex precipitate was formed. This precipitate was filtered, washed with ether and ethanol, and dried in desiccators using silica gel as an absorbent.

Co(II) complexes with ligand (L^1)

Ligand (L^1) was found to be soluble in water, so its aqueous solution was prepared and mixed with aqueous solution of metal salts in 1:2 ratio. The mixture was heated under reflux with constant stirring for 6 h. On cooling, a colored complex precipitate was formed. This precipitate was filtered, washed with ether and ethanol, and dried in desiccators containing silica gel as an absorbent.

RESULTS AND DISCUSSION

On the basis of elemental analyses, the complexes were found to have general composition CoL_2X_2 (where $L = L_1$ and L_2 and $X = Cl^-$, NO_3^- , OAc^- , and $\frac{1}{2}SO_4^{2-}$). The elemental analysis values are indicated in Table 1. The molar conductance values lie between 11 and 19 ($\Omega^{-1}cm^2 mol^{-1}$), indicating that all the cobalt complexes are non-electrolytic in nature and have composition (CoL_2X_2) . All complexes and ligands were found to be biologically active toward test fungi and bacteria. Complexes were found to be more biologically active than ligands. The results obtained from antimicrobial susceptibility testing are depicted in Table 1.

Magnetic Moment

The ground state (4T_1) is orbitally degenerate and would cause an orbital angular momentum contribution to

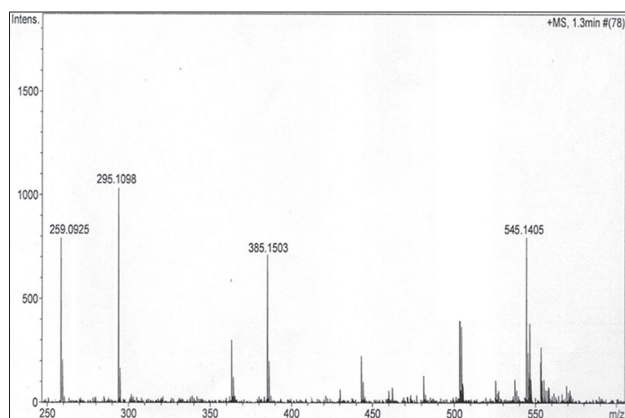


Figure 3: Mass spectrum of ligand (L^3)

the magnetic moments in octahedral field. That is why the moments would lie in between the limits of $\mu_{\text{eff}} = [4S(S+1)]^{1/2} = 3.38$ B.M. and $[4S(S+1)+L(L+1)]^{1/2} = 5.2$ B.M., where S is the total spin angular momentum of $(3/2)h$ and L is the total orbital angular momentum of $3h$. The amount of L depends on the actual value remaining associated with the ground state orbital triplet.^[16] Literature survey indicates that experimental magnetic moment values lie in the range of 4.7–5.2 B.M. to account electron delocalization and a low symmetry ligand component.

However, in case of tetrahedral cobalt(II) complexes, the ground state is orbital singlet 4A_2 . By the action of spin-orbit coupling, the higher lying 4T_1 and 4T_2 states are mixed into the ground state 4A_2 . Thus, the magnetic moment for these complexes is given by the expression $\mu_{\text{eff}} = 2(1-4\lambda/10Dq) [S(S+1)]^{1/2}$ B.M., in the free ion, $\lambda = -178 \text{ cm}^{-1}$. There is an evidence of a small degree of delocalization. The T.I.P. contribution is very large in this case, which may be estimated from the temperature dependence of the susceptibility, with a certain degree of accuracy. Thus, for tetrahedral complexes, magnetic moment lies in the range of 4.4–4.7 B.M.

In Co(II) complexes for the square planar strong field, the seven electrons of Co(II) would be distributed as follows: $b_{2g}^2, e_g^4, a_{1g}^1$, in which one unpaired electron is present in the a_{1g} orbital ($S = 1/2$). Therefore, magnetic moment of the square planar complexes of Co(II) lies in the range of 2.1–2.8 B.M.,^[17] which do not change with the temperature. Mixing of higher ligand field term into ground $^4A_{2g}$ term of the $b_{2g}^2, e_g^4, a_{1g}^1$ configuration by spin-orbit coupling is expected to give some orbital contribution to the moment

by raising g. Mixing takes place, for example, with the $^4A_{2g}$ term of $b_{2g}^2, e_g^4, a_{1g}^1$, giving a $-2[(1-2\lambda/(2A_{2g} - 2A_{1g}))]$.

Thus, magnetic moment is very helpful to assign the geometry of complexes. Magnetic moment also varies with configuration. In the present study, six coordinated complexes of Co(II) with L^1 and L^2 ligands show magnetic moment at room temperature in the range of 4.54–5.12 B.M. corresponding to three unpaired electron.

IR Spectra

The ligand mode of coordination is determined by the principal IR bands and their assignments [Figure 4]. The bands appeared at 1604 cm^{-1} , 1602 cm^{-1} , 1600 cm^{-1} , and 1606 cm^{-1} correspond to $\nu(\text{C}=\text{N})$ group, and the bands appeared at 738 cm^{-1} , 742 cm^{-1} , 756 cm^{-1} , and 736 cm^{-1} correspond to $\nu(\text{C}=\text{S})$ group for the complexes of ligand L^1 . Further, the coordination is supported by the appearance of $\nu(\text{M}-\text{N})$ band in the range of $435\text{--}452 \text{ cm}^{-1}$, whereas in case of ligand L^2 , the bands appeared at 1543 cm^{-1} , 1538 cm^{-1} , 1552 cm^{-1} , and 1562 cm^{-1} correspond to shift in $\nu(\text{C}=\text{O})$ group and the bands at 1641 cm^{-1} , 1617 cm^{-1} , 1631 cm^{-1} , and 1641 cm^{-1} indicate the shift in $\nu(\text{C}=\text{N})$ group, and the appearance of band in the range of $433\text{--}684 \text{ cm}^{-1}$ also supports the M-O coordination. The comparison of spectra of the ligand and their complexes shows that the ligands (L^1 , L^2) behave as bidentate ligand.^[18] The values are listed in Table 2.

Bands Due to Anion

The free nitrate ion has relatively high symmetry (D_{3h}) and its IR spectrum consists of three IR bands at $1419\text{--}1491 \text{ cm}^{-1}$, $1310\text{--}1316 \text{ cm}^{-1}$, and $1209\text{--}1293 \text{ cm}^{-1}$. According

Table 1: Color, melting point, and elemental analysis of Co(II) complexes

Complexes	Color	Molar conductance	Melting point (°C)	Molecular weight Found (Calc.)	Found (calculated)%		
					C	H	N
(Co[L ¹] ₂ SO ₄)	Brown	9.9	220	670	46.57 (46.01)	3.58 (3.60)	16.71 (16.24)
CoC ₂₆ H ₂₄ S ₃ N ₈ O ₄							
(Co[L ¹] ₂ [NO ₃] ₂)	Brown	11.0	230	633	49.29 (49.98)	3.79 (3.44)	19.90 (19.28)
CoC ₂₆ H ₂₄ S ₂ N ₁₀ O ₆							
(Co[L ¹] ₂ [OAc] ₂)	Shiny brown	9.7	248	689	52.26 (52.78)	4.35 (4.67)	16.25 (16.58)
CoC ₃₀ H ₃₀ S ₂ O ₂ N ₈							
(Co[L ¹] ₂ Cl ₂)	Brown	9.5	237	642	48.60 (48.93)	3.73 (3.56)	17.44 (17.89)
CoC ₂₆ H ₂₄ S ₂ N ₈ Cl ₂							
(Co[L ²] ₂ Cl ₂)	Light brown	12.2	221	610	51.15 (51.01)	3.93 (3.65)	18.36 (18.32)
CuC ₂₆ H ₂₄ O ₂ N ₈ Cl ₂							
(Co[L ²] ₂ [NO ₃] ₂)	Light brown	11.9	235	663	47.06 (47.89)	3.62 (3.21)	21.11 (21.87)
CoC ₂₆ H ₂₄ O ₈ N ₁₀							
(Co[L ²] ₂ SO ₄)	Light brown	12.9	245	635	49.14 (49.780)	3.78 (3.01)	17.64 (17.09)
CoC ₂₆ H ₂₄ O ₆ N ₈							
(Co[L ²] ₂ [OAc] ₂)	Shiny brown	13.9	254	657	47.50 (47.02)	4.57 (4.98)	17.05 (17.43)
CoC ₃ OH ₃₀ O ₆ N ₈							

to Gatehouse,^[19] if the nitrate ion is coordinated, its symmetry gets reduced to C_{2v} and shows absorption bands in the region of 1419–1491, 1310–1316, and 1209–1293 cm^{-1} . If the separation of ν_5 and ν_1 lies in the range of 115–186 cm^{-1} indicates the unidentate nature of nitro group.^[18] But if the separation is <186 indicates the bidentate nature of nitrate group.^[19]

The sulfato complexes [Figure 1] under study with ligand L^1 and L^2 show bands in the region of 1139–1143 cm^{-1} , 1015–1049 cm^{-1} , and 933–957 cm^{-1} which correspond to unidentate behavior of sulfate ion.

IR spectra of acetate complexes show two bands $\nu(C=O)$ and $\nu(C-O)$ band in the region of 1436–1463 and 1209–1282, and the difference of ν_5 and ν_1 lies in the range of 180–210 cm^{-1} which corresponds to unidentate behavior of acetate. The values are listed in Table 3.

Electronic Spectra

The electronic spectra of the present study complexes $[Co(L)_2X_2]$ ($X = Cl^-, NO_3^-,$ and OAc^-) show spin allowed bands at

Table 2: Important IR spectral bands (cm^{-1}) and their assignments

Complexes	$\nu(C=O)$	$\nu(C=N)$	$\nu(C=S)$	$\nu(M-N)$	$\nu(M-O)$
Ligand (L^1)	-	1618	781	-	-
$(Co[L^1]_2Cl_2)$	-	1604	738	435	-
$(Co[L^1]_2[OAc]_2)$	-	1602	742	459	-
$(Co[L^1]_2[SO_4])$	-	1600	756	452	-
$(Co[L^1]_2[NO_3]_2)$	-	1606	736	451	-
Ligand (L^2)	1577	1660	-	-	-
$(Co[L^2]_2Cl_2)$	1543	1641	-	-	684
$(Co[L^2]_2[NO_3]_2)$	1538	1617	-	-	433
$(Co[L^2]_2[SO_4])$	1552	1631	-	-	456
$(Co[L^2]_2[OAc]_2)$	1562	1641	-	-	542

Table 3: Important IR spectral bands (cm^{-1}) due to anions

Complexes	ν_1	ν_2	ν_3	$\nu_5-\nu_1$	Results
Ligand 1	-	-	-	-	-
$(Co[L^1]_2Cl_2)$	-	-	-	-	-
$(Co[L^1]_2[OAc]_2)$	$\nu(C=O)$ 1437	$\nu(C-O)$ 1209	-	228	Unidentate acetate
$(Co[L^1]_2[SO_4])$	1142	1014	957	-	Unidentate sulfate
$(Co[L^1]_2[NO_3]_2)$	1473	1321	1249	124	Unidentate nitrate
Ligand 2	-	-	-	-	-
$(Co[L^2]_2Cl_2)$	-	-	-	-	-
$(Co[L^2]_2[NO_3]_2)$	1418	1310	1293	125	Unidentate nitrate
$(Co[L^2]_2[SO_4])$	1139	1049	934	-	Unidentate sulfate
$(Co[L^2]_2[OAc]_2)$	$\nu(C=O)$ 1463	$\nu(C-O)$ 1282	-	181	Unidentate acetate

9680–11025 (ν_1) cm^{-1} , 14650–14,480 (ν_2) cm^{-1} , and 22471–23419 (ν_3) cm^{-1} . These transitions may be assigned to ${}^4T_{1g} \rightarrow {}^4T_{2g}$ (F), ${}^4T_{1g} \rightarrow {}^4A_{2g}$ (F), and ${}^4T_{1g} \rightarrow {}^4T_{1g}$ (P), respectively. The position of bands [Table 4] indicates that these complexes have distorted octahedral geometry and might possess D_{4h} symmetry.

The electronic spectra of sulfato complexes of cobalt display three bands at 10010–10140 (ν_1), 20263–22000 (ν_3), and 26,809–27397 cm^{-1} (ν_4) [Figure 5] corresponding to five-coordinate square pyramidal geometry^[20] and might possess C_{4v} symmetry.

Ligand Field Parameter

The various ligand field parameters were calculated for the Co(II) complexes. The value of Dq has been calculated from Orgel energy level diagram using ν_3/ν_1 ratio. Our results correspond to respective position of anions in the spectrochemical series. The nephelauxetic parameter β is readily obtained using the relation:

$$\beta = B(\text{complex})/B(\text{free ion})$$

Where $B(\text{free ion})$ is 1120 cm^{-1} . The value of β lies in the range of 0.735–0.975. The value of β indicates that the covalent character of metal-ligand σ bond is low. The ligand field stabilization energy is calculated [Table 4].

Electron Paramagnetic Resonance (EPR) Spectra

For cobalt square planar like cobaltous phthalocyanin $g_{11} = 2.0$, $g_{\perp} = 2.9$. These results are compatible with the

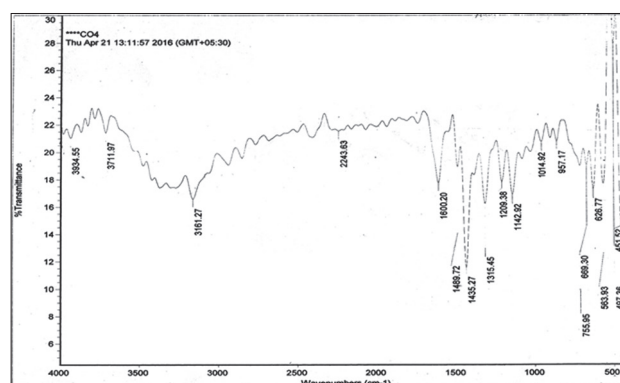


Figure 4: Infrared spectrum of $[Co(L^1)_2(SO_4)]$

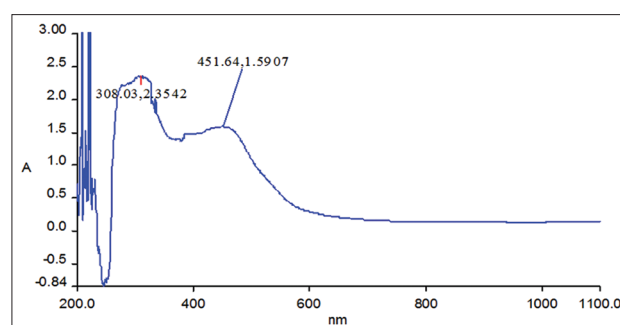


Figure 5: Ultraviolet spectrum of $Co(L^2)_2(OAc)_2$

spin-paired configuration $b_{2g}^2 e_{g}^4 a_{1g}^1$, provided that b_{1g} orbital lies only some 2000 cm^{-1} higher than the a_{1g} orbital.

The EPR spectra of Co(II) complexes were recorded as polycrystalline samples [Figure 6]. No EPR was observed at room temperature because the rapid spin–lattice relaxation of Co(II) broadens the lines at higher temperature. All the complexes show a very broad signal at liquid nitrogen temperature. The deviation of “g” values from the free electron value (2.0023) may be due to angular momentum contribution in the complexes. The present values for such complexes are listed in Table 5.

Mass Spectroscopy

Mass gives the important information regarding the proposed formula of the synthesized compound. The proposed molecular formula of these compounds was confirmed by comparing their molecular formula weight with m/z values. The mass spectrum of the complex $[\text{Co C}_{26}\text{H}_{23}\text{O}_2\text{N}_8\text{Cl}_2]^+$ shows a molecular ion peak at $m/z = 609$ amu which justifies the proposed formula of the synthesized complex under study. In addition to the peaks due to the molecular ion, the spectra exhibit the peak assignable to various fragments arising from the thermal cleavage of the compounds. The mass spectrum of both the complexes is shown in Figure 7.

Table 4: Electronic spectral bands (cm^{-1}) and magnetic moment (B.M.) of Co (II) complexes

Complexes	Spectral bands in (cm^{-1})	μ_{eff}
$(\text{Co}[\text{L}^1]_2\text{Cl}_2)$	10,965, 17614, 21,371, 23,147, 27,019, 31,606, 38,592	4.96
$(\text{Co}[\text{L}^1]_2[\text{OAc}]_2)$	10,593, 13,247, 23,148, 26,961, 31,666, 38,607	4.76
$(\text{Co}[\text{L}^1]_2[\text{SO}_4])$	9329, 10,894, 11,363, 23,091, 26,854, 27,242, 31,684	4.87
$(\text{Co}[\text{L}^1]_2[\text{NO}_3]_2)$	11,015, 11,918, 17241, 22,324, 23,548, 30,853	4.56
$(\text{Co}[\text{L}^2]_2\text{Cl}_2)$	9,398, 11,721, 22,142, 32,464	4.67
$(\text{Co}[\text{L}^2]_2[\text{NO}_3]_2)$	9,320, 9,606, 10,960, 21,316, 26,252, 29,069, 29,941, 30,861	4.98
$(\text{Co}[\text{L}^2]_2[\text{SO}_4])$		4.75
$(\text{Co}[\text{L}^2]_2[\text{OAc}]_2)$	10,625, 13,426, 24,530, 26,815, 27,923, 28,408, 28,754	4.58

Table 5: Electron paramagnetic resonance spectral data of cobalt complexes (II) complexes at lnt (as polycrystalline sample)

Complexes	Dq	v_2/v_1	B	β	LFSE	giso
$(\text{Co}[\text{L}^1]_2\text{Cl}_2)$	1285	2.26	918	0.819	122	2.008
$(\text{Co}[\text{L}^1]_2[\text{OAc}]_2)$	1421	2.38	990	0.884	135	2.0041
$(\text{Co}[\text{L}^1]_2[\text{SO}_4])$	1295	2.31	996	0.889	123	2.0124
$(\text{Co}[\text{L}^1]_2[\text{NO}_3]_2)$	1345	2.26	961	0.858	128	-
$(\text{Co}[\text{L}^2]_2\text{Cl}_2)$	1195	2.41	996	0.889	114	-
$(\text{Co}[\text{L}^2]_2[\text{NO}_3]_2)$	1085	2.36	823	0.735	103	-
$(\text{Co}[\text{L}^2]_2[\text{SO}_4])$	1120	2.28	990	0.883	107	-
$(\text{Co}[\text{L}^2]_2[\text{OAc}]_2)$	1170	2.09	980	0.875	111	-

Antimicrobial Activity

All the synthesized Co(II) complexes were screened for antibacterial and antifungal activity *in vitro* by broth dilution method^[21,22] with two Gram-positive bacteria *Staphylococcus aureus*, one Gram-negative bacteria *Escherichia coli*, and two fungal strains *Candida parapsilosis* and *Candida krusei*. Serial dilutions of the test compounds and biological activities of ligands and their metal complexes were prepared in Mueller-Hinton agar. Drugs (0.005, 0.050, and 0.500 mg) were dissolved in DMSO, 1 mL. 0.5 McFarland

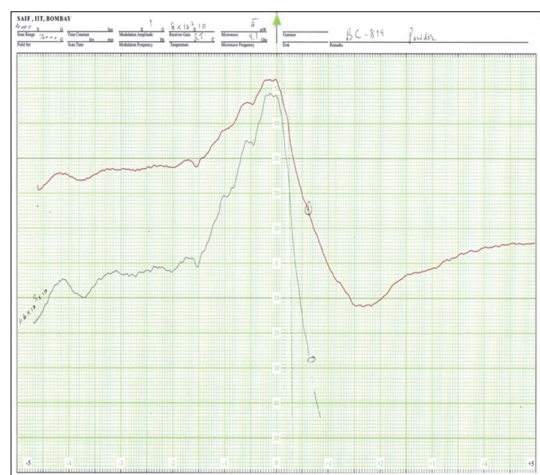


Figure 6: Electron paramagnetic resonance spectrum of $\text{Co}(\text{L}^1)_2\text{Cl}_2$

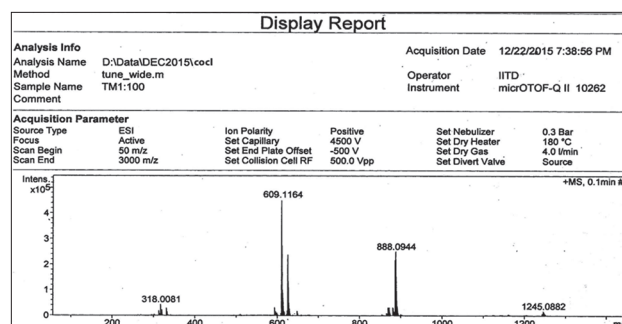


Figure 7: Mass spectrum of $\text{Co}(\text{L}^1)_2\text{Cl}_2$

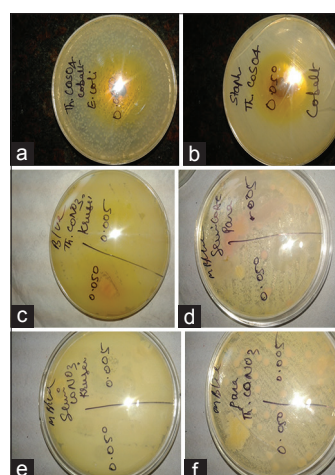


Figure 8: (a-f) Antibacterial and antifungal activity of complexes under study

Table 6: Antibacterial screening results of ligand (L1, L2, L3) and its complexes

Name	Concentration (μg)	<i>E. coli</i> diameter (mm)	<i>S. aureus</i> diameter (mm)
Ligand 1	0.005	NA	10
	0.050	10	14
	0.500	14	17
$L_1\text{CoSO}_4$	0.050	20	20
	0.005	23	24
$L_1\text{CoNO}_3$	0.050	28	29
	0.005	NA	NA
$L_1\text{CoCl}_2$	0.050	20	18
	0.005	NA	NA
$L_1\text{CoAc}$	0.005	NA	NA
	0.050	14	16
	0.500	15	19
L_2	0.005	10	NA
	0.050	14	14
	0.500	18	15
$L_2\text{CoCl}_2$	0.050	22	30
	0.005	NA	NA
$L_2\text{CoAc}$	0.050	14	15
	0.005	NA	NA
$L_2\text{CoNO}_3$	0.005	NA	NA
	0.050	11	30
	0.005	NA	NA
$L_2\text{CoAc}$	0.005	NA	NA
	0.050	13	18
	0.500	13	18
L_3	0.005	NA	10
	0.050	10	12
	0.500	13	18
$L_3\text{CoAc}$	0.005	11	12
	0.050	19	26
$L_3\text{CoSO}_4$	0.005	NA	NA
	0.050	10	11
	0.500	16	13

E. coli: *Escherichia coli*, *S. aureus*: *Staphylococcus aureus*

solution of *E. coli*, *S. aureus*, and *C. parapsilosis* and *C. krusei* was prepared and applied on Mueller-Hinton agar contained in a Petri plate with the help of sterilized swab. Then, 10 μL solution of concentration (0.005, 0.050, and 0.500 mg) in 1 mL DMSO was dropped on it with the help of micropipette. This Petri plate was incubated for 24 h at $22 \pm 29^\circ\text{C}$. The growth of fungi and bacteria was measured diametrically. The values are listed in Tables 6 -8.

To make sure that the DMSO had no effect on the bacterial growth, a control test was performed with the test medium supplemented with DMSO at the same dilutions as used in the experiments and it was observed that solvent had no effect on the microorganisms in the concentrations studied.

CONCLUSION

The antimicrobial screening of all investigated compounds provided information about the biological activity of

Table 7: Antifungal screening results of ligand 1 and its complexes

Name	Concentrations (μg)	<i>C. krusei</i> diameter (mm)	<i>C. parapsilosis</i> diameter (mm)
Ligand L^1	0.005	10	R
	0.050	15	10
	0.500	17	17
$L_1\text{CoSO}_4$	0.050	13	15
	0.005	10	10
$L_1\text{CoNO}_3$	0.050	12	13
	0.005	11	11
$L_1\text{CoCl}_2$	0.050	12	14
	0.005	10	11
$L_1\text{CoAc}$	0.050	11	13
	0.005	NA	NA
L_2	0.005	NA	NA
	0.050	10	10
	0.500	14	12
$L_2\text{CoCl}_2$	0.050	13	15
	0.050	13	15
$L_2\text{CoAc}$	0.050	13	15
	0.005	NA	NA
$L_2\text{CoNO}_3$	0.050	10	18
	0.005	18	22
$L_2\text{CoAc}$	0.500	19	26
	0.005	10	10
L_3	0.050	12	10
	0.500	15	12
	0.005	NA	NA
$L_3\text{CoAc}$	0.005	13	10
	0.050	13	10

C. krusei: *Candida krusei*, *C. parapsilosis*: *Candida parapsilosis*

ligands and its complexes, and it was found that complexes are more biologically active than ligands. On the basis of elemental analysis, molar conductance measurement, IR, electronic, EPR data, and subsequent discussion given above the octahedral and square planar geometry are suggested, and the following structures may be proposed for all the complexes under study.

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