

**Potentially Active N_2O_2 Type Metal Complexes Derived From 4-Aminoantipyrine,
4-Chlorobenzaldehyde and Acetylacetone**

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Abstract

*Transition metal complexes of Schiff bases (L_1) derived from the condensation of 4-aminoantipyrine, 4-chlorobenzaldehyde and acetylacetone has been synthesized by template method and characterized by elemental analysis, IR, 1H NMR, EPR spectroscopy, conductivity, thermal analysis, magnetic measurements and a microbial study. The magnetic measurements and EPR spectral data of the complexes suggest a square-planar geometry around the central metal ion. The molar conductance data revealed that all the complexes were electrolytes in the ratio 1:2 (metal:ligand). The thermal stability of the complexes were studied by thermogravimetry. The ligands and their metal complexes were screened for antimicrobial activity against *S. typhi*, *S. aureus*, *E. coli* and *B. subtilis*.*

Keywords: Schiff bases, Transition metal complexes, Antimicrobial activity, Characterization

1. Introduction

Azomethine group containing Schiff bases and their complexes have been derived for their biological properties and chelating abilities [1-3]. Several Schiff base ligands with oxygen and nitrogen atoms in their skeleton showed remarkable biological activities like diuretic activities [4-7], antibacterial [8-12], antifungal [13-15], and anticancer [16]. Many complexes of pyrazol-5-one derivatives such as antipyrine [17-20], 4-dimethylaminoantipyrine [21], 4-aminoantipyrine [22-24], and 3-methyl-1-phenylpyrazol-5-one [25] have been synthesized and some of them found to be DNA cleavage agents with or without sequence specificity. Moreover, the ligand or the metal in these complexes can be varied in an easily controlled manner to facilitate the individual applications [26].

The synthetic protocol for the preparation of complexes derived from 4-aminoantipyrine, 3-hydroxy, 4-nitrobenzaldehyde and acetylacetone involves three steps namely synthesis of β -diketone, Schiff base and metal complexes under reflux conditions.

In the present work, effort have been made to synthesize new series of N_2O_2 type complexes derived from 4-aminopyridine, 4-chlorobenzaldehyde and acetylacetone using solid-supported perchloric acid as a catalyst in two steps and less time period than the reported method.

2. Experimental

2.1 Material and Methods of Analysis

Analytical grade chemicals, 4-aminoantipyrine, 4-chlorobenzaldehyde, acetylacetone metal salts were purchased from Sigma-Aldrich, INC. IR spectra ($400-4000\text{ cm}^{-1}$) were recorded on Shimadzu FTIR spectrophotometer using KBR discs, and the absorption bands are expressed in cm^{-1} . 1H NMR spectra were recorded in DMSO- d_6 with tetramethyl silane as an internal standard. CHN analysis of the compounds was recorded at the Sophisticated Analytical Instrument Facility, (SAIF), Chennai. The X-band ESR spectra of the complexes were recorded at 300 K on a Varian ESR spectrophotometer using diphenylpicrylhydrazyl (DPPH) as internal standard at RSIC, IIT, Chennai. Magnetic susceptibility measurements of the complexes were carried out by Gouy balance using

copper sulphate as the calibrant. The molar conductance of the complexes was measured using a Systronic conductivity bridge at room temperature in DMSO solution. TG/DTA scans were recorded on Mettler-Toledo-851 TGA-DTA instrument at linear heating rate of 10⁰ per minute under inert atmosphere in a temperature range 25-1000 °C. X-ray powder diffraction patterns of complexes were recorded in the 2θ range of 10-80 ° on Bruker X-D 8 advanced diffractometer and XRD scans with the help of powder X- programme. The antimicrobial activities of the ligands and complexes were carried out by disc diffusion method.

2.2 Present Work

Herein attempt have been made to synthesized novel complexes of type [M(C₃₄H₃₅N₆O₂)]X₂ by non-template method utilizing solid-supported perchloric acid (HClO₄-SiO₂) as a catalyst at room temperature (Scheme 1 and 2). The investigated complexes were characterized and evaluated for their antimicrobial activity against four bacterial strains.

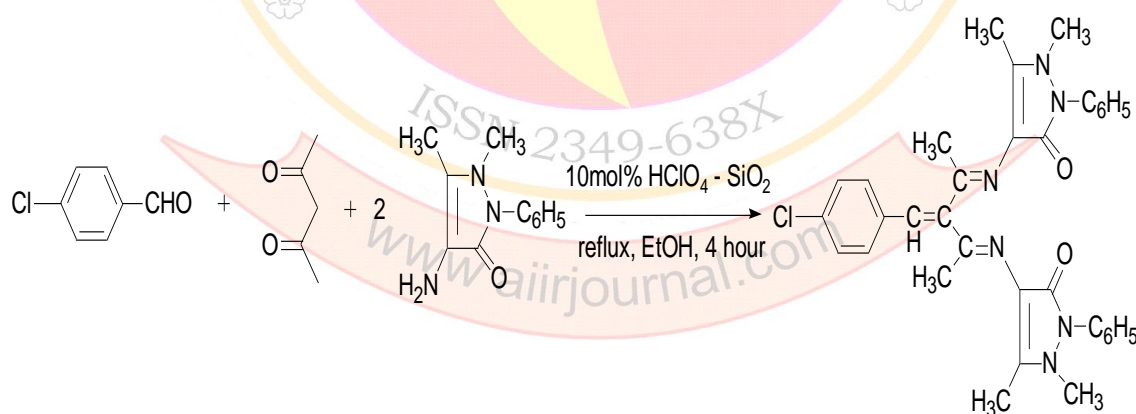
3. Typical procedure

3.1 Synthesis of 3(4'-chlorobenzalidene)-2,4-di(imino-4''-antipyrinyl) pentane (L₃)

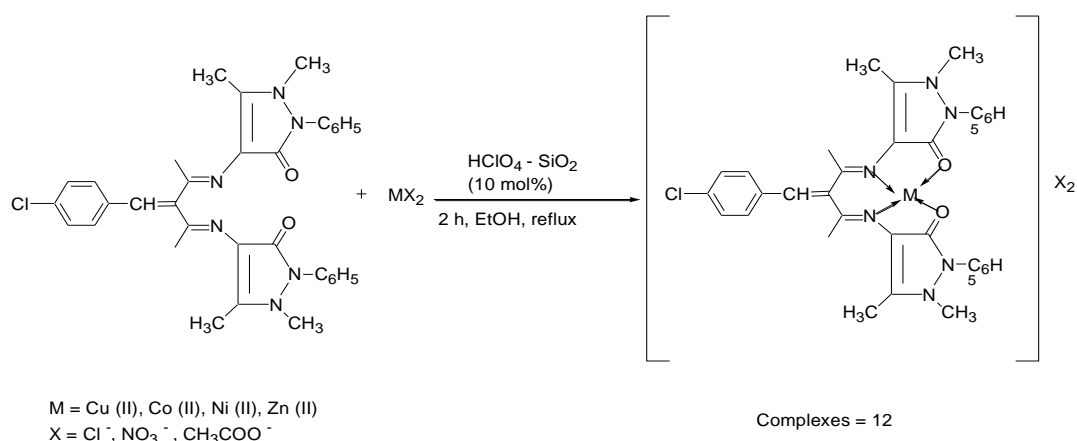
A mixture of acetyl acetone (10 mmol), 4-aminoantipyrine (20 mmol), and 4-chlorobenzaldehyde (10 mmol) along with 10 mol% solid-supported perchloric acid in ethanol (50 mL) was refluxed until completion of the reaction, as monitored by thin layer chromatography (TLC). The catalyst was filtered, washed with ethanol and the filtrate was concentrated under reduced pressure. The crude product was purified by recrystallization with hot ethanol. The recovered catalyst was activated at 180 °C for 2 h and reused four times for the preparation of complexes.

3.2 Synthesis of metal complexes

A mixture of 3(4'-chlorobenzalidene)-2,4-di(imino-4''-antipyrinyl)pentane (2 mmol), metal salt (2 mmol) along with 10 mol% solid-supported perchloric acid in ethanol (15 mL) was refluxed for 1 h. The resulting colored complex along with insoluble catalyst was filtered, wash with ethanol, acetone and petroleum ether. To separate the catalyst, complex was dissolved in DMSO (2 x 15 mL) and then filtered. The filtrate was then concentrated under reduced pressure to afford shiny blue colored copper complex, which was dried over calcium chloride (65% yield)



Scheme 1



Scheme 2

4. Result and discussion

4.1 Chemistry

The analytical data suggest the formula of complexes as $[\text{ML}_1]\text{X}_2$ where $M = \text{Co(II), Ni(II), Cu(II), Zn(II)}$ and $X = \text{Cl}^-, \text{NO}_3^-$ and CH_3COO^- . Conductivity measurements in DMSO indicate them to be electrolytic in nature ($40\text{-}60 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$). The melting point of all complexes was above 250°C and all complexes are intensively colored. Magnetic moment values suggest square-planar environment around metals (Table 1)

Table No. 1: Analytical Data of complexes of type $[\text{M}(\text{C}_{34}\text{H}_{35}\text{N}_6\text{O}_2)]\text{X}_2$

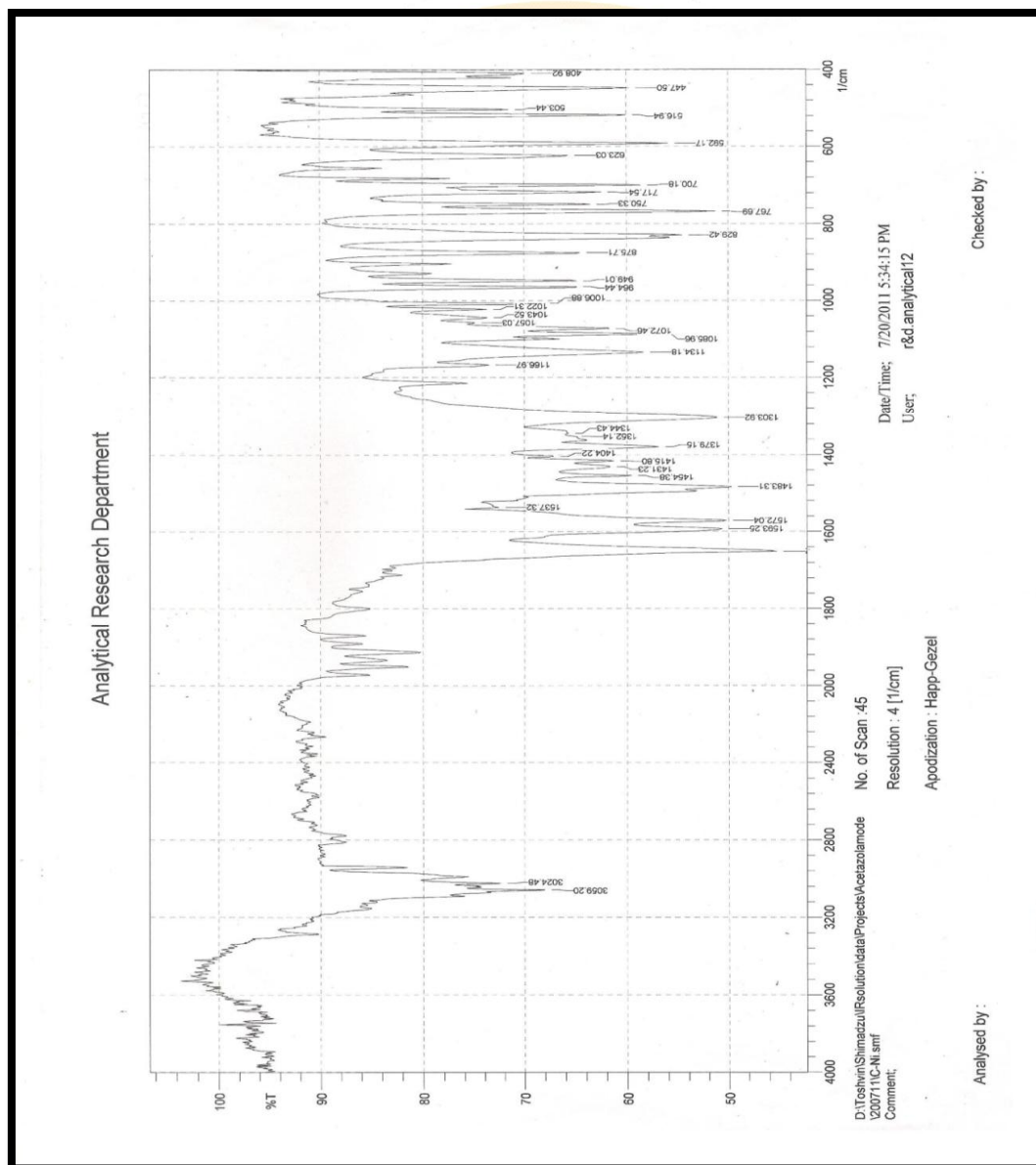
Sr. No.	Mol. For. of Complex	Mol. Wt.	Colour	Melting Point	Elemental Analysis %			IM cm^2	M.M. m_B
					Calcd.	(Found)	% N		
01	$[\text{Cu}(\text{C}_{34}\text{H}_{35}\text{N}_6\text{O}_2)]\text{Cl}_2$	694.14	Bluish	250	58.831 (58.415)	5.082 (4.865)	12.107 (11.867)	107	1.72
02	$[\text{Cu}(\text{C}_{34}\text{H}_{35}\text{N}_6\text{O}_2)](\text{NO}_3)_2$	747.242	Green Blue	250	54.650 (54.135)	4.721 (4.487)	14.995 (14.335)	116	1.72
03	$[\text{Cu}(\text{C}_{34}\text{H}_{35}\text{N}_6\text{O}_2)](\text{CH}_3\text{COO})_2$	741.322	Blue	250	61.568 (60.997)	5.574 (5.165)	11.336 (11.001)	102	1.72
04	$[\text{Co}(\text{C}_{34}\text{H}_{35}\text{N}_6\text{O}_2)]\text{Cl}_2$	689.533	Pink	250	59.224 (58.935)	5.116 (4.887)	12.188 (11.836)	111	2.85
05	$[\text{Co}(\text{C}_{34}\text{H}_{35}\text{N}_6\text{O}_2)](\text{NO}_3)_2$	742.635	Light Pink	250	54.989 (54.547)	4.750 (4.239)	15.088 (14.885)	119	2.86
06	$[\text{Co}(\text{C}_{34}\text{H}_{35}\text{N}_6\text{O}_2)](\text{CH}_3\text{COO})_2$	736.715	Pink	250	61.953 (61.530)	5.609 (5.227)	11.407 (11.002)	123	2.85
07	$[\text{Ni}(\text{C}_{34}\text{H}_{35}\text{N}_6\text{O}_2)]\text{Cl}_2$	689.31	Yellow	250	59.243 (58.985)	5.118 (4.839)	12.192 (11.833)	114	-
08	$[\text{Ni}(\text{C}_{34}\text{H}_{35}\text{N}_6\text{O}_2)](\text{NO}_3)_2$	742.412	Yellowish Green	250	55.006 (54.748)	4.752 (4.289)	15.093 (14.879)	119	-
09	$[\text{Ni}(\text{C}_{34}\text{H}_{35}\text{N}_6\text{O}_2)](\text{CH}_3\text{COO})_2$	736.492	Yellow	250	61.971 (61.635)	5.611 (5.275)	11.411 (10.936)	124	-
10	$[\text{Zn}(\text{C}_{34}\text{H}_{35}\text{N}_6\text{O}_2)]\text{Cl}_2$	695.97	Buff	250	58.676 (58.175)	5.069 (4.879)	12.075 (11.835)	109	-
11	$[\text{Zn}(\text{C}_{34}\text{H}_{35}\text{N}_6\text{O}_2)](\text{NO}_3)_2$	749.072	Buff	250	54.517 (54.017)	4.709 (4.335)	14.959 (14.435)	105	-
12	$[\text{Zn}(\text{C}_{34}\text{H}_{35}\text{N}_6\text{O}_2)](\text{CH}_3\text{COO})_2$	743.152	Buff	250	61.416 (60.997)	5.561 (5.036)	11.308 (10.915)	111	-

4.2 Infrared spectra

The important absorption bands of the free ligand and those of the complexes are presented in Table 2. The characteristic band at 1677 cm^{-1} and 1729 cm^{-1} indicate the presence of C=N, and C=O group in the free Schiff base. In the IR spectra of complexes, these bands shifts to lower frequencies which indicates that the nitrogen of azomethine group and oxygen of keto group are coordinated to metal ion.[27-29] furthermore, the appearance of new bands in the region $460\text{-}510\text{ cm}^{-1}$ $410\text{-}460\text{ cm}^{-1}$ are due to $\nu\text{M-N}$ and $\nu\text{M-O}$ [30-31]

Table No. 2: IR spectra of complex.

Compound	$\nu(\text{C} = \text{N})$	$\nu(\text{C} = \text{O})$	$\nu(\text{M} - \text{N})$	$\nu(\text{M} - \text{O})$
$[\text{Ni}(\text{C}_{34}\text{H}_{35}\text{N}_6\text{O}_2)]\text{Cl}_2$	1572-1593	1645	516	447

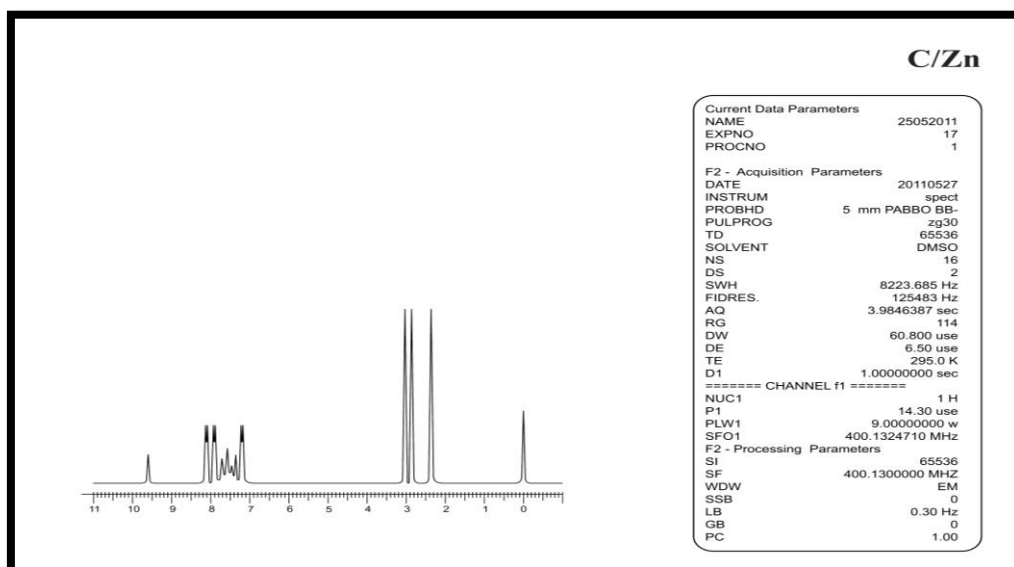


4.3 NMR spectra

The ^1H NMR spectra of complexes in DMSO- d_6 at room temperature shows following signals $\delta = 2.4(\text{s}, 6\text{H}, =\text{C}-\text{CH}_3)$, $\delta = 2.90(\text{s}, 6\text{H}, \text{N}=\text{C}-\text{CH}_3)$, $\delta = 3.10(\text{s}, 6\text{H}, -\text{N}-\text{CH}_3)$, $\delta = 7.20-8.20(\text{m}, 14\text{H}, \text{Ar}-\text{H})$ (Table 3)

Table No. 3: ^1H NMR Spectral data of the complex.

Complex	=C-CH ₃	-N-CH ₃	-N = C-CH ₃	Phenyl Multiplate
[Zn(C ₃₄ H ₃₅ N ₆ O ₂)]Cl ₂	2.35	3.05	2.85	7.10 to 8.10

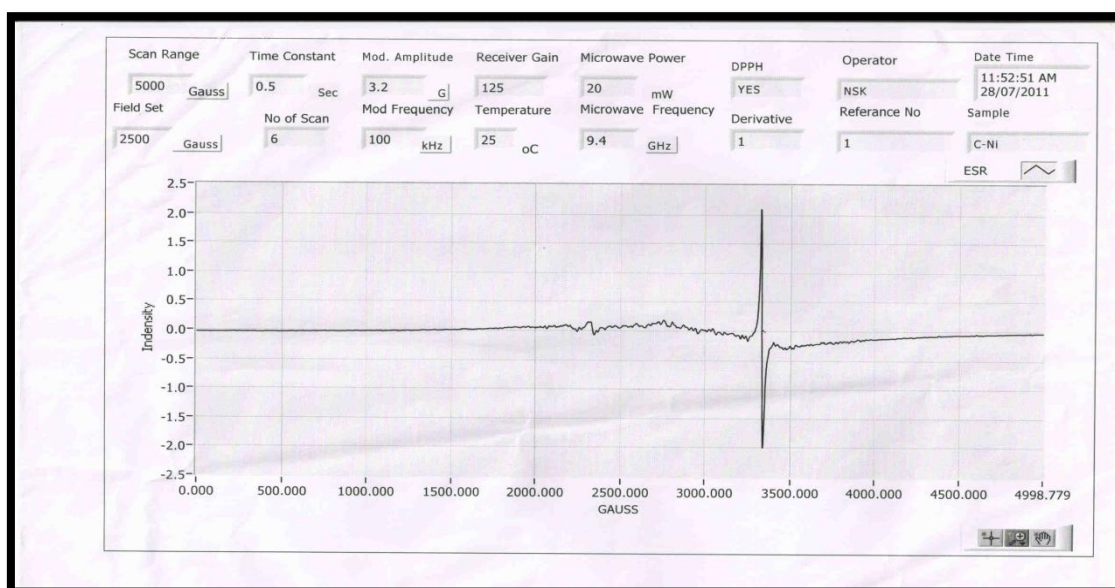


4.4 EPR spectra

The EPR spectra of the [Ni(C₃₄H₃₅N₆O₂)](NO₃)₂ complex in powder form at room temperature shows anisotropic signals with $g_{\parallel} = 1.9972$, $g_{\perp} = 1.9946$, and $g_{\text{iso}} = 1.9954$, $A_{\parallel} = 16.66\text{G}$, $A_{\perp} = 25.00\text{G}$, exchange coupling interaction constant $G = 0.6486$. This finding indicates that the observed 'g' values for the complex are less than 2.3 in agreement with the covalent character of the metal ligand bond. The trend $g_{\parallel} > g_{\perp} > 2.0023$ observed for the Ni (II) complex indicated that unpaired electron is localized in the dx^2-y^2 orbital [32-37].

Table No. 4: EPR parametrs of metal complex

Complex	Gyromatric ratio g	A gauss	G	e/gm*10 ²¹
[Ni(C ₃₄ H ₃₅ N ₆ O ₂)](NO ₃) ₂	$g_{\parallel} = 1.9972$ $g_{\perp} = 1.9946$ $g_{\text{av}} = 1.9954$	$A_{\parallel} = 16.66$ $A_{\perp} = 25$	0.6486	1.5047



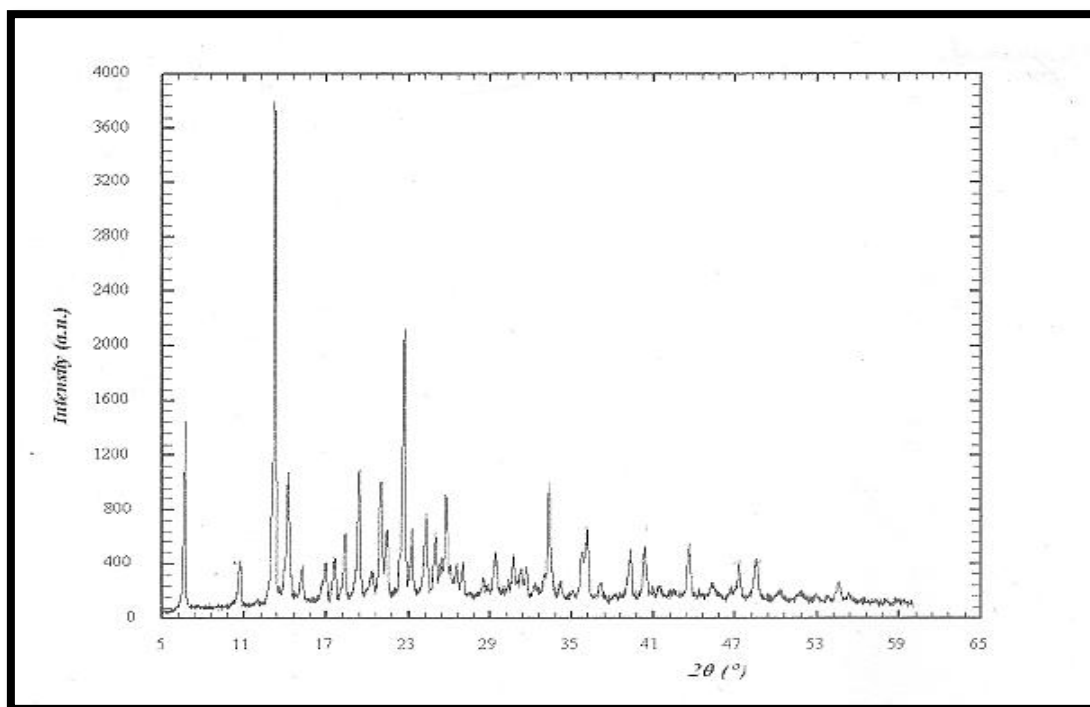
4.5 Powder X-ray analysis

Powder XRD diffractogram of Co (II) complexes were recorded in the range $20-80^\circ$ at wavelength 1.5447°A . The diffractogram and associated data depict the 2θ value for each peak, relative intensity and inter-planar spacing (d-values). Major reflexes were used to determined corresponding interplaner distances. The X-ray diffraction pattern of Co(II) complexes with respect to major peaks having relative intensity greater than 10% has been indexed by using computer programme. Miller indices (hkl), unit cell parameters and unit cell volume were also obtained from above indexing method. The unit cell of Co(II) complex yielded values of lattice constants, $a = 18.194798^\circ\text{A}$, $b = 13.448669^\circ\text{A}$, $c = 3.908525^\circ\text{A}$ and unit cell volume 956.40°A^3 . Also, in association with these cell parameters, the conditions such as $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$ required for sample to be orthorhombic were tested and found satisfactory. In conclusion the complexes Co(II) have orthorhombic crystal system[38-39].

The experimental density values of complexes were determined using specific gravity method and found to be 0.7732 g cm^{-3} for the Co(II) complexes respectively. Using the experimental density values ρ , the molecular weight of the complexes (M), Avogadro's number (N), and the volume of unit cell (V), the number of molecules per unit cell (n) were calculated using the equation $\rho = nM/NV$ and they were found to be one. With these values, the theoretical densities were computed and found to be 0.7758 g cm^{-3} for respective complexes. Comparison of experimental and theoretical density value shows good agreement within the limits [40-44].

Table No. 5: Millar indices and inter planer distances

Complex	h k l	2θ observed	2θ observed	d
[Co(C ₃₄ H ₃₅ N ₆ O ₂)(NO ₃) ₂]	0 1 0	6.577	6.567	13.4281
	0 2 0	13.176	13.156	6.7140
	1 2 0	14.046	14.030	6.3002
	4 0 0	19.502	19.499	4.5482
	0 0 1	22.744	22.733	3.9066
	1 1 1	24.167	24.193	3.6797
	2 1 1	25.669	25.655	3.4676



4.6 Thermal analysis

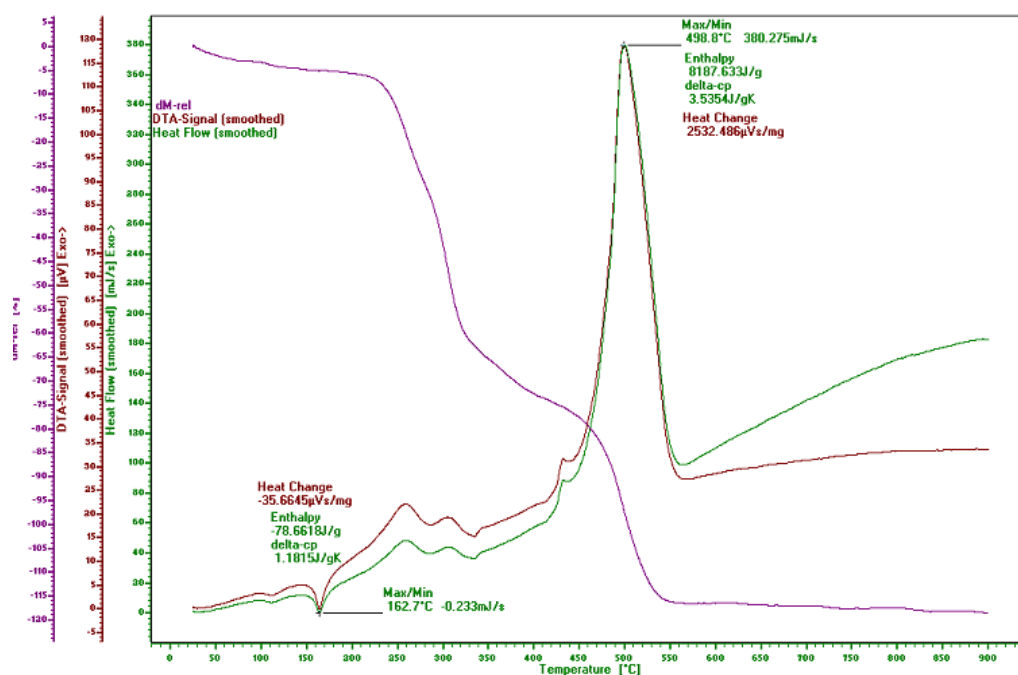
On the TG curve of Co (II) complex, the mass loss of 8.10% (calcul. 8.04%) in the range of 30-240°C indicating the removal of non-coordinated nitrate. An endothermic peak on DTA curve at 160°C also corresponds to the loss of nitrate. The second step of the decomposition between 250-320°C with 58.06% mass loss (calcul. 58.28%) is attributed to the removal of the coordinated organic moiety and remaining part of nitrate of the complex. The third step of decomposition between 320-550°C indicating the removal of remaining coordinated organic moiety. An exothermic peak on DTA curve at 510°C also corresponds to the removal of organic moiety. The mass loss continued with slow decomposition of the remaining part up to 770°C corresponds to final residue of cobalt oxide [45-54].

4.7 Kinetic Data

The kinetic and thermodynamic parameters viz, order of reaction (n), energy of activation (E_a), three exponential factor (Z) etc. for non- isothermal decomposition of metal complexes were determined by the Horowitz and Metzger approximation method. The data obtained are given in (Table 6). The calculated values of the activation energy of the complexes are relatively low, indicating the autocatalytic effect of the metal ion on the thermal decomposition of the complex. The negative activation entropy values suggest that the activated complex were more ordered than the reactants and that the reactions were slow. The more ordered nature may be due to polarization of bonds in activated state [55].

Table No. 6: Thermal decomposition and kinetic parameters of complex

Complex	DTA peak °C	Temp. range °C	Mass loss (%) observed (calculated)	Nature of decomposition	Order of reaction	ΔE kg/mole	ΔS JK/mole	GKJ/ mole	Frequency factor Z
[Co(C ₃₄ H ₃₅ N ₆ O ₂)] (NO ₃) ₂	160	0-240	8.10(8.04)	Nitrate	1.9	4.283	-291.694	20.877	5.758x10 ⁻³
	260	250-470	58.06(58.28)	Nitrate + Ligand	1.9	61.203	-179.812	74.873	5.359x10 ³
	510	470-550	27.42(26.07)	Ligand	1.9	11.780	-266.577	36.928	1.957x10 ⁻¹



4.8 Antimicrobial activity

The *in vitro* antibacterial activities of synthesized complexes have been studied by disc diffusion method. The antibacterial activities were done at 100 µg/ml concentrations in DMF solvent using four bacterial strains (*S. typhi*, *S. aureus*, *E. coli* and *B. subtilis*) by the minimum inhibitory concentration (MIC) method. These bacterial strains were incubated for 24 h at 27°C. Standard antibacterial (Cefodox and Linazoid) were used for comparison under similar conditions. Activity was determined by measuring the diameter of the zone of inhibition (mm) [56]. It is observed that Zn(II) and Cu(II) complexes are more active against the bacterial strains *S. typhi* and *E. coli* as compared to other bacterial strains. Co (II) and Ni(II) complexes were found to be moderately active against all bacterial strains.

Table 7: Antibacterial activity of complexes of type $[M(C_{34}H_{35}N_7O_4)]X_2$

Sr. No.	Complex	Inhibition zone (mm)			
		<i>S. typhi</i>	<i>S. aureus</i>	<i>E. coli</i>	<i>B. subtilis</i>
1	[Cu(L ₁)]Cl ₂	6.8	5.2	6.9	5.1
2	[Cu(L ₁)](NO ₃) ₂	6.9	5.6	7.0	5.0
3	[Cu(L ₁)](CH ₃ COO) ₂	6.8	5.5	6.7	5.3
4	[Co(L ₁)]Cl ₂	5.3	5.0	4.9	4.7
5	[Co(L ₁)](NO ₃) ₂	5.6	5.1	4.6	4.3
6	[Co(L ₁)](CH ₃ COO) ₂	5.2	5.1	4.7	4.6
7	[Ni(L ₁)]Cl ₂	6.1	5.2	5.1	5.0
8	[Ni(L ₁)](NO ₃) ₂	6.0	5.0	5.2	5.0
9	[Ni(L ₁)](CH ₃ COO) ₂	6.1	5.1	5.0	5.1
10	[Zn(L ₁)]Cl ₂	6.7	5.9	4.9	5.3
11	[Zn(L ₁)](NO ₃) ₂	6.5	5.8	5.0	5.6
12	[Zn(L ₁)](CH ₃ COO) ₂	6.7	5.7	5.1	5.2
13	Ligand (L ₁)	4.4	4.6	4.9	4.2
14	Cefodox	7.0	7.4	7.3	6.8
15	Linazoid	7.6	6.9	7.8	7.2

L₁ = (C₃₄H₃₅N₇O₄)

5. Conclusion

Based on elemental analysis, molar conductance, infrared, magnetic moment, EPR, all the complexes are assigned to be in square planer geometry and exhibit coordination number four. Biological studies of these complexes reveal that these complexes are potentially active than their respective ligands. The value of orbital reduction factor and covalency factor suggest the covalent nature of the complexes. Thermal decomposition of complexes reveals that Co- complex decompose in three steps and transform into the corresponding metal oxide.

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