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Synthesis and spectrochemical characterization of Cu (II) and Co (II) new imine metal complexes - Biological activity

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ABSTRACT

The new azomethine and its solid metal complexes derived from 2-amino 6-picoline and 2, 4, 5 trimethoxy benzaldehyde (2TMBAMP) by using modified Sand Mayer's method. The derived colored complexes of Cu & Co with 2TMBAMP are characterized by physicoelectrochemical techniques like IR, NMR, ESR, Elemental analysis, Magnetic susceptibility, and UV-Vis Spectrophotometer, TGA-DTA and conductometric measurements. In addition the authors have been screened the compounds for biological activity. It was found that the compounds have shown activity against the organisms like Escherichia coli, Bacillus subtilis and Klebsiella.

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KEYWORDS

2TMBAMP Schiff base;
Biological activity;
Organisms.

INTRODUCTION

Schiff base of various transition metal ions were investigated for their Coordinating capability, Pharmaceutical and biological activities^[1-3] these complexes are used as catalysts for water photolysis^[4] and for oxygen reduction at modified carbon cathode^[5]. Some compounds have been used industry and catalytic hydrogenation of unsaturated hydrocarbons^[6] Schiff bases are also used for analytical purpose^[7] in the determination of metal ions, and some Schiff base derivatives have been used in the biological extraction of metals^[8], paint industry and medicinal bioinorganic fields^[12-16]. The applications of such complexes depend to a large extent on their molecular structure. The author in the present study provides a new series of metal complexes of Cu (II) and Co (II) with Schiff base ligand derived from 2-amino 6-picoline and 2,4,5 trimethoxy benzaldehyde (2TMBAMP). These complexes were characterized

by elemental analysis IR, NMR, ESR, VSM, UV-Vis Spectrophotometer, TGA-DTA and conductometric measurements determine the mode of bonding and geometry, biological activities of the ligands and metal complexes were also studied.

EXPERIMENTAL

All chemicals used in the present investigation were pure BDH chemicals.

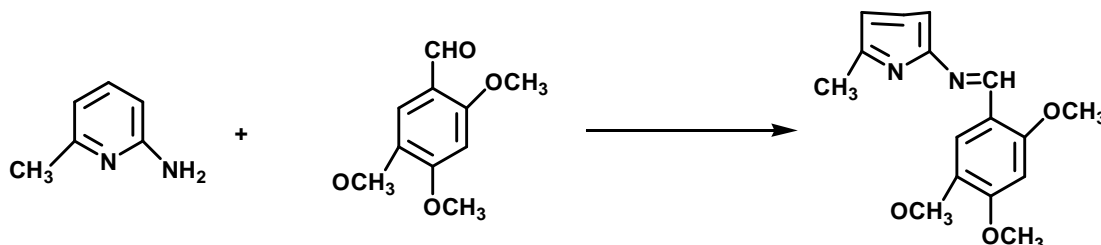
Preparation of the ligand & its metal complexes

2-amino-6-methyl pyridine and 2, 4, 5 trimethoxy benzaldehyde Schiff base (2TMBAMP)

2, 4, 5 trimethoxy benzaldehyde (0.018 moles) and 2 amino-6-methyl pyridine (0.018mole) were dissolved in 50 ml of methanol were taken in 250ml borosil reflection flask and two drops of HCl was added. The mixture was refluxed for 1 hour on water bath and then

cooled at room temperature, yellow coloured sharp needles were separated out and washed with methanol and dried in vacuum. This compound was recrystallized from methanol, then it proceeds for preparation of metal complexes by adding requisite amount of Schiff base 2gm (0.0076 moles) in 50 ml of 50% methanol to the Copper and Cobalt metal ions 2.2 gm (0.0076 moles) in water in the presence of sodium ac-

etate and refluxed the mixture for two hours on a water bath. The reaction mixture poured in excess of cold water. Light yellow and green colour precipitates of metal complexes were obtained with good yield. These products were washed several times with hot water and cold methanol to free them from unreacted metal salt ligand respectively and finally with ether and dried in a vacuum desiccator.



RESULT AND DISCUSSION

Conductivity measurements

The molar conductance of complexes in DMF ($\sim 10^{-3}$ M) was determined at $27 \pm 2^\circ\text{C}$ using Systronic 303 direct reading conductivity bridge. Copper (II) and Cobalt (II) complexes of azomethine compounds formed due to the condensation of 2-amino 6-methyl pyridine and 2, 4, 5- trimethoxy benzaldehyde (2TMBAMP) ligand was prepared. It was observed

that highly these complexes are soluble in dimethylformamide (DMF). Therefore, these metal chelates are dissolved in DMF to perform conductivity measurements. A known amount of solid complexes is transferred into 25ml standard flask and dissolved in dimethyl formamide (DMF). The contents are made up to the mark with DMF. The complex solution is transferred into a clean and dry 100ml beaker. The molar conductance values of these metal complexes are given in the TABLE 2. These values suggest non-electrolytic nature^[9] of the present complexes.

TABLE 1 : Analytical data of the ligands and their metal complexes.

Molecular Formula X=H ₂ O	Molecular Weight In gms	Colour	Yield in %	Elemental analysis							
				Carbon %		Hydrogen %		Nitrogen %		Metal %	
				Calc.	Found	Calc	Found	Calc	Found	Calc	Found
L=C ₁₆ H ₁₇ N ₂ O ₃	286.31	Yellow	78	67.13	66.18	5.94	6.32	9.79	10.54	-----	-----
[Cu.L ₂] ₂ X	653.54	Light Yellow	71	58.75	58.64	4.84	4.58	8.56	8.47	9.7	9.5
[Co.L ₂] ₂ X	648.93	Green	73	59.17	59.11	4.93	4.87	8.62	8.54	9.0	7.9

TABLE 2 : Molar conductivity of copper and cobalt complexes

Metal Complexes	Molar conductance (ohm ⁻¹ cm ² mol ⁻¹)
Cu (2TAMBAMP) ₂	22
Co (2TMBAMP) ₂	19

Electronic spectra

In UV-Visible electromagnetic radiation, the transitions are associated with the electronic energy levels of the compound under investigation. The electronic spectra were recorded on a Thermo Spectronic Heylos α Spectrophotometer. The transition metal ions occur

in a variety of structural environments. Because of this, the electronic structures are extremely varied. The electronic structures have been identified with UV-Visible spectroscopy.

2TMBAMP and its metal complexes

The electronic spectra of the aqueous solutions of Cu⁺² and Co⁺² individual ions are compared with the corresponding complexing nature. The data is given in TABLE 3, Figure 1 (a, b and c). The data indicates that the energy of the d-d transitions in the complexes is slightly less when compared to the corresponding aqua

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ions, either because of slight covalent interaction of the 3d vacant orbitals with ligands, leading to some delocalization with consequent reduction in interelectronic repulsion, or by increased nuclear shielding of the orbitals due to slight covalent ligand-metal electron drift.

TABLE 3 : Electronic spectral data

Complexes	λ_{\max} of metal ions in nm	λ_{\max} of the complex in nm	λ_{\max} of the ligand in nm
Cu(2TMBAMP) ₂	328.5	329	303.5
Co(2TMBAMP) ₂	313.5	314	303.5

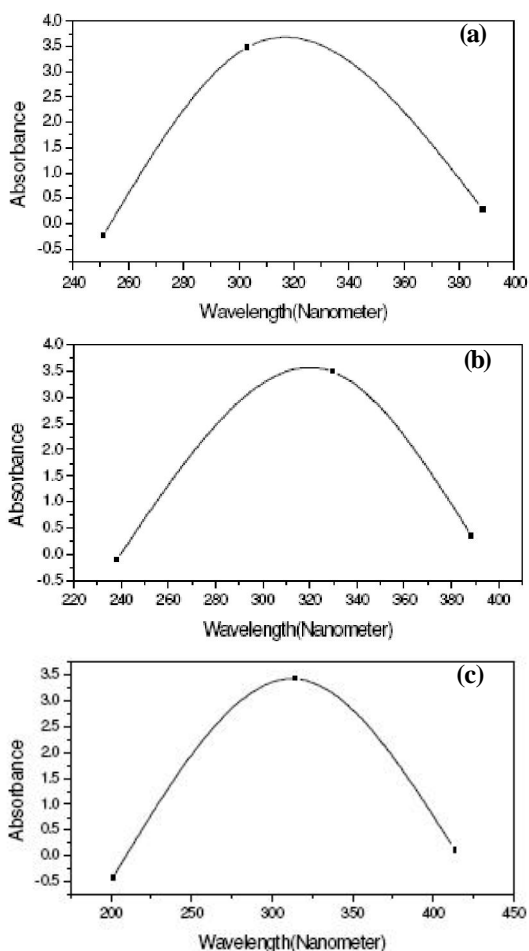


Figure 1 : Spectrophotometric determination of 2TMBAMP and its Cu & CO metal complexes

The observation showed that the transitions occurred at 303.5 nm for the ligand. But on complexation with the different metal ions like copper and cobalt, new bands appeared at 328.5 nm, 313.5 nm respectively corresponding to the transition charge transfer from the ligand to the different metal ions^[10]. Bands occurring in the region of 372nm to 327nm for all complexes are assigned to charge transfer transition (L → M).

Based on the above results octahedral structure is proposed for Cu⁺² and Co⁺² complexes.

Infrared spectra

Infrared spectra were recorded with a Perkin-Elmer IR 598 Spectrometer (4000-400 cm⁻¹) using KBr pellets. Infrared spectroscopy is one of the many valuable analytical techniques currently available to the chemist which is based on the interaction of electromagnetic radiation with the matter. By utilizing this spectroscopy, the presence of important functional groups in the compound can be identified.

2TMBAMP and its metal complexes

TABLE 4 through light on the observation made in analyzing IR spectra of ligand and metal complexes. The typical IR spectra are presented in the Figure 2 and 3 (a, b).

TABLE 4 : The important IR bands of the ligand and their metal complexes

Compound	OH (water)	$\nu_{\text{(OH) phenolic}}$	$\nu_{\text{(C=N)}}$	$\nu_{\text{(C=N) Ring}}$	$\nu_{\text{(M-O)}}$	$\nu_{\text{(M-N)}}$
2,TMBAMP SB	-	3408.20	1659.95	1608.76	-	-
2,TMBAMP Cu	3340.44	-	1660.20	1634.12	640.04	579.12
2TMBAMP Co	3854	-	1660.01	1608.79	640.22	579.88

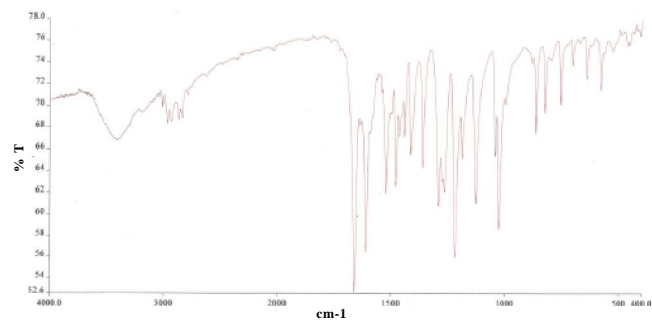


Figure 2 : IR spectrum of 2TMBAMP ligand.

The bands due to $\nu_{\text{(C=N)}}$ showed that the free picoline moiety is^[11] located at 1608.76 cm⁻¹. In the IR spectra of the ligand under investigation corresponding to the picoline moiety $\nu_{\text{(C=N)}}$ of free ligand shifted^[12] to 1634.12 cm⁻¹. Hence it was found that the nitrogen atom of the picoline moiety coordinated to the metal (II) ion in the complex under investigation.

The IR spectra of metal chelates show the disappearance of the $\nu_{\text{(OH) phenolic}}$ ^[13] and $\nu_{\text{(C-OH)}}$ bands at 3408.20-1218.41 cm⁻¹ respectively. It indicates the proton displacement from the phenolic (OH)

group on complexation. Thus bonding of the metal ions to the ligands under investigation takes place

through a covalent link with oxygen of the phenolic group.

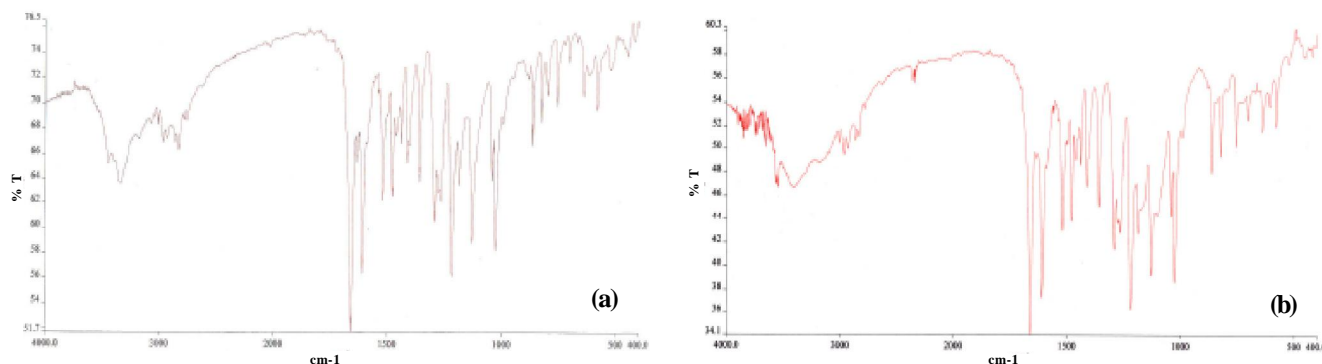


Figure 3 : IR spectrum of (a) Cu (2TMBAMP)₂ and (b) Co (2TMBAMP)₂ complex.

The Infrared spectrum of all solid metal complexes under investigation exhibit a broad band^[18] around 3340.44-3854 cm⁻¹ which is attributed to $\nu_{(OH)}$ of water or methanol molecules associated with complex formation. The mono and bi nuclear Cu (II) and Co (II) complexes showed new bands of ranges 823.32-863.86 cm⁻¹ respectively. These are attributed to OH rocking and wagging vibrations of coordinated water molecules.

Bangalore in DMSO-d₆ solvent at room temperature.

2TMBAMP and its metal complexes

The observation noted in the chemical shift values of the ligand and metal complexes were shown in TABLE 5, Figure 4 and 5 (a, b).

TABLE 5 : ¹HNMR spectrum of the ligands and its metal complexes in DMSO-d₆ in ppm

Compound	H-C=N	CH ₃	-OCH ₃	Ar-H
2TMBAMPSB	10.32	1.81	3.98,3.93&3.88	
2TMBAMPCu	10.0-10.4	-	4.0	6.51-7.50
2TMBAMPCo		-	4.0	6.6-7.4

It was noted that the ligand at 1661.70 cm⁻¹ corresponds to^[17] azomethine group $\nu_{(C=N)}$ of free ligand reduced by 1-30 cm⁻¹. Hence the nitrogen atom of the azomethine group coordinates the existence of new bands in the IR spectrum of the complex at 640.04-640.22 and 579.12-579.88 cm⁻¹ which are associated to $\nu_{(M-O)}$ and $\nu_{(M-N)}$ respectively^[19-21].

¹H Nuclear magnetic resonance spectra

¹H Nuclear magnetic resonance (NMR) spectroscopy is an analytical technique based on the magnetic properties of nuclei. By using this spectroscopy, the nature of protons and the number of protons present in the molecule.

In the present study, ¹H nuclear spectra were recorded on av-400MHZz NMR spectrometer in IISc

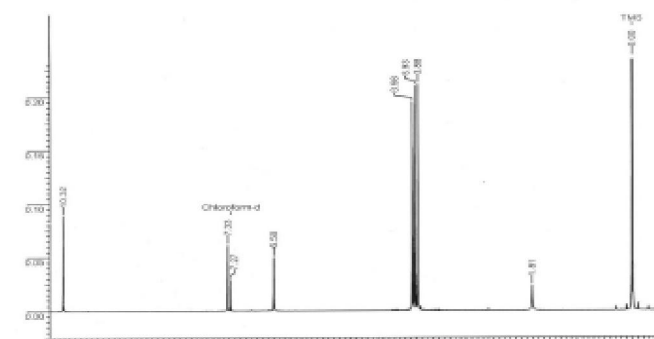


Figure 4 : NMR spectrum of 2TMBAMP ligand.

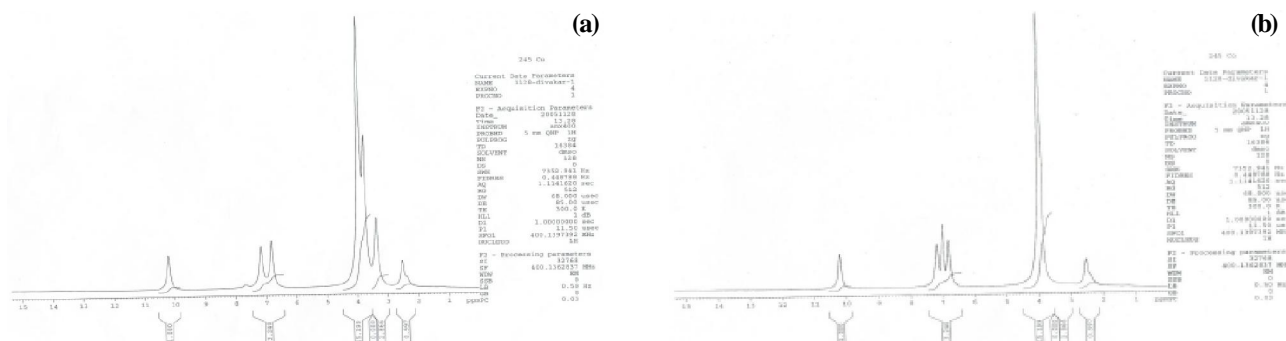


Figure 5 : NMR spectrum of a) Cu (2TMBAMP)₂ and b) Co (2TMBAMP)₂ complex.

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The methoxy protons of the 2TMBAMP Schiff bases were observed at^[22] 3.98, 3.93 and 3.88 ppm. The peaks in the aromatic region were seen as a singlet in the range of 7.27 ppm. A singlet at 10.32 ppm due to the azomethine proton.

In the case of the Cu and Co complexes the signal due to the azomethine protons were shifted from 10.32 ppm to 10.0 and 10.04 ppm respectively. This shifting indicates the shielding of the azomethine proton on coordination through nitrogen atom of the azomethine group. The aromatic ring protons that are seen in the range of 6.51-7.50 ppm^[22] become broad and less intense compared with the corresponding Schiff base. This effect may be due to the drifting of ring electron towards the metal ion following complexation to the metal ion. The singlet at 2.5 ppm in the case of copper (II) & cobalt (II) complexes indicates the complexation of water molecules by coordination with metal ion.

Electronic spin resonance spectra

In the present study the X-band (~9.3 GHz) ESR

spectra of Cu (II) & Co(II) complexes in DMF were recorded at room temperature and at liquid nitrogen temperature (LNT) on a Bruker ESP 300E spectrometer. The ESR spectrum obtained from the instrument is a plot of the first derivative of the absorption curve as a function of the magnetic field which was calibrated with an NMR gauss meter and the exact frequency was determined using DPPH radical as a field maker.

Analysis of 2TMBAMP through ESR spectra of copper & cobalt complexes

The ESR spectra of the complex in polycrystalline state exhibit only one broad signal, which is attributed to dipolar broadening and enhanced spin-lattice relaxation. Anisotropic spectra obtained for these complexes in DMF at LNT and representative ESR spectra of Cu (II) & Co (II) complexes were presented in Figure 6 (a) & (b). In this low temperature spectrum, four peaks of small intensity have been identified which are considered to originate from g_{\parallel} component.

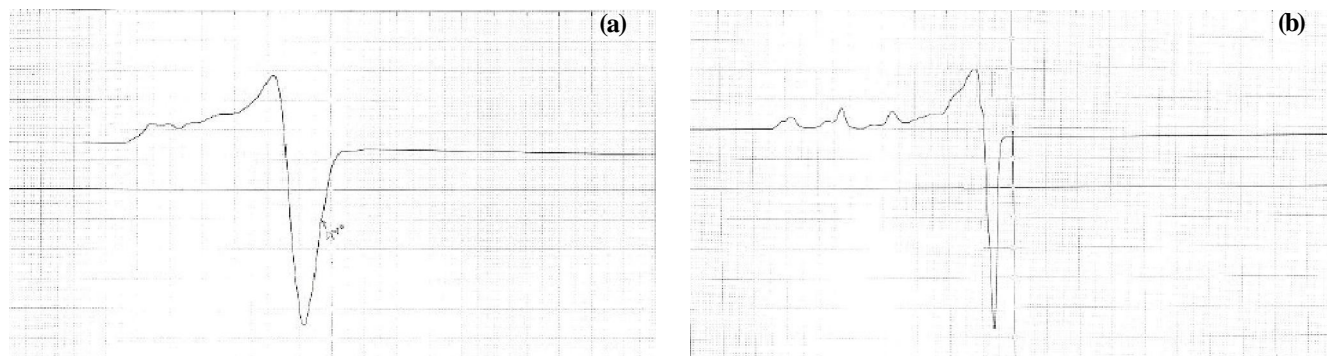


Figure 6 : ESR spectrum of (a) Cu (2TMBAMP)₂ and (b) Co (2TMBAMP)₂ complex.

The spin Hamiltonian, orbital reduction and bonding parameters of the Cu & Co complexes were presented in TABLE 6. The g_{\parallel} and g_{\perp} are computed from the spectrum using DPPH free radical as g marker. Kvelson & Neiman^[23] have reported that g_{\parallel} value is less than 2.3 for covalent character and is greater than 2.3 for ionic character of the metal-ligand bond in complexes. Applying this criterion, the covalent bond char-

acter can be predicted to exist between the metal and the ligand complexes^[24]. The trend $g_{\parallel} > g_{ave} > g_{\perp} > 2.0023$ observed for the complex suggest that the unpaired electron is localized in $d_{x^2-y^2}$ and d_{z^2} orbital of the copper (II) ions for the complex. It is observed that G value for these complexes are greater than four and suggest that there are no interactions between metal-metal centers in DMF medium.

TABLE 6 : Spin hamiltonian and orbital reduction parameters of copper and cobalt complexes in DMF solution

Complex	g_{\parallel}	g_{\perp}	g_{ave}	G	A_{\parallel}^*	A_{\perp}^*	A_{ave}^*	$d-d$	K_{\parallel}	K_{\perp}	P^*	α^2
Cu(2TMBAM) ₂	2.5864	2.2038	2.3313	4.29	0.0194	0.0042	0.0092	16000	1.8871	2.2129	0.031	0.4832
Co(2TMBAM) ₂	2.211	2.014	2.079	4.18	0.0178	0.0039	0.0085	15896	1.8038	2.3110	0.029	0.4150

The ESR parameters g , g_{\parallel} , A_{\parallel} and A_{\perp} of the complexes and the energies of d-d transitions are used to evaluate the orbital reduction parameters (K_{\parallel} , K_{\perp}) the bonding parameters (α^2), the dipolar interaction (P)^[25]. The observed $K_{\parallel} < K_{\perp}$ indicates the presence of out of plane Pi-bonding. The α^2 values for the present chelates lie in the range 0.41-0.48 and support the covalent nature of these complexes. Giordano and Bereman suggested the identification of bonding groups from the values of dipolar term P . The reduction of P values from the ion value (0.036cm^{-1}) might be attributable to the strong covalent bonding. The values of P obtained for the present complexes in between 0.029 - 0.031cm^{-1} and remain consistent with bonding of metal ions to oxygen and nitrogen donor atoms respectively. The shape of ESR lines, ESR data together with the electronic spectral data suggest an octahedral geometry for these complexes^[26].

Magnetic susceptibility measurements of copper and cobalt complexes

The magnetic susceptibility values of the copper complex at room temperature are consistent with the range 5.2 BM present in TABLE 7. There is considerable orbital contribution and effective magnetic moments for octahedral complex at room temperature. For high spin octahedral complexes, the magnetic moments are around 5.2 B.M in magnetically dilute compounds. The magnetic properties of cobalt complex are useful to know the geometry. In the case of cobalt complex the magnetic moment value of 6.2. The magnetic moments of $(2\text{TMBAMP})_2\text{Co(II)}$ complexes are very close to spin only value.

TABLE 7 : Magnetic moments of copper and cobalt complexes

Complex	Magnetic moment (B.M)
$(2\text{TMBAMP})\text{Cu}$	5.2
$(2\text{TMBAMP})_2\text{Co}$	6.2

Thermal analysis

The thermal studies of these complexes are carried out to know the stability of the complexes on thermal decomposition, as well as to know the different final products that are obtained in thermal decomposition having novel catalytic properties. Thermo gravimetric analyses of the metal complexes were carried out by using the Perkin Elmer system in thermal analysis centre: STIC KOCHIN. All possible precautions were taken to optimize conditions, so as to carry out all the thermogravimetric analysis experiments under the same conditions.

Study of 2TMBAMP and its copper & cobalt metal complexes by TGA-DTA spectra

The complexes of thermo analytical data are given in the TABLE 8. The copper and cobalt complexes are thermally stable up to 110 and 181.50°C respectively. The first stage of decomposition corresponding to endothermic dehydration of the complexes and the two lattice water molecules are lost in the temperature range^[28] 110-222.10°C and 181.50-219.31°C to give anhydrous complex. The second decomposition stage with two (or) three endothermic peaks are known as stable intermediate formed around 450°C and 565.38°C respectively and they undergo decomposition resulting in the loss of ligand moiety up to 600°C and 720.09°C. Exothermically decomposition product at high temperature^[29] i.e. above 600°C and 720.09°C respectively. The decomposition behavior of the complexes observed in nitrogen atmosphere. All the experimental mass loss and total mass loss percentage values found were shown in the TABLE III.7. The DTA peak temperature for the removal of the anhydrous ligand complex^[30] follows the order of $\text{Co } 250 > \text{Cu } 215.58$ and suggests the strength of the metal-ligand bond.

TABLE 8 : Thermal analytical data of the ligand and their metal complexes

Complex $\text{X}=\text{H}_2\text{O}$	Molecular Weight in Gram	Weight of the Complex taken in mgs	Stage	Temperature	Probable assignment	Mass loss (%)	Total mass loss (%)
				range decreasing weight loss in°C			
$\text{Cu L}_2 2\text{X}$ $\text{L} = \text{C}_{16}\text{H}_{17}\text{N}_2\text{O}_3$	653.54	6.084	1	110-222.10	Loss of 2H ₂ O molecules	4.5	70.22
			2	450-600	Loss of 2L molecules	25.53	
			3	600 above	Corresponds to CuO	40.35	
$\text{Co L}_2 2\text{X}$ $\text{L} = \text{C}_{16}\text{H}_{17}\text{N}_2\text{O}_3$	648.93	7.934	1	181.50-219.31	Loss of 2H ₂ O molecules	4.1	88.83
			2	565.38-720.09	Loss of 2L molecules	32.35	
			3	728.09 above	Corresponds to CoO	52.38	

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Biological activity

The author in this present investigation attempted to find out antibacterial activity of ligand and their metal complexes against Escherichia coli, Klebsiella and Bacillus subtilis choosing serial paper disc method TABLE 9. The results of the biological activity of the metal complexes indicated the following facts.

TABLE 9 : Antibacterial activities of ligands and their transition metal complexes (Zone formation in mm)

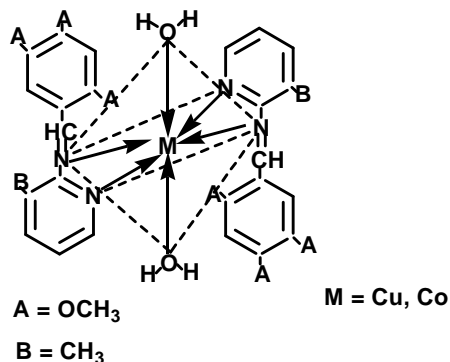
Compound	E.Coli	Klebsiella	Bacillus.subtilis
2TMBAMP	15	16	17
2TMBAMPCu	20	20	20
2TMBAMPCo	16	20	18

A comparative study of the ligand and their complexes indicates that the metal chelates exhibited higher antibacterial activity than that of the free ligand. The increase in the antibacterial activity of metal chelates was found due to the effect of metal ion on the metal chelates which could be explained on the basis of overtones concept and chelation theory.

On chelation the polarity of the metal ion reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of positive charges of metal ion with donor groups. It was further noted that the delocalization of π -electrons over the whole chelate ring enhanced the lipophilicity of the complexes. This increased lipophilicity^[31] enhanced the penetration of the complexes into lipid membrane and blocking the metal sites on enzymes of microorganism.

CONCLUSION

Based on the above results, the structure of the complexes under investigation can be formulated as follows.



Suggested the structure of 2-TMBAMP metal complexes

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