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Synthesis, Characterization and Antimicrobial Activities of Cobalt (II) Complexes-Mannish Base Ligands

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ABSTRACT

Single crystals of $[Co(DP)(H_2O)_4NO_3](NO_3)_2.H_2O$, $[Co(DMP)\ (H_2O)_4NO_3](NO_3)_2.H_2O$ *were grown by the slow evaporation technique from the super saturation solution. The samples obtained were characterized by the X-ray (Powder) Diffraction and spectroscopic (IR), thermal analysis (TGA and DTA), electronic spectra, magnetic measurements and conductance measurement. The complexes were also evaluated for their antimicrobial activities using in vitro agar diffusion methods*

High lights

- The method is easy to synthesize the complexes.
- The synthetic method of complex formation is eco-friendly.
- The synthesized complexes have good antibacterial and antifungal activities.

Keywords: Metal complexes, crystal structure, antimicrobial activity.

INTRODUCTION

Coordination chemistry describes compounds that are classically termed complexes involving bonds between a Lewis acidic centre and one or many Lewis basic centres. A vast series of representative examples are known for all s-block, b-block, d-block, and f-block elements as Lewis acids. Metal coordination complexes with catalytic function have attracted extensively attention owing to their unique features for catalysis and promising application in organic reaction including Knoevenagal, Suzuki, Sonogashira, Aldol, Friedel-Crafts alkylation, acylation and alkene epoxidation reactions [1-20]. Additionally, metal coordination complexes possess potential for optics, gas separation and storage, magnetism, drug delivery and sensoring many natural compounds and drugs contain piperidine, pyran, thianone, pyrimidine and cyclohexanone ring system as a structural element. As these class of compounds exhibit pharmacological properties [21].The elaboration of versatile, flexible regio and stereo selective synthesis of chiral piperidines, pyrans, thianones, pyrimidines and cyclohexanones are a major interest to organic chemists [22] Indeed piperidones, pyrans, pyrimidines and cyclohexanones are the constituents of a number of alkaloids which possess broad spectrum of biological activities [23].

In recent years there has been a great deal of interest in exploring proximal functional groups for designing novel structures capable of performing a variety of functions. The design and synthesis of conformationally restricted molecules is an important approach towards improving the potency, selectivity etc. It is well known that a number of heterocyclic compounds containing nitrogen and sulphur exhibit a wide variety of biological activities.

The study of coordination compounds has emerged as one of the major centres of attraction for the inorganic chemists. It covers a comprehensive range of fascinating theoretical applications and synthetic works. In industries, coordination compounds play a vital role in homogenous and heterogeneous catalysis, solvent extraction, purification of water, photography, metallurgy, electrochemistry and analytical chemistry. They are also used for the formulation and improvement of semiconductors, super conductors, advanced ceramic materials and pharmaceuticals. They are essential for many life processes such as oxygen transfer, metal ion control etc.

The rapidly developing field of bioinorganic chemistry focuses on several metal complexes present in the biological system. The presence of coordination compounds in living system such as haemoglobin, myoglobin, ferredoxin and chlorophyll have created an interest among the inorganic chemists to make significant progress in refining the concept of chemical bonding and to explain the influence of bonding on the various properties of the compounds.

The role of metal atom in enzyme catalysis is currently an active subject of research, which depends upon the metal ion present. Metal containing compounds are also important in the process of chemical and energy transfer reactions which involve the transport of oxygen to the site of oxidation and various redox reactions. In this research, the synthesis and spectral characterization of two Mannich base ligands and their cobalt complexes are reported. The antimicrobial activities of the synthesized compounds were also investigated against Gram-positive and Gram-negative bacteria.

MATERIALS AND METHODS

Preparation ofpiperidin-4-ones (1): The compound (1) was prepared by adopting the following procedure. A mixture of acetone (14.5 g, 0.25 mol), benzaldehyde (53g, 0.5 mol), ethanol (20 mL) and anhydrous ammonium acetate (19.3 g, 0.25 mol) were heated on a water bath with constant shaking till the content became pale orange in color. The flask was then cooled; ether (125 mL) was added to the cold mixture and filtered. Addition of concentrated hydrochloric acid (13 mL) to the clear filtrate afforded the hydrochloride of piperidone (m.p 214-216°C) (lit 216-217°C), which was collected after washing several times with ethanol – ether (1:5). The base was liberated by suspending the hydrochloride in acetone and adding ammonia (1:1) till the hydrochloride dissolved and the free base (1) was generated by diluting with water, which was crystallized from ethanol. Yield: 90%, m. p: 104-105°C (Lit 104–105°C). (Anal. calc. %) for ligand: C-81.2, H-6.77, N-4.9 Molecular weight 249.2. Found C-80.9, H-6.77, N-5.88, Molecular weight 251. IR (cm^{-1}) : 3305(s), 3062(s), 2975(s), 1724(s), 1637(s), 1458(sd), 1078(b), 1002(s), 933(b), 821(b), 754(w), 698(b), 663(b), 611(s), 522(l).

Preparation of 2, 6–diphenyl-3-methyl piperidin-3-methyl piperidin-4-one (2): To a solution of dry ammonium acetate (9.2 g, 0.12 mol) in glacial acetic acid (12.5 g, 0.21 mol), a mixture of benzaldehyde (29 g, 0.25 mol) and n-butanone (9 g, 0.125 mol) was added, then it was heated to boiling and allowed to stand at room temperature to overnight. Concentrated hydrochloric acid (13 mL) was added. The precipitated hydrochloride was collected and washed with ethanol-ether mixture (1:5). Crystallization of the pure hydrochloride, 16g (40%) was done in ethanol-ether. M.p. 223-225°C (Lit 224-226°C). A suspension of the hydrochloride in acetone was treated with ammonia (1:1) and the free base was obtained by dilution with large quantity of water. The pure form of piperidin-4-one [3-7] was crystallized from ethanol. M.p. 96°C (Lit 96-97°C). (Anal. calc. %) for ligand: C-81.48, H-7.12, N-5.27 Molecular weight 263. Found C-81.51, H-7.17, N-5.28, Molecular weight 265. IR

(cm^{-1}): 3294(s), 3032(s), 2960(s), 1701(s), 1607(s), 1497(Sd), 1110(b), 1090(s), 930(b), 822(b), 750(w), 694(b), 663(b), 600(s), 524(l).

Preparation of Co (II) complexes with compounds (1-2): The corresponding ligands (1 and 2) (0.04 mol) and cobalt nitrate (0.002 mol) were dissolved in ethanol separately, mixed the solutions and refluxed on a water bath for 2 h at 35-40°C. A color change was observed indicating the complex formation. The complexes were separated out by evaporating the solvent, filtered, washed with ethanol, then with ether and dried in vacuum.

Elemental Analysis: Elemental analysis (C, H and N) was determined using a Carlo Erba1106 micro analytical instrument available at RSIC, IIT, Chennai. The metal content of the complexes was determined by complex metric EDTA titration method.

Estimation of Co(II) ions: The complex (100 mg) was treated with Conc. HNO_3(5 mL) and evaporated to dryness. The process of addition of conc.HNO_3 and subsequent evaporation were repeated at least four times till the residue was clearly soluble in distilled water. By addition of two drops of conc. H_2SO_4 and four drops of xylenol orange indicator to get the yellow color solution. The solution was titrated against standard EDTA solution (0.01M) until the color changes from red to yellow and the titre value, Co(II) ion content was calculated.

Conductance Measurements: Molar conductance of an electrolyte in a particular solvent depends on various factors such as dielectric constant, viscosity, specific conductivity of the solvent etc. The conductance behaviour of different type of electrolytes in various solvents has been studied by Geary Conductance measurement was performed in 10^{-3} moldm^{-3} solution of the complexes in DMF or DMSO using a Cm-82 type Elico conductivity bridge with a dip type conductivity cell fitted with a platinum electrode (cell constant = 1.0 cm^{-1}).

Magnetic Susceptibility Measurements: The magnetic susceptibility of the complexes was measured at room temperature by vibrational magnetometer available at RSIC, IIT, Chennai. From the measured magnetic susceptibilities, the effective magnetic moments were calculated using the formula,

$$\mu_{eff} = 2.84\left(\sqrt{\chi_m^{corr} XT}\right)BM$$

where μ_{eff} - Magnetic Moment, χ_m-Magnetic susceptibility , T -Absolute temperature

Infrared Spectra: The IR spectra of the different ligands and their complexes were recorded on a Schimadsu FT–IR 8400 series spectrophotometer in the region 400-4000 cm^{-1} using KBr disc technique.

Electronic Spectra: The electronic spectrum of solid complexes was recorded using Schimadsu UV-1700 pharma spec UV-Vis Spectrophotometer in the range of 200-800 nm.

Nuclear Magnetic Resonance Spectra: The proton magnetic resonance spectroscopy of the ligands and their complexes were recorded in 400 JEOL GSX spectrometer operating at 399.65 and 100.4MHz respectively using DMSO-d_6 as the solvent and TMS as internal standard.

Thermogravimetric Analysis (TGA): Thermogravimetry was a technique in which the mass of a sample is continuously recorded as it is heated at a constant rate in a suitable environment. The resulting mass versus temperature TGA curve gives valuable information about the thermal stabilities and composition of the original sample, intermediate products and ultimate decomposition residue. The instrument used for getting TGA curve was called thermo balance. The horizontal portions in a TGA curve, called plateus indicate regions of temperature where there were no mass changes and curved portions show mass losses. The curve was quantitative and hence calculations on compound stoichiometry can be made at a given temperature. A closely related application of TGA consists of (i) Determination of proper drying temperature and (ii) detailed information about thermal stabilities of analytical reagents. The general principle of TGA and its applications were discussed by Wendlandt and Mackenzie *et al*.

Differential Thermal Analysis (DTA): This was the technique of recording the difference in temperatures between the sample and the reference material as the two materials were subjected to identical temperature regions in an environment heated or cooled at controlled rate. Usually α-alumina (α-Al_2O_3) was used as the reference material. This material was known to undergo no decomposition or phase transition, i.e., no process involving enthalpy change in the temperature ranges often encounter in DTA studies. The temperature of the reference material will go on increasing uniformly, but that of sample under study will sometimes lag behind or rush fast, depending on whether an endothermic or exothermic process, was taking place. Thus, a DTA curve gives an idea of the enthalpy changes occurring in the sample as it was continuously heated or cooled. In DTA, a plot is made with ΔT against temperature. Chemical reactions, be accompanied by enthalpy changes and these would therefore be indicated in DTA curve. The simultaneous thermo gravimetry (TGA) and differential thermal analysis (DTA) measurements were carried out using a STA 1500 Shimadzu DT 40 thermal analyzer. The thermal experiments were carried out in Nitrogen atmosphere using 3-5 mg sample at a heating rate 10°C min^{-1} in the temperature from ambient to 800°C using platinum cup as the sample holder.

Cyclic Voltammetry: The electrochemical measurements were performed with an EG and G instrument model 270/250 research electrochemistry hardware and software at PSG College of Arts and Science, Coimbatore. The system consisted of a glassy carbon working electrode, silver/silver chloride reference electrode and a platinum foil counter electrode. Tetrabutylammonium perchlorate was used as the supporting electrolyte. Measurements were made at room temperature in a specially designed glass cell. The compounds were dissolved in purified and deaerated dimethyl formamide and the solutions were flushed with nitrogen gas.

X-ray (Powder) Diffraction Studies: X-ray (Powder) diffraction patterns were recorded on a Joel JDX-8030 X-ray diffractometer at the Central Electrochemical Research Institute, Karaikudi, using CuKα radiation (λ = 1.54Å). It yields a great deal of structural information about the material under investigation. Basically, this method involves the diffraction of monochromatic X-rays by a powder specimen.

Antimicrobial studies of various ligands and their complexes of Cobalt (II): The compounds synthesized were evaluated for their antibacterial and antifungal activities. The results of these studies indicate that the biological activity of the ligands increases on complexation. The evaluations were carried out using "Paper disc diffusion method" for antibacterial activity and the "Turbidity method" for antifungal activity.

Principle: Standard suspension of rapidly growing bacteria was inoculated on the surface of Muller-Hinton agro plates. Filter paper disc containing specific concentration of antimicrobial agents were pressed on to the surface and incubated at 35°C to overnight. Zone of inhibition of growth around each disc was measured and from the susceptibility was determined.

Antibacterial Activity: The synthesized ligands and their complexes were evaluated for their invitro antibacterial activity against the pathogenic microorganisms Escherichia Coli (Gram-positive) and Staphylococcus aureus (Gram-negative) using paper disc-diffusion-method. A nutrient agar at 45°C was poured into the Petridishes (25-30 mL each) and allowed to solidify. To this, 0.5-0.6 mL of 18-24 h old culture was added and inoculum was spread evenly by using a spreader. Thereafter, filter paper discs (6 mm) were dipped into the complex solution ($2x10^{-3}\mu$) and were place on seeded medium.

These plated were incubated at 37°C and extend of inhibition was measured by the zone of inhibition produced after 24 h. All the experiments were done in triplicate. Phenol was taken as a standard.

Antifungal activity: Antifungal activity of the synthesized ligands and their complexes were determined invitro against Aspergillus Niger by adopting the turbidity method. In this method 0.1mL of the sample solution (200 µg in DMF) in 5mL sterilized fungi medium were treated with 3-4 drops of 48h and old culture in a test tube. The test tubes were then shaken well and incubated for 48 h, at 37°C. The extent of inhibition was determined by measuring the decrease in turbidity in terms of % transmission at 660 µ. Salicylic acid was taken as a standard.

Minimum Inhibitory Concentration (MIC): The MIC was defined at the lowest concentration at which an antimicrobial substance will inhibit microbial growth under specified test conditions. For the MIC of any tested antimicrobial agent to have meaning, a standard protocol must be followed for each test. The protocol was detailed by publications from the national committee for clinical laboratory standards (NCCLS). Included instructions on how to prepare and store antimicrobials before testing and how to interpret test results. It was determined with slight modification in concentrations which showed better zone of inhibition in Disc diffusion method. Taking it as a centre value, many different concentrations were prepared. It was then added on the Mueller Hinton broth which was inoculated with 12 h subculture of microorganisms. It was incubated at 37°C for 37 h and measured colorimetrically at 650nm.

RESULTS AND DISCUSSION

All the Co (II) ion complexes were non-hygroscopic and pink in color. They were insoluble in benzene, carbon tetrachloride, chloroform etc. but moderately soluble in methanol, DMF and DMSO. The analytical data and composition of the complexes were presented in table 1.

Table 1. Analytical Data of Co (II) Complexes

Complex	Carbon % found (Cal)	Hydrogen % Found (Cal)	Nitrogen % Found (Cal)	Metal % Found (cal)	M.Wt Found (Cal)	M.P °C
1.	38.91 (38.94)	5.95 (5.15)	8.73 (8.02)	12.01 (11.24)	523.69 (523.9)	212- 214
2.	41.03 (40.16)	5.63 (5.39)	7.97 (7.81)	11.20 (10.95)	538.18 (537.9)	200- 203

Electrical Conductance: Molar conductance values of the different Cobalt (II) Complexes (10^{-3}M) in DMF were given in table 2. The values are in the range of 62-80ohm^{-1} cm^{2} mol^{-1}.

Table 2. Molar conductance of Co (II) complexes with ligands (1-2) (ohm^{-1}cm^{-2}mol^{-1})

Complex	Molar conductance
[Co (DP) $(H_2O)_4NO_3]NO_3.H_2O$	65
[Co (DMP) $(H_2O)_4NO_3]NO_3.H_2O$	68

Magnetic Behaviour: Magnetic moment values of different cobalt (II) complexes with ligands (1-2) were given in table 3. These values were very useful in establishing the geometry of the complexes.

Table 3. Magnetic moment of Co (II) complexes with ligands (1-2)

Complex	Magnetic moment (µeff)
[Co (DP) $(H_2O)_4NO_3]NO_3.H_2O$	4.00 BM
[Co (DMP) $(H_2O)_4NO_3]NO_3.H_2O$	4.15 BM

For an octahedral Co(II) complex, the ground state was $^4T_{1g}$. It causes an orbital angular momentum which contributes to its magnetic moment. As a result the experimental value usually lies in the range of 4.7-5.2 DM. The observed magnetic moment value of Co (II) complexes of ligands (1-2) were found to be in the range 4.0-5.2 BM. It was in good agreement with the reported values for various octahedral complexes and confirms an octahedral geometry for the synthesized Co (II) complexes. Magnetic μ_{eff} ranges from 5.02 to 5.18BM. These values were in accordance with high spin d^7complexes and they were diamagnetic in nature.

Electronic Spectra: The solid state electronic spectra of Co (II) complexes of ligands (1-2) were found to be the same. Their absorption frequencies and their assignments were recorded in table 4.

Table 4. Electronic spectra of Co (II) Complexes with Ligands (1-2) in cm^{-1}

Complex	$^4T_{1g}\rightarrow{}^4T_{2g}$ (F)	$^4T_{1g}\rightarrow{}^4T_{2g}$ (F)	$^4T_{1g}\rightarrow{}^4T_{2g}$ (F)	γ_2 / γ_1	10Dq	B	β
1.	7845	14972	18750	1.91	8923	798	0.82
2.	7799	14852	18518	2.37	8866	785	0.80

They were in accordance with the values expected for high spin octahedral configuration. A weak absorption band at 7194 – 8547 cm^{-1} (γ_1) and a shoulder at 15858 cm^{-1} (γ_2) with a multiple structured band in the visible region at 17556 – 18750 cm^{-1} (γ_3) are observed and are assigned to $^4T_{1g}(F)\rightarrow{}^4T_{2g}$ (F), $^4T_{1g}$ (F) $\rightarrow{}^4A_{2g}$ (F) and $^4T_{1g}$ (F) $\rightarrow{}^4T_{1g}$ (P) transitions respectively. The γ_2/γ_1 ratio falls within 1.87 - 2.06. All these observations lead to the conclusion, that the complexes were spin free with an octahedral geometry. The various ligand field parameters such as 10Dq, B and β are given in table 4, which were calculated from the band positions of γ_1 and γ_3 by using the relations

$$Dq = \{(2\gamma_1 - \gamma_3) + [(\gamma_3)^2 + \gamma_1\gamma_3 - (\gamma_1)^2]^{1/2}\}/20 \quad --- \quad (1)$$

$$B = \gamma_3 - 2\gamma_1 + 10Dq/15 \quad --- \quad (2)$$

The calculated β values indicate considerable covalence in the metal-ligand bond in these complexes. The values of B fall below 972.6 cm^{-1} (observed for free Co(II) ion) suggesting an appreciable covalent nature of the metal–ligand bond in these complexes. It also indicates an orbital overlap and delocalization of d-orbitals. The UV-visible spectra of complexes were shown in fig.1. The calculated values of 10Dq, B and β of the complexes lie in the same range as reported by Hussain Reddy and Figgis. Cobalt(II) complexes with ligands (1-2) have higher 10Dq values and were presumably due to the higher stability facilitated by high density of these ligands.

The ligand field parameters were recorded. The splitting energies 10Dq of Co(II) complexes lie in the range 3570-3845 cm^{-1}. The Racah parameter B^1 were in the range 714-769 cm^{-1} which were less than the B value of free Co(II) ion (971 cm^{-1}) indicating that the Co(II) ion was involved in complex formation. The covalent factor β was around 0.75 which was an indication of the covalent nature of metal to ligand bonds in all these complexes. The 10Dq value was nothing but the frequency ν_1 which would be observed in IR region.

The UV-Visible spectra of the Co (II) nitrate complexes were similar. Their absorption frequencies and assignments were shown in the table 4. The spectra of the complexes display three spin-allowed bands at 7936 -7692cm^{-1} (ν_1), 16,950-15,400cm^{-1} (ν_2) and 20,410-17,857cm^{-1} (ν_3) which are assigned to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$ transitions respectively. The ν_2/ν_1 ratio falls within 2.00 – 2.20. All these observations along with high magnetic moments of these complexes (5.02–5.18BM) indicate octahedral geometry for all Cobalt (II) nitrate complexes.

The B^1 values (731-867cm^{-1}) and the β values (0.75–0.89) suggest the involvement of cobalt ion in complexation.

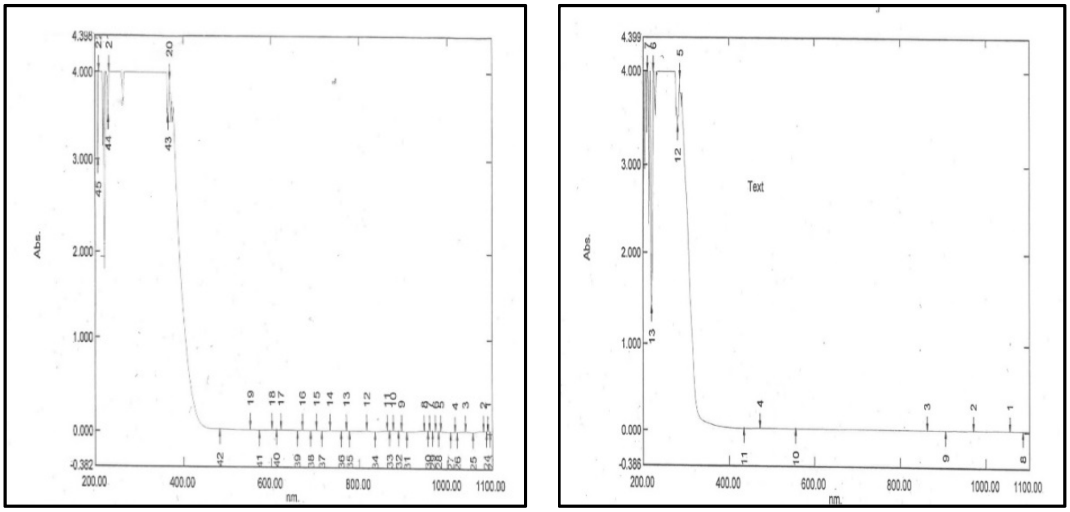

Figure 1. UV spectrum of the Co(II) complexes with ligands(1-2).

Infrared Spectra: The IR spectra of the complexes have been analyzed for those specific frequencies which were directly involved in complex formation and the values were indicated in table 5 and shown in fig.2. The moderately strong bands around 3300 cm^{-1} in the IR spectra of the free ligands (1-2) are attributed to the stretching mode of N-H vibration. In IR spectra of the complexes, these bands exhibit a considerable downward shift of 30-50cm^{-1}. This spectral observation suggests that the coordination of the ligands to the metal ion takes place through the lone pair electrons of secondary amine nitrogen atom of the ligands (1-2) moiety [26]. The piperidin-4-one has been shown to exist in the chair conformation with alkyl and phenyl groups in equatorial orientations. The band around 3182 -3085cm^{-1} due to N-H stretching were found to be present at about some frequencies in spectra of the complexes suggesting that these two nitrogen atoms were not involved in coordination. Due to presence of new medium intensity band in the region 546-515cm^{-1} assignable to M-O stretching vibration.

Table 5. Important IR bands (in cm^{-1}) of Co(II) complexes with ligands (1-2)

Complex	$\gamma_{C=O}$	$\gamma^*_{C=O}$	γ_{N-H}	γ^*_{N-H}	γ^*_{M-N}	γ^*_{M-O}	γ^*_{O-H}	γ^*_{N-C}	γ^*_{H-O-H}
1.	1724	1637	3305	3552	838	530	3049	1112	1637
2.	1703	1708	3298	3105	825	503	3307	1128	1602

γ = Ligand, γ* = complex

The presence of water molecules in the complexes is shown by a strong sharp band in the region 3560-3456 cm^{-1} due to O-H stretching and a strong band around 1655-1574 cm^{-1} due to H-O-H bending vibration. The Bohlmann bands in the IR spectra of Cobalt (II) nitrate complexes were either missing or reduced in number or intensity, indicating that nitrogen lone pair was involved in coordination with a consequent change in conformation of the heterocyclic ring.

Inspection of ν (C=O) values of Cobalt (II) complexes reveals that the carbonyl stretching frequencies were either unaffected or only slightly affected. This observation rules out the possibility of the participation of carbonyl group in coordination. Thus in the present study it was reasonable to assume that Cobalt (II) complexes of the ligands (1-2) were monodentate ligand, coordinating only through ring nitrogen and not through carbonyl group. This conclusion was similar to that obtained for -NH-piperidin-4-ones.

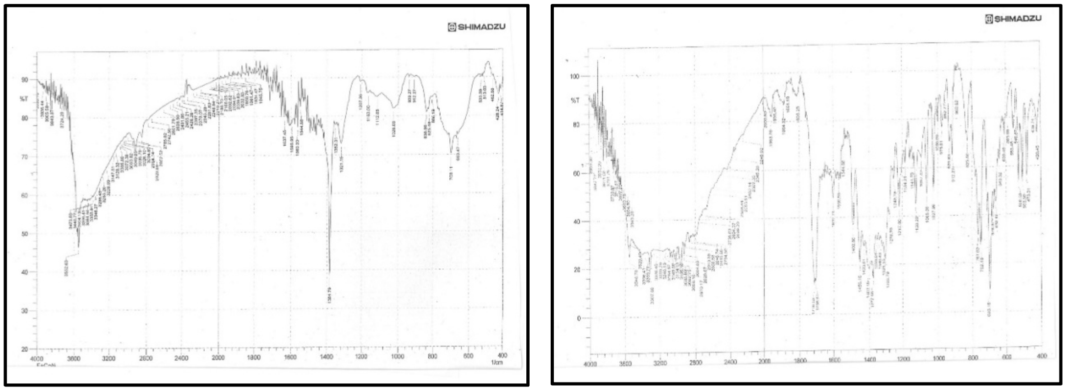

Figure 2. IR spectrum of the Co(II) complexes with ligands(1-2).

Piperidin-4-ones also exhibit these bands in the region 3000–2800cm^{-1} and these bands disappear on complexation through nitrogen due to the lack of antiper planarity with respect to the lone pair of electrons as a result of the change in conformation. The sharp band around 3300cm^{-1} due to N-H stretching for the ligands (L^1)–(L^2) has also been shifted to higher frequency (3400cm^{-1}) and was broadened in the corresponding complexes of piperidin-4-ones. The IR spectra of the ligands contain additional peaks in the region 3000–2800cm^{-1} due to C-H stretching modes of N-CH_3 group. These bands were missing in the IR spectra of the corresponding complexes and presumably overlap with the broad absorption bands in the 3600-3200cm^{-1} region. Thus it was inferred that the lone pair of electrons of ring nitrogen was involved in coordination and as a result there was a change in the conformation of piperidin-4-one ring. The presence of water molecules in the complexes were confirmed by accounting a broad absorption band in the region around 3556-3551cm^{-1} due to υ(O-H) stretching and a sharp medium peak at 1629-1618 cm^{-1} region due to H-O-H bending vibrations. In addition to these absorption bands, the observed two new bands at 526-511 and 431-410 cm^{-1} were due to the presence of υ(M-O) and υ (M-N) frequencies.

Thermal Analysis: The thermal data of $[Co(DP)(H_2O)_4NO_3]NO_3.H_2O$ and $[Co(DMP)(H_2O)_4NO_3]NO_3.H_2O$ complexes are listed in table 6. The composition of the intermediates and the final products fits with the observed mass loss in TGA. Thermogravimetric results were in good agreement with the DTA data. The simultaneous TG-DTA traces of the synthesized compounds were given in fig. 3 and can be taken as a representative model for all the Co(II) complexes of ligands (1-2).

Table 6. Thermal Analysis of Co(II) Complexes with DP and DMP ligands

Complex	DTA Peak Temp (°C)	Thermogravimetry		
		Temperature Range (°C)	Mass Loss %	
			Observed	Calculated
1.	256 (+)	195-273	13.33	14.01
	399 (+)	273-357	80.19	81.12
	450 (-)	357-515	95.29	96.05
	519 (-)			
2.	149 (+)	134-228		
	228 (+)	228-325	13.63	10.95
	418 (+)		60.13	60.22
	561 (+)	325-404	94.75	96.65
	166 (-)			
	509 (-)	404-519		

[Co(DP)(H_2O)$_4$$NO_3$]$NO_3$.$H_2O$: From the TG/ DTA curve, it was found that the complex undergoes in five decomposition stages. The first stage of decomposition occurs at a temperature range of 195-273°C, the mass loss of 13.33% (theoretical value 14.01%) was observed endothermically at 256°C and can be attributed to the release of one water molecule. Such a high temperature endothermic dehydration confirmed the co-ordination of water molecules to the metal ion.

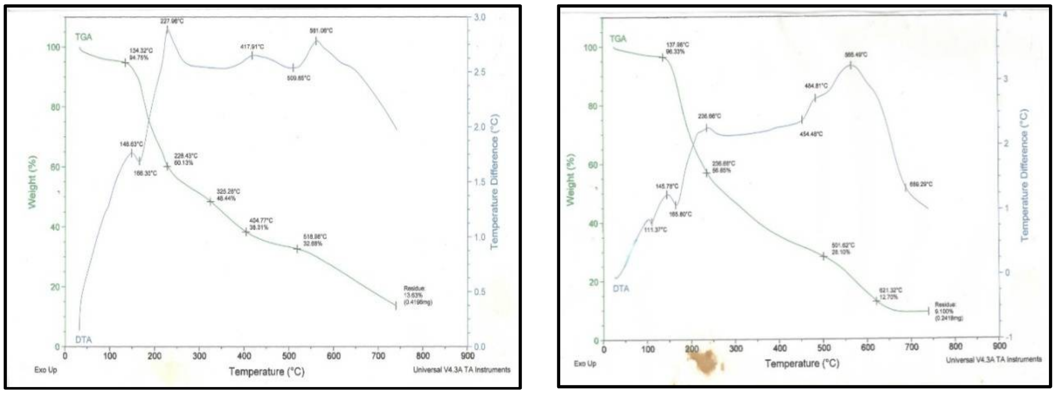

Figure 3. Simultaneous TGA and DTA of Co(II) complexes with ligands(1-2).

The second stage of decomposition ranges from 273-357°C with a mass loss of 80.19% (theoretical value 81.12%) corresponds to the removal of one outer nitrate ion. The corresponding endothermic peak temperature from DTA curve was 399°C. The third and the fourth stages correspond to the exothermic decomposition of coordination sphere nitrate ion and ligand at 450°C and 519°C respectively, which finally decomposes into Co_2O_3 in an exothermic way [25]. The theoretical mass loss for the formation of Co_2O_3 was 96.05%, which agreed well with the observed value of 95.29%. The decomposition scheme of the complex was given as follows

$$
\begin{aligned}
&[\mathrm{Co\,(DP)\,(H_2O)_4NO_3]NO_3.H_2O} \xrightarrow{195^\circ-273^\circ C} [\mathrm{Co\,(DP)\,(H_2O)_4NO_3]NO_3}\\
&\xrightarrow{273^\circ-357^\circ C} [\mathrm{Co\,(DP)\,(H_2O)_4NO_3}]\\
&\xrightarrow{357^\circ-515^\circ C} \mathrm{CO_2O_3}
\end{aligned}
$$

[Co (DMP) (H_2O)$_4$$NO_3$]$NO_3$.$H_2O$: The decomposition of the above complex follows in three steps. The first with 13.63% endothermic mass loss observed at 149°C was attributed to the release of non coordinated water molecule. In the second step, the remaining coordinated water molecules and nitrate ions were eliminated endothermically at 228°C. The final decomposition occurred at the temperature range between 325-519°C with a violet exothermic peak to give Co_3O_4. The various processes occurred in the thermal changes of the Co(II) complex was presented in the following sequence of reactions.

$$
\begin{aligned}
&[\mathrm{Co\,(DMP)\,(H_2O)_4NO_3]NO_3.H_2O} \xrightarrow{134^\circ-228^\circ C} [\mathrm{Co\,(DMP)\,(H_2O)_4NO_3]NO_3}\\
&\xrightarrow{228^\circ-325^\circ C} [\mathrm{Co\,(DMP)}]\\
&\xrightarrow{325^\circ-519^\circ C} \mathrm{Co_3O_4}
\end{aligned}
$$

In both cases, a high temperature endothermic dehydration confirmed the coordination of water molecules with the metal ion. IR studies also indicated the presence of water molecules in coordination sphere. The first and second arrested in TG curve of these complexes show a mass loss corresponding to four water molecules. The DTA curve of cobalt (II) complexes showed a sharp endothermic peak at 195-353°C. Decomposition of the anhydrous complexes occurred in two distinct exothermic steps. The residue obtained was the metal oxide either (Co_2O_3 or Co_3O_4). Thus, it was confirmed from the thermal studies that four water molecules were coordinated with the central metal ion in the complexes.

Cyclic Voltammetric studies: The cyclic voltammogram of the cobalt complex comprises two reduction peaks at 0.16 and -0.88 V, which was shown in the table 7. The peak at 0.16V probably corresponds to the reduction Co(II) – Co(I).

Table 7. Cyclic voltammetric data with ligand (1-2) and Cobalt (II) Complex

Compounds	E_{PC} (V)	E_{Pa} (V)	ΔE_P (V)
DP	1.70	-8.27	1.1
DMP	1.66	-8.13	2.7
Cobalt (II) Complex	0.16	-0.88	1.22

X-ray (Powder) Diffraction study: The X-ray (powder) diffraction photograph was recorded for the Cobalt complex with ligands (1-2). For instance, $[Co(DMP)(H_2O)_4NO_3](NO_3)_2.H_2O$ photograph reveals 13 reflex ions with maximum reflection at 10.46 (2θ) with the spacing of 8.45 Å. All the lines in the powder photograph were indexed based on Ito's method. The Co(II) complexes crystallizes in a triclinic lattice. The agreement between observed and computed Q_{hkl} (within 1%) was displayed in table 8 and 9. The direct cell dimensions calculated from the reciprocal cell dimensions were collected in table 10. The molecules is non-centro symmetric and it was a neutral monomer in the Co(II) complex was octahedral coordinated by two each of crystallographically independent N-coordinated ligands. The NH, NCH_3 groups were quasilinear with 178.1° and 169.2° bonded to the Co(II) ion through an angle of 169.5° and 165.3° respectively. Interestingly the respective N atoms of the ligands are cis-located whereas the same were trans-positioned in the reported Co (II) complexes [24].

Table 8. X-ray (Powder) Diffraction data for complex $[Co(DP)(H_2O)_4NO_3]NO_3.H_2O$

D	2θ	$Q_{obs} = 1/d^2$	d-spacing [Å]	Rel. Int. [%]	Q_{cal}	Index (h k l)
10.4659	100.07	0.1338	8.45279	100.00	0.002475	Q_{100}
14.6723	56.68	0.1673	6.03756	56.64	0.006582	Q_{010}
16.2471	18.97	0.2676	5.45572	18.96	0.004270	Q_{001}
17.8540	82.87	0.2007	4.96814	82.81	0.007211	Q_{101}
18.3427	22.98	0.2007	4.83687	22.96	0.010809	Q_{111}
19.3674	29.75	0.2007	4.58322	29.73	0.015486	Q_{101}
19.9752	20.48	0.2007	4.44510	20.47	0.019662	Q_{102}
20.5868	43.23	0.2342	4.31442	43.20	0.031702	Q_{301}
21.6958	21.79	0.2676	4.09632	21.78	0.031592	Q_{122}
23.0451	20.40	0.2676	3.85944	20.39	0.033193	Q_{310}
25.6179	40.92	0.1338	3.47738	40.89	0.035253	Q_{122}
26.8440	55.55	0.2342	3.32126	55.51	0.035131	Q_{310}
39.3283	21.32	0.4015	2.29101	21.31	0.049385	Q_{122}

NMR studies: ^1H NMR data obtained were found to be in good agreement with the structure proposed for the ligands and complexes. The singlet signals observed at 9.99 and 9.78 ppm in the H NMR spectra of Co(II)complex 1 and complex 2 respectively, corresponds to the proton of the hydroxyl group as was supported by deuterium exchange when D_2O was added to their DMSO solution. The aromatic protons of all synthesized compounds lie in the range of 6.76-8.02 ppm as multiplet signals. In addition, the signals related to CH_3 of the cation appear in the range 1.13-1.14 ppm. The structure of the ligands and complexes were also supported by C^{13} NMR spectra of ligands DP and DMP, the chemical shift of the methane carbon atom are observed at 150.28ppm. upon coordination, these signals shifts to lower field showing that the methane nitrogen of ligand were now connected to the cobalt central metal atom [24].

Table 9. X-ray (Powder) Diffraction data for complex $[Co(DMP)(H_2O)_4NO_3]NO_3.H_2O$

D	2θ	$Q_{obs} = 1/d^2$	d-spacing [Å]	Rel. Int. [%]	Q_{cal}	Index (h k l)
13.2901	284.48	0.1338	6.66221	100.00	0.006475	Q_{100}
13.6793	43.55	0.1673	6.47351	15.31	0.003092	Q_{010}
15.5564	32.45	0.1673	5.69637	11.41	0.002270	Q_{001}
16.7110	106.09	0.1171	5.30529	37.29	0.007201	Q_{101}
18.1369	77.86	0.2676	4.89129	27.37	0.011809	Q_{111}
20.7658	184.23	0.1338	4.27762	64.76	0.014486	Q_{101}
21.6610	209.45	0.1338	4.10283	73.62	0.019562	Q_{102}
24.6636	204.52	0.1171	3.60972	71.89	0.021702	Q_{301}
27.1071	38.50	0.2676	3.28963	13.54	0.031592	Q_{122}
28.1259	102.65	0.1840	3.17274	36.08	0.033193	Q_{310}
31.2995	49.02	0.2676	2.85790	17.23	0.035151	Q_{122}
32.2674	33.04	0.2676	2.77436	11.62	0.038130	Q_{310}
54.4734	20.56	0.3264	1.68310	7.23	0.039384	Q_{122}

Table 10. Crystal Parameters of $[Co(DMP)(H_2O)_4NO_3](NO_3)_2.H_2O$

Cell length (Å)	Angular parameters (°)	Cell Volume $(Å)^3$
a = 16.77	α = 122.1	3935.43
b = 14.82	β = 107.7	
c = 14.30	γ = 118.0	

APPLICATIONS

Antibacterial and antifungal study: In this work and many previous reports, the coordination of ligands to metal improves Antibacterial and antifungal activity. The overtones concept and tweedys chelation theory were used for explanation of increased activity of the complexes respect to parent ligands. As mentioned earlier, the in-built spiro carbocyclic or heterocyclic systems in a ring increases the biological potency, with the systems having smaller rings. On this basis, the synthesized compounds were evaluated for their in-vitro antibacterial and antifungal activities.

The evaluations were carried out using "paper disc diffusion method" for antibacterial activity and the "Turbidity method" for antifungal activity. All the synthesized compounds (1-2) were evaluated for their in-vitro antibacterial activity against the pathogenic micro-organisms, Escherichia coli (gram-positive) and Staphylococcus aureus (gram-negative) using paper disc diffusion method. Sterilized 10 mm Whitman No.1 paper discs were taken, impregnated with 0.1mL of the sample solutions (200 µg in DMF) and placed in the petridish containing 25-30 mL of nutrient agar inoculated with 18-24 h test culture. Incubation was carried out at 37°C for 24 h and the zone of inhibition was measured in mm. All the experiments were done in triplicate. Phenol was taken as standard.

Antifungal activity of the compounds was determined in-vitro against Aspergillus Niger adopting the turbidity method. In this method, 0.1 mL of the sample solutions (200 µg in DMF) in 5mL sterilized fungi medium were treated with 3-4 drops of 48 h old culture in a test tube. The test tubes were then shaken well and incubated for 48 h at 37°C. The extent of inhibition was determined by measuring the decrease in turbidity interms of % transmission at 660µ. Salicyclic acid was taken as standard [26-28]. Antibacterial and antifungal activities of all the compounds in-vitro against the pathogenic micro-organisms *Escherichia coli* (gram activity) with solvent control: DMF (positive), *Staphylococcus aureus* (gram-negative) and *Asperigillus Niger* fungal are given in table 11.

Table 11. Result of the Antibacterial and Antifungal activities with Co (II) complexes (1-2)

Compounds	Antibacterial Activity		Antifungal Activity
	E.C	S.A	A.N
1	-	-	+
2	+	+	++

CONCUSSIONS

The complexes were non-hygroscopic and pink in nature. Based on the analytical and spectral data, the general formula assigned to the complexes were $[Co(L)(H_2O)_4NO_3]NO_3.H_2O$. The conductance values of these complexes were in the range of 62-80ohm-1cm^{2}mol^{-1}, indicating that they are 1:1 electrolyte behaviour in nature. The IR spectra of Cobalt (II) complexes confirmed the presence of respect to N-H, C=O, N-CH_3, benzylidene carbonyl and O-H stretching and H-O-H bending vibrations. Thermal curves (TG and DTA) indicate the presence of four water molecules and one nitrate ion along with a ligand in coordination sphere and a nitrate ion and one water molecule in outer sphere of the complexes. The magnetic moment values of these complexes (4.0-5.2 BM) were in accordance with the values expected to high spin octahedral complexes. The electronic spectra of these complexes exhibit three bands in the region at 7194-8547 cm^{-1} (r_1) and a shoulder at 15858 cm^{-1} (r_2) with a multiple structured band in the visible region at 17556 -18750 cm^{-1} (r_3) assignable to $^4T_1g(F) \rightarrow {}^4T_2g(F)$, $^4T_1g(F) \rightarrow {}^4A_2g(F)$, and $^4T_1g(F) \rightarrow {}^4T_2g(P)$ transitions respectively. The r_2/r_1 ratio falls within 1.87 -2.06. All these observations lead to the conclusion that the complexes were spin free with an octahedral geometry. The various ligand field parameters such as ligand field splitting energy (10Dq), Racah interelectronic repulsion parameter (B) and Covalent factor (β) have also been calculated and the results have been rationalized. Based on the above factors, it was concluded that the Co(II) complexes with the ligands (1-2) were spin free with an octahedral geometry and the ligands are monodentate in nature. Cyclic voltammetric studies indicate that the metal ion of the complexes was reversible and XRD showed that the complexes were in triclinic lattice arrangement.

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