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Synthesis, Characterization and Antibacterial Studies of VO(IV), Cu(II), Ni(II), Co(II) Chelates of Tetradentate Schiff Base Derived from Benzil and Anthranilic Acid

N. GAYATHRI and M.S. SURESH*

Department of Chemistry, Government Arts College, Udthagamandalam-643002, India

*Corresponding author: E-mail: mssgacooty@gmail.com; sanjeevigk@gmail.com

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A novel tetradentate N_2O_2 type Schiff base, synthesized from benzil and 2-aminobenzoic acid (anthranilic acid) in the ratio 1:2, form stable complexes with transition metal ions such as VO(IV), Cu(II), Ni(II) and Co(II) in ethanol. Microanalytical data, magnetic susceptibility, molar conductance measurements, FTIR, UV-visible, ESR spectroscopic techniques and thermal analysis were used to confirm their structures. These complexes show very low conductance values supporting non-electrolytic nature. The infrared spectra supports the involvement of azomethine nitrogens and oxygen from carboxylate ion are coordinated to the metal. Electronic spectra of the complexes suggest a square pyramidal geometry for oxovanadium(IV) complex [VO(L)], distorted octahedral geometry for Cu(II) and Co(II) complexes and octahedral geometry for Ni(II) complexes with general formula $[M(L)(H_2O)_2]$ where $M = Cu(II), Ni(II), Co(II)$. The X-band ESR spectra of VO(IV) and Cu(II) complexes were recorded in DMSO at LNT and their parameters were calculated. All these complexes are paramagnetic and thermal studies show that in all the cases a stable metal oxide was obtained as the residue. The metal complexes have been screened for their antibacterial activity against organisms like *E. coli*, *S. aureus*, *Serratia* sp, *P. aeruginosa* and *B. cereus* and it was found that the complexes were more active than the corresponding ligand.

Keywords: Schiff base, Benzil, Anthranilic acid, Metal complexes, Antibacterial studies.

INTRODUCTION

Addition of an amine to a compound containing a carbonyl functional group produces an imine ($N=CH-$) known as Schiff bases. Schiff bases have been playing an important part in the development of coordination chemistry. Schiff base metal complexes have been studied extensively because of their attractive chemical and physical properties and their wide range of applications in numerous scientific areas. They play an important role in both synthetic and structural research, because of their preparative accessibility and structural diversity [1]. These complexes are extensively examined due to their wide applications in various fields like biological, pharmacological, clinical, analytical [2-4] and industrial area [5]. A search through the literature reveals that no work has been done on transition metal complexes of Schiff bases formed by the condensation of benzil and anthranilic acid. So in this paper we describe the synthesis, structural characterization and antibacterial studies of Schiff base complexes derived from benzil and anthranilic acid [N_2O_2 donor].

EXPERIMENTAL

Benzil, anthranilic acid, $VOSO_4 \cdot 5H_2O$, $CuCl_2 \cdot 2H_2O$, $NiCl_2 \cdot 5H_2O$, $CoCl_2 \cdot 6H_2O$, ethyl alcohol, etc. were purchased

from Merck and used as such without any further purification. The elemental analysis (CHNS) were performed using EL elemental analyser at Central Electrochemical Research Institute (CECRI). The FT infrared spectra were recorded in the range $4000-400\text{ cm}^{-1}$ on a Shimadzu FTIR 8400S spectrometer using KBr pellet techniques. Electronic (UV-VIS) spectra were recorded on a Shimadzu UVspectrophotometer in the range $200-1100\text{ cm}^{-1}$ using DMSO solvent. The thermal analyses were carried out using universal V4.5A Thermal analysis instrument in an atmosphere of static air with a heating rate of $10K/min$. The ESR spectra of various Schiff base complexes were recorded on a JES-X3 series in the scan range of 2300-4300 Gauss at LNT. The magnetic susceptibility measurements of the complexes were carried out using Gouy balance. The molar conductance was measured on ELICO-CM180 using DMSO as the solvent at room temperature. The antibacterial studies was carried out with disc diffusion method.

Synthesis of Schiff base of benzil and anthranilic acid (BEA): To the ethanolic solution of benzil (4.20 g, 0.02 mol in 20 mL ethanol) an ethanolic solution of 2-anthranilic acid (5.48 g, 0.04 mol in 20 mL ethanol) was added, followed by the addition of anhydrous sodium acetate (3 g) and the mixture was refluxed for 1 h. The hot solution was poured into ice

cold water where upon a grey precipitate of the Schiff base was separated, filtered, washed with water, and dried *in vacuo* [6]. The scheme of preparation is shown in Fig. 1.

Synthesis of metal complexes

- The vanadium complex was prepared by refluxing 1:1 molar ethanolic mixture of the vanadium salt, $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ (2.530 g, 0.01 mol) with the ligand (4.484 g, 0.01 mol) for 3 h followed by dropwise addition of ammonia until metal chelate separated. It was suction filtered washed with ethanol and ether before dried in vacuum dessicator. The compound was recrystallized from rectified spirit and dried.

- The same method was adopted for other complexes in which $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1.704 g, 0.01 mol), $\text{NiCl}_2 \cdot 5\text{H}_2\text{O}$ (2.376, 0.01 mol), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (2.379 g, 0.01 mol), was added to the ligand (4.484 g, 0.01 mol) in ethanol medium.

RESULTS AND DISCUSSION

Elemental analysis and molar conductance studies: The analytical data (Table-1) suggests 1:1 metal:ligand stoichiometry and the synthesized complexes have the molecular formula $[\text{VO}(\text{BEA})]$ and $[\text{M}(\text{BEA}) \cdot (\text{H}_2\text{O})_2]$ where $\text{M} = \text{Cu}^{2+}$, Ni^{2+} and Co^{2+} . These complexes are stable and green in colour. These complexes have molar conductance in the range of 12.5-17.5 $\text{S cm}^2 \text{mol}^{-1}$ indicating that they are non-electrolytic in nature. The microanalytical data and its molar conductance are presented in Table-1.

Infrared analyses: IR spectra provide valuable information regarding the nature of functional group attached to the

metal ion. Coordination to the metal through the nitrogen atom is expected to reduce the bond strength of azomethine group and lowers the $\nu(\text{C}=\text{N})$. The spectrum of the free Schiff base ligand BEA shows $\text{C}=\text{N}$ bands at region 1658 cm^{-1} shifted to lower frequency in the complexes $1615\text{--}1606 \text{ cm}^{-1}$ showing the involvement of the coordination of $\text{C}=\text{N}$ to the metal [7-10]. The frequency corresponding to $\nu(\text{COO})^-$ present in the ligand 1480 cm^{-1} is shifted to lower values $1470\text{--}1450 \text{ cm}^{-1}$ in the complexes, indicating the coordination through the oxygen atom of the carboxylate COO^- anion. The $\nu(\text{OH})$ due to water is present in the range $3845\text{--}3308 \text{ cm}^{-1}$ except vanadyl complex indicating the presence of hydrated water [11,12]. It was further supported by M-N peak at $483\text{--}426 \text{ cm}^{-1}$ and M-O peak in the range $592\text{--}585 \text{ cm}^{-1}$ [13,14]. A new peak at 998 cm^{-1} in vanadyl complex is due to $\nu(\text{V}=\text{O})$ [15]. The IR spectral data are given in Table-2.

UV-visible electronic spectra and magnetic susceptibility measurement: The free ligand shows absorption maxima appearing around 38461 and 31250 cm^{-1} due to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition respectively. The electronic spectrum of $[\text{VO}(\text{BEA})]$ shows peaks at 11792 , 15337 and 21276 cm^{-1} assigned to be ${}^2\text{B}_2 \rightarrow {}^2\text{E}$, ${}^2\text{B}_2 \rightarrow {}^2\text{B}_1$ and ${}^2\text{B}_2 \rightarrow {}^2\text{A}_1$ transitions respectively supports the square pyramidal structure of the complex [16-20] and confirmed by its magnetic moment of 1.78 BM [19]. The three peaks obtained at 10869 , 16666 and 19011 cm^{-1} in Co(II) complexes is assigned to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})\nu_1$, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})\nu_2$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})\nu_3$, respectively suggesting a distorted octahedral geometry [17] around Co(II) ion. It was also supported by its magnetic moment

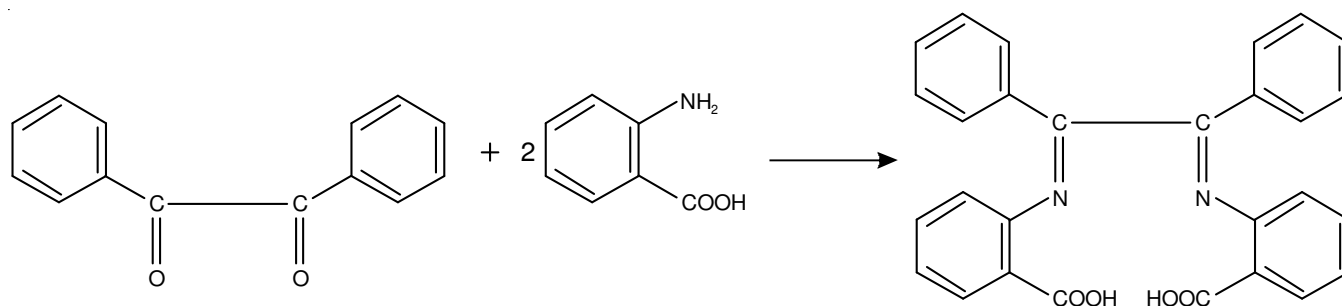


Fig. 1. Schematic representation of the synthesis of tetradentate ligand BEA

TABLE-1
PHYSICAL CHARACTERISATION, ANALYTICAL AND MOLAR CONDUCTANCE DATA

| Compound | m.w. | Colour | Yield (%) | Elemental analysis (%): Found (calcd.) | | | | $\Lambda_M (\text{S cm}^2 \text{mol}^{-1})$ |
|--|--------|------------|-----------|--|-----------------|---------------|---------------|---|
| | | | | C | H | N | M | |
| $\text{C}_{28}\text{H}_{20}\text{N}_2\text{O}_4(\text{BEA})$ | 448.46 | Grey | 80 | 72.79 (74.98) | 4.221 (4.495) | 6.013 (6.248) | — | — |
| $[\text{VO}(\text{BEA})]$ | 515.4 | Dark green | 75 | 65.24 (65.24) | 3.9115 (3.9115) | 5.411 (5.436) | 12.90 (12.98) | 13.5 |
| $[\text{Cu}(\text{BEA}) \cdot (\text{H}_2\text{O})_2]$ | 548.04 | Green | 75 | 60.55 (61.36) | 4.257 (4.414) | 5.100 (5.112) | 11.00 (11.59) | 13.5 |
| $[\text{Ni}(\text{BEA}) \cdot (\text{H}_2\text{O})_2]$ | 543.20 | Green | 70 | 60.55 (61.92) | 4.257 (4.453) | 5.100 (5.158) | 11.00 (10.80) | 17.5 |
| $[\text{Co}(\text{BEA}) \cdot (\text{H}_2\text{O})_2]$ | 543.42 | Green | 70 | 60.90 (61.88) | 4.233 (4.451) | 4.989 (5.156) | 11.10 (10.80) | 12.5 |

TABLE-2
INFRARED SPECTRAL DATA OF THE SCHIFF BASES AND ITS METAL COMPLEXES

| Compound | $\nu(\text{OH})$ | $\nu(\text{C}=\text{N})$ | $\nu(\text{COO})^-$ | $\nu(\text{M}-\text{O})$ | $\nu(\text{M}-\text{N})$ | $\nu(\text{V}=\text{O})$ |
|--|------------------|--------------------------|---------------------|--------------------------|--------------------------|--------------------------|
| $\text{C}_{28}\text{H}_{20}\text{N}_2\text{O}_4(\text{BEA})$ | — | 1658 | 1480 | — | — | — |
| $[\text{VO}(\text{BEA})]$ | — | 1615 | 1450 | 590 | 467 | 998 |
| $[\text{Cu}(\text{BEA}) \cdot (\text{H}_2\text{O})_2]$ | 3345 | 1606 | 1459 | 590 | 483 | — |
| $[\text{Ni}(\text{BEA}) \cdot (\text{H}_2\text{O})_2]$ | 3305 | 1614 | 1457 | 592 | 450 | — |
| $[\text{Co}(\text{BEA}) \cdot (\text{H}_2\text{O})_2]$ | 3308 | 1613 | 1457 | 585 | 426 | — |

value of 4.40 BM [21]. The electronic spectrum of Cu(II) complex shows *d-d* transition band in the range 13037, 19083 and 24038 cm^{-1} corresponds to $^2A_{1g} \rightarrow ^2B_{1g}$ ($d_{z^2} \rightarrow d_{x^2-y^2}$) ν_1 , $^2B_{2g} \rightarrow ^2B_{1g}$ ($d_{xy} \rightarrow d_{x^2-y^2}$) ν_2 and $^2E_g \rightarrow ^2B_{1g}$ ($d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$) ν_3 transition respectively [17]. The spectrum is typical for a distorted octahedral geometry. The magnetic moment of 1.86 BM, also supports this [21]. The electronic spectrum of Ni(II) complex shows three absorption maxima at 12315, 14450 and 20283 cm^{-1} . These are characteristic of octahedral Ni(II) complexes and assigned to be $^3A_{2g} \rightarrow ^3T_{2g}(F)$ (ν_1), $^3A_{2g} \rightarrow ^3T_{1g}(F)$ (ν_2) and $^3A_{2g} \rightarrow ^3T_{1g}(P)$ (ν_3) transition respectively [22]. Its magnetic moment was found to be 3.01 BM supporting octahedral environment [21] around Ni(II) ion (Table-3).

TABLE-3
UV-VISIBLE SPECTRAL DATA AND
MAGNETIC MOMENTS OF THE COMPLEXES

| Compound | Absorption max (cm^{-1}) | Assignments | μ_{eff} (BM) |
|--|-------------------------------------|---|-------------------------|
| $\text{C}_{28}\text{H}_{20}\text{N}_2\text{O}_4(\text{BEA})$ | 38461 31250 | $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$ | |
| $[\text{VO}(\text{BEA})]$ | 11792 15337 21276 | $^2B_2 \rightarrow ^2E$ $^2B_2 \rightarrow ^2B_1$ $^2B_2 \rightarrow ^2A_1$ | 1.78 |
| $[\text{Cu}(\text{BEA}) \cdot (\text{H}_2\text{O})_2]$ | 13037 19083 24038 | $^2A_{1g} \rightarrow ^2B_{1g}(\nu_1)$ $^2B_{2g} \rightarrow ^2B_{1g}(\nu_2)$ $^2E_g \rightarrow ^2B_{1g}(\nu_3)$ | 1.86 |
| $[\text{Ni}(\text{BEA}) \cdot (\text{H}_2\text{O})_2]$ | 12315 14450 20283 | $^3A_{2g} \rightarrow ^3T_{2g}(F)(\nu_1)$ $^3A_{2g} \rightarrow ^3T_{1g}(F)(\nu_2)$ $^3A_{2g} \rightarrow ^3T_{1g}(P)(\nu_3)$ | 3.01 |
| $[\text{Co}(\text{BEA}) \cdot (\text{H}_2\text{O})_2]$ | 10869 16666 19011 | $^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$ $^4T_{1g}(F) \rightarrow ^4A_{2g}(F)$ $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$ | 4.40 |

Thermal studies: From the thermogram of $[\text{VO}(\text{BEA})]$ given in Fig. 2, it was observed that the compound is thermally stable upto 130 $^{\circ}\text{C}$ indicated by a well defined horizontal plateau. The first stage decomposition is seen starting at 130 $^{\circ}\text{C}$ and progressing till 290 $^{\circ}\text{C}$. The weight loss during this stage was 70 %. The second stage of decomposition starts at 290 $^{\circ}\text{C}$ itself and ends at 600 $^{\circ}\text{C}$ with mass loss of 12.5 %. Above 600 $^{\circ}\text{C}$ the residue is seen stable at static air atmosphere, with a mass percentage of 17.5 %. The compound was stable upto 130 $^{\circ}\text{C}$, indicates that there is no water molecules attached to it. The first and second stage of decomposition was due to the breaking of bulky tetradentate Schiff bases from the complex, leaving behind a residue, V_2O_5 , stable oxide of vanadium. The calculated value of the residue 17.63 % is in good agreement with the observed value of 17.5 %.

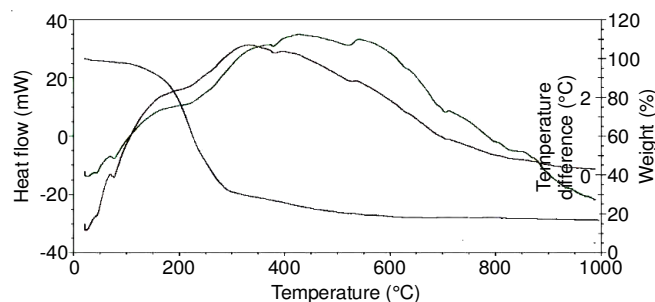
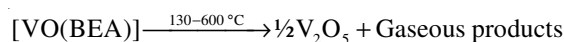


Fig. 2. TG/DTA curve of $[\text{VO}(\text{BEA})]$ in static air



Thermal curve of Ni^{2+} complex $[\text{Ni}(\text{BEA})(\text{H}_2\text{O})_2]$ in static air atmosphere is given in Fig. 3. It shows an initial mass loss of 6.5 % in the range 50-100 $^{\circ}\text{C}$ itself, due to the loss of two water molecules from the complex. The calculated value of 6.62 % is in good agreement with this. The second stage of decomposition starts at 100 $^{\circ}\text{C}$ and progressing till 363.56 $^{\circ}\text{C}$ with a mass loss of 53.5 % and third stage was in the range 363.56-650 $^{\circ}\text{C}$ with a mass loss of about 25.8 % leaving behind a residual percentage of 14.2 %. Above 650 $^{\circ}\text{C}$ a horizontal plateau was observed. The second and third stage of decomposition corresponds to the decomposition of bulky ligand from the complex leaving NiO , as the stable residue. The calculated value of the residue 13.75 % is in good agreement with the observed value of 14.2 %.

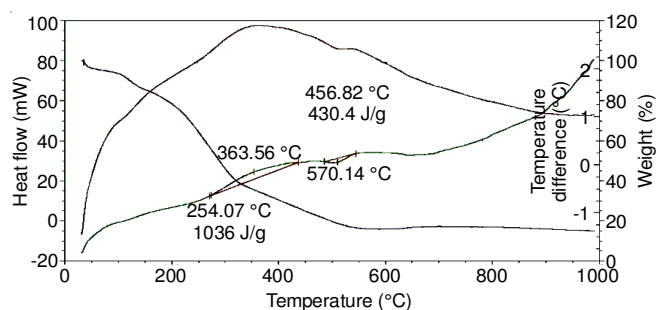
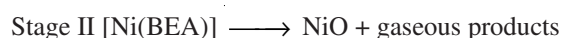
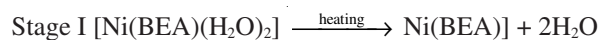


Fig. 3. TG/DTA curve of $[\text{Ni}(\text{BEA}) \cdot (\text{H}_2\text{O})_2]$ in static air

ESR spectroscopy: The X-band ESR spectrum of the complex $[\text{VO}(\text{BEA})]$ was recorded in DMSO at LNT (77 K), given in Fig. 4. In the frozen state, it shows two sets of eight lines which are due to parallel and perpendicular resonance feature of VO^{2+} . The eight line peaks are due to hyperfine splitting originating from the interaction of unpaired electrons with ^{51}V nucleus having a nuclear spin of $I = 7/2$. This confirms the presence of single oxovanadium(IV) in the complex [23,24]. The g_{\parallel} , g_{\perp} , $g_{(\text{av})}$, A_{\parallel} , A_{\perp} and $A_{(\text{av})}$ are calculated using the equation:

$$g\beta H = h\nu$$

$$g_{(\text{av})} = 1/3(g_{\parallel} + 2g_{\perp})$$

$$A_{(\text{av})} = 1/3(A_{\parallel} + 2A_{\perp})$$

The observed values are $g_{\parallel} = 1.97$, $g_{\perp} = 1.99$, $g_{(\text{av})} = 1.9833$; $A_{\parallel} = 194 \text{ G}$, $A_{\perp} = 74 \text{ G}$, $A_{(\text{av})} = 114 \text{ G}$.

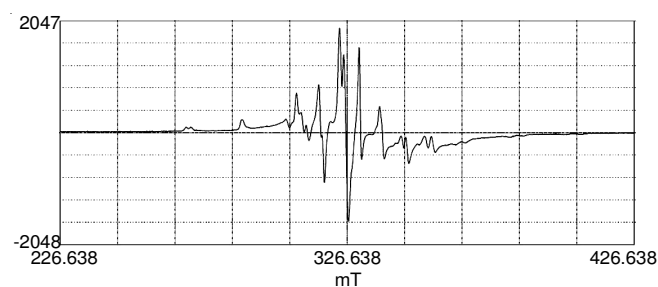


Fig. 4. ESR spectrum of $[\text{VO}(\text{BEA})]$ in LNT

It was found that $g_{\parallel} < g_{\perp}$ in the complex which is in good agreement with its square pyramidal geometry.

The X-band ESR spectrum of $[\text{Cu}(\text{BEA}) \cdot (\text{H}_2\text{O})_2]$ in DMSO in the frozen state at 77 K shows four well resolved peaks of low intensities in the low field region and one intense peak in the high field region given in Fig. 5. It was found that the g_{\parallel} value is 2.3463, $g_{\perp} = 2.0645$ and $g_{\text{av}} = 1/3(g_{\parallel} + 2g_{\perp}) = 2.1524$. The g tensor values of copper(II) complex can be used to derive the ground state of the complex. If $g_{\parallel} > g_{\perp} > 2.0023$, the unpaired electron lies in the $d_{x^2-y^2}$ orbital and $g_{\perp} > g_{\parallel} > 2.0023$, the unpaired electron is in the d_{z^2} orbital. The interaction term G is calculated using the equation $G = (g_{\parallel} - 2.0023)/(g_{\perp} - 2.0023)$ and is greater than 4. The local tetragonal axes are aligned parallel or only slightly misaligned, while $G < 4.0$, significant exchange coupling is present and the misalignment is appreciable. From the observed value it was clear that $g_{\parallel} (2.3463) > g_{\perp} (2.0645) > 2.0023$ and the value of G in a complex 5.53 suggests that the local tetragonal axes are aligned parallel or slightly misaligned, the unpaired electron is present in $d_{x^2-y^2}$ orbital [25-27] and the complex is distorted octahedral.

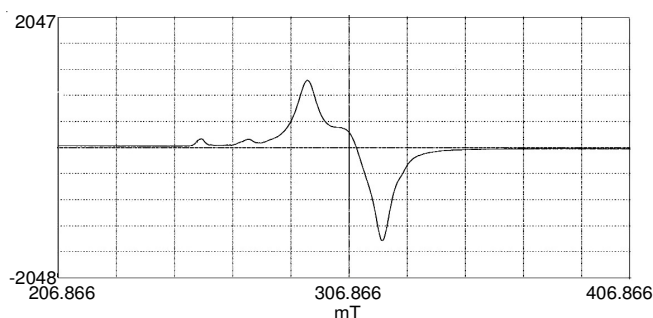


Fig. 5. ESR spectrum of $[\text{Cu}(\text{BEA}) \cdot (\text{H}_2\text{O})_2]$ in LNT

Antibacterial studies: The ligand and its metal complexes were assayed for their antimicrobial activities against *E. coli*, *S. aureus*, *P. aeruginosa*, *Serratia* sp and *Bacillus cereus* by the disc diffusion method [28,29]. It was found that all the metal complexes have better activity than the ligands explained by the theory of Tweedy. This is probably due to the greater lipophilicity nature of the complexes. Such increased activity of metal chelates can be explained on the basis of overtones concept and chelation theory. According to overtone's concept of cell permeability the lipid membrane that surrounds the cell favours the passage of lipid soluble materials. On chelation, the polarity of metal ion will be reduced to a greater extent due to overlap of the ligand orbitals and partial sharing of positive charge of the metal ion with donor groups. Therefore the delocalization of π electrons in the chelate ring increases and enhances the penetration of the complexes into lipid membranes. The antibacterial data are presented in Table-4.

Conclusion

In this work, the synthesis and characterization of tetradentate Schiff base ligand derived from benzil and anthranilic acid and its interaction with various transition metals like VO^{2+} , Cu^{2+} , Ni^{2+} and Co^{2+} are reported. The metal complexes formed were non-electrolytic in nature. The synthesized systems were characterized by micro-analysis, molar conductance values, FTIR, ESR, UV spectroscopy and TG analyses. These analytical and spectral data suggests that azomethine N atoms, oxygens from carboxyl group are coordinated to oxovanadium(IV) resulted into $\text{VO}(\text{N}_2\text{O}_2)$ square pyramidal structure and due to two molecules of coordinated water, octahedral geometry was predicted for the others. The antibacterial screening tests were also performed against bacteria which indicate that the complexes exhibit good antibacterial activity than the ligand. Based on the above results, the structure of coordination compounds under investigation are formulated in Fig. 6.

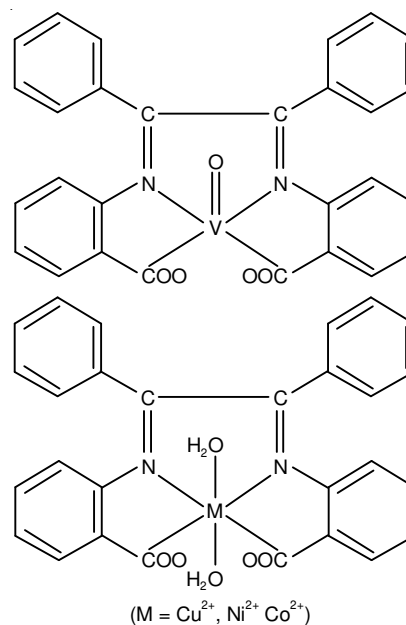


Fig. 6. Proposed structure of the metal complexes

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TABLE-4
ANTIBACTERIAL ACTIVITY DATA OF THE LIGAND AND ITS METAL COMPLEXES

| Compound | <i>Escherichia coli</i> | <i>Staphylococcus aureus</i> | <i>Pseudomonas aeruginosa</i> | <i>Serratia</i> sp | <i>Bacillus cereus</i> | Inference |
|--|-------------------------|------------------------------|-------------------------------|--------------------|------------------------|-----------|
| $\text{C}_{28}\text{H}_{20}\text{N}_2\text{O}_4(\text{BEA})$ | 9 | 12 | 8 | 9 | 12 | ++ |
| $[\text{VO}(\text{BEA})]$ | 15 | 14 | 12 | 11 | 12 | +++ |
| $[\text{Cu}(\text{BEA}) \cdot (\text{H}_2\text{O})_2]$ | 9 | 14 | 8 | 8 | 8 | ++ |
| $[\text{Ni}(\text{BEA}) \cdot (\text{H}_2\text{O})_2]$ | 10 | 16 | 6 | 9 | 11 | +++ |
| $[\text{Co}(\text{BEA}) \cdot (\text{H}_2\text{O})_2]$ | 9 | 15 | 8 | 10 | 9 | ++ |

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