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Synthesis, Spectral, Redox and Antimicrobial Activities of Mixed Ligand Complexes Derived from 1-Phenyl-2,3-dimethyl-4-imino-benzylidene-pyrazol-5-one and Dimethylglyoxime

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ABSTRACT

Novel complexes of Cu(II), Ni(II), Co(II), Zn(II) and VO(II) have been prepared using a Schiff base derived from 1-phenyl-2,3-dimethyl-4-imino-benzylidene-pyrazol-5-one and dimethylglyoxime. The structural features of the chelates have been confirmed by microanalytical data, IR, UV-Vis., ^{1}H NMR and ESR spectral techniques. Electronic absorption and IR spectra of the complexes indicate an octahedral geometry around the central metal ion except VO(II) complex which shows square pyramidal geometry. The monomeric nature of the complexes is confirmed from their magnetic susceptibility. Low conductance data of the chelates support their non-electrolytic nature except vanadyl complex which shows electrolytic in nature due to the presence of sulphate ion outside the coordination sphere. The cyclic voltammogram of the copper and vanadyl complexes in MeCN at 300 K were well studied. The ESR spectra of copper and vanadyl complexes in DMSO solution at 300 and 77 K were recorded and their salient features are reported. The molecular orbital coefficients were calculated for the complexes. The antimicrobial activity of the ligand and its complexes has been extensively studied on microorganisms such as *Staphylococcus aureus, Klebsiela pneumoniae, Bacillus subtilis, Escherichia coli and Salmonella typhi*. Most of the complexes have higher activity than that of the free ligand.

1. Introduction

Schiff bases play an important role in coordination chemistry because they easily form stable complexes with most transition metal ions. Chelating ligands containing N, S and O donor atoms show broad biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions. Some pyrazolone derivatives are potential analgesic, antipyretic, anti-inflammatory and antirhematic agents. Among the pyrazolone derivatives, 4-aminoantipyrine forms a variety of Schiff bases with aldehydes/ketones and is reported to be superior reagents in biological, pharmacological, clinical and analytical applications [1-7]. A search through the literature reveals that no work has been done on the syntheisis of mixed ligand transition metal complexes derived from 4-aminoantipyrine derivatives and dimethyl glyoxime [8-27]. This paper reports the synthesis of mixed ligand Cu(II), Co(II), Ni(II), VO(II) and Zn(II) complexes from benzylidene-4-iminoantipyrine and dimethyl glyoxime. The synthesized complexes were characterized by analytical, IR, UV-Vis., ^{1}H NMR, ESR, magnetic susceptibility and molar conductance methods. The biological activities of the metal chelates against the bacteria like *Staphylococcus aureus, Klebsiela pneumoniae, Bacillus subtillis, Escherichia coli and Salmonella typhi* were performed by using nutrient agar as medium.

2. Experimental Methods

All of the chemicals and reagents used in the synthesis were purchased from Fluka and Merck Chemical companies and were used without further purification. Spectroscopic grade solvents were used for spectral and cyclic voltammetric measurements. Elemental analyses were carried out with Thermofinger –Flash CA 1112 series at Sophisticated Analytical Instrumentation facility, Indian Institute of Technology, Mumbai. The molar conductance of the complexes in 10^{-3} M MeCN solution was measured using a 305 type systronic conductivity bridge with a dip type cell. H^1-NMR spectra of the Schiff base and its zinc complex were recorded in $CDCl_3$ solution on a Brucker 300 MHz FT-NMR spectrometer using TMS as internal standard at Madurai Kamaraj University, Madurai. The UV-Visible spectra of the compounds were recorded on a systronics UV-Vis., spectrophotometer. The IR spectra were recorded on a FT-IR 8400S Shimadzu spectrophotometer in the 4000 – 400 cm^{-1} range using KBr as solvents. Cyclic voltammogram of the copper complexes was recorded in MeCN solution at 300 K using a BAS CV50 electrochemical analyzer. The three electrode cell contains a reference Ag/AgCl electrode, Pt wire auxiliary electrode and glassy carbon working electrode. Tetra butyl ammonium bromide (TBAB) was used as supporting electrolyte. The X-band ESR spectra of the copper and vanadyl complexes in DMSO solution at 300 K and 77 K were recorded on a Varian E-112 ESR spectrometer using DPPH as the g – marker at Sophisticated Analytical Instrumentation facility, IIT, Mumbai.

2.1 Synthesis of Schiff Base

An ethanolic solution (20 mL) of 1-phenyl-2,3-dimethyl-4-aminopyrazol-5-one (4-aminoantipyrine) (2.03 g, 0.01 mol) and benzaldehyde (1.08 g, 0.01 mol) was stirred for *ca.* 30 minutes. On cooling, the yellow solid, benzylidene-4-iminoantipyrine (B4AAP) obtained was filtered and recrystallised from ethanol.

2.2 Synthesis of Cu(II), Co(II), Ni(II) and Zn(II) Complexes

An ethanolic solution of dimethyl glyoxime (10 mmol), 4-aminoantipyrine (2.03 g, 10 mmol) and Cu(II)/Co(II)/Ni(II)/Zn(II) chloride salt (10 mmol) was taken in a 250 mL RB flask. To this solution, 1 g of sodium hydroxide was added and the resulting solution was boiled under reflux on a water bath for 12 h with constant stirring. Then, the solution was filtered and cooled for 12 h at 0 °C. The solid product crystallized out was collected by filtration and washed by ethanol. The preparation for the Cu(II), Ni(II), Zn(II) and Co(II) complexes was given by the Scheme 1. Oxovanadium(II) complex was synthesized by utilizing the same procedure using vanadyl sulphate as a metal salt and the reaction is carried out in presence of 5% aqueous sodium acetate solution (instead of 1 g NaOH). The preparation for the vanadyl complex was given by Scheme 2.

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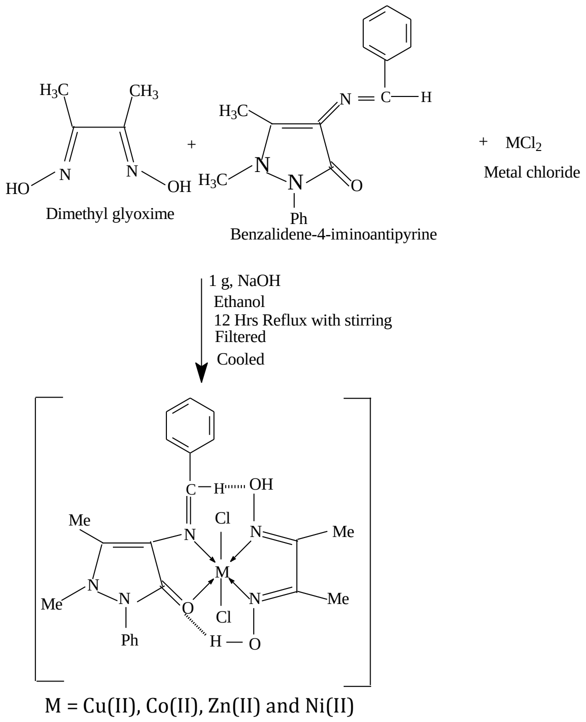
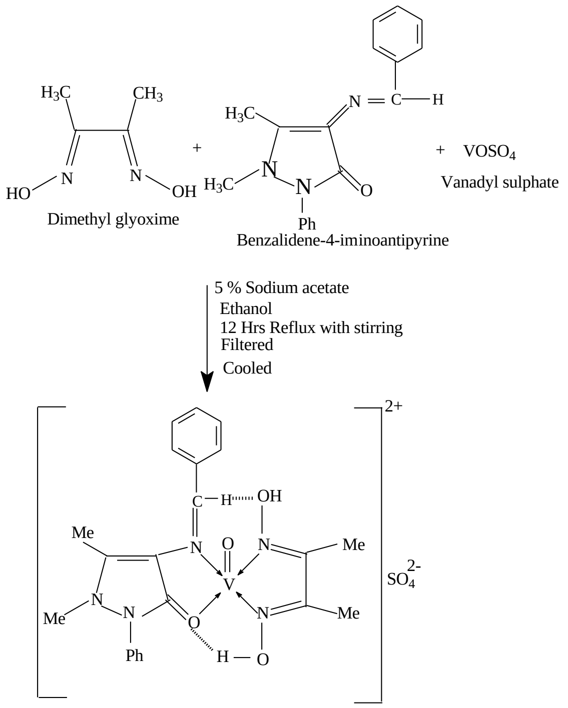


Scheme 1 Preparation of Cu(II), Ni(II), Zn(II) and Co(II) complexes



Scheme 2 Preparation of vanadyl complex

Table 1 Analytical and physical data of the chelates

Compound	Melt./ Decomp. Point (°C)	Colour	Found (Calcd) (%)					Λ_M x 10^{-2} (mho cm^2 mol^{-1})	$\mu_{eff.}$ (B.M.)
			M	C	*H*	N	Cl		
[CuB4AAP(DMG)Cl_2]	196	Green	11.98 (11.73)	48.65 (48.75)	4.18 (4.62)	12.14 (12.93)	13.32 (13.11)	1.2	1.81
[NiB4AAP(DMG)Cl_2]	216	Green	10.12 (10.94)	48.17 (49.19)	4.68 (4.66)	13.18 (13.04)	12.86 (13.23)	3.6	2.87
[CoB4AAP(DMG)Cl_2]	214	Pink	10.82 (10.98)	48.67 (49.16)	4.58 (4.66)	13.12 (13.04)	13.46 (13.22)	3.9	3.86
[VOB4AAP(DMG)]SO_4	198	Green	8..52 (8.94)	46.68 (46.32)	4.32 (4.39)	12.47 (12.28)	-- --	96.4	1.85
[ZnB4AAP(DMG)Cl_2]	187	Yellow	12.06 (12.12)	48.34 (48.54)	4.51 (4.60)	12.16 (12.87)	12.83 (13.05)	2.3	-

3. Results and Discussion

The analytical data of the ligands and complexes along with some physical properties are summarized in Table 1.

The analytical data of the complexes correspond well with the general formula [MB4AAP(DMG)Cl_2] while the vanadyl complex having the general formula [VOB4AAP(DMG)]SO_4, where, M= Cu(II), Co(II), Zn(II) and Ni(II), B4AAP = $C_{18}H_{17}N_3O$ and DMG = $C_4H_8N_2O_2$. Their magnetic susceptibilities at room temperature are consistent with octahedral geometry around the central metal ion, except for the vanadyl complex which exists in square pyramidal geometry. The low conductance of the chelates supports their non-electrolytic nature where as higher conductance data of the vanadium chelate exhibits their electrolytic nature [28].

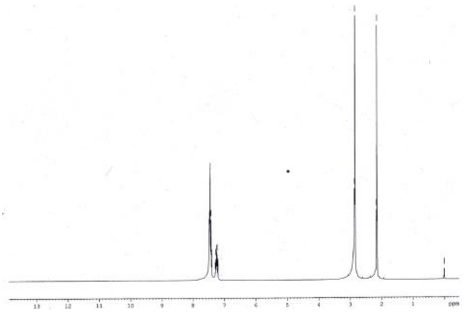


Fig. 1 The ^1H NMR spectrum of the Schiff base in $CDCl_3$ solution

3.1 ^1H NMR spectra

The ^1H NMR spectrum of the Schiff base in $CDCl_3$ solution (Fig. 1) shows the following signals: C_6H_5 multiplet at 6.9 - 7.2 δ, =C-CH_3 at 2.2 δ and -N-CH_3 at 2.9 δ. The ^1H NMR spectrum of the dimethyl glyoxime in $CDCl_3$ (Fig. 2) solution shows the following signals: CH_3 singlet at 1.6 δ range and -N-OH at 10.8 δ. The ^1H NMR spectrum of the [ZnB4AAP(DMG)Cl_2] complex in $CDCl_3$ (Fig. 3) solution shows the following signals: C_6H_5 multiplet at 7.1 - 7.8 δ, =C-CH_3 at 2.3 δ and -N-CH_3 at 3.0 δ.CH_3 doublet at 1.3 δ range and -N-OH at 9.9 δ. The strong upfield shift of -OH group of oxime moiety indicates that the involvement of azomethine nitrogen atoms of the dimethyl glyoxime. It also suggests that –OH groups are not involved in chelation [29, 30].

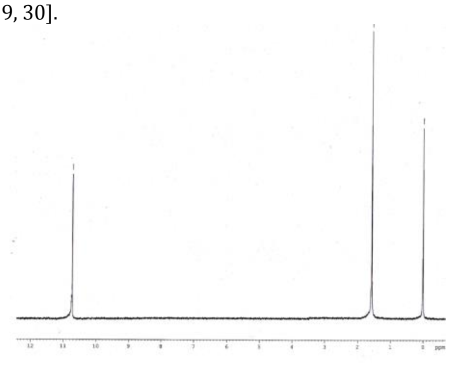


Fig. 2 The ^1H NMR spectrum of the dimethyl glyoxime in $CDCl_3$ solution

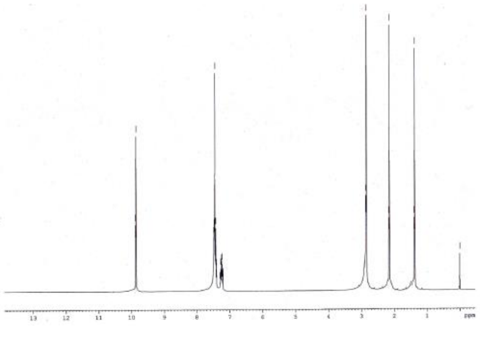


Fig. 3 The ^1H NMR spectrum of the [ZnB4AAP(DMG)Cl_2] complex in $CDCl_3$ solution

3.2 IR Spectra

The spectra of the dimethyl glyoxime shows the characteristic -C=N bands in the region 1630-1600 cm^{-1}, which are also shifted to lower frequencies in the all the spectra of the complexes (1600-1560 cm^{-1}) indicates that the coordination of azomethine group present in the DMG. It also shows a broad band for the -OH group at 3500-3300 cm^{-1}. The existence of this peak in all the spectra of the complexes indicates that the -OH group of oxime moiety not involved in coordination. The band at 1650 cm^{-1} is assigned as the characteristic frequency of keto group in a pyrazolone ring. This band is shifted to *ca.* 1600-1620 cm^{-1} region in all the complexes which is due to the chelation of carbonyl group with the central metal ion. Besides the ligand vibrations, characteristic V=O vibrations of vanadyl complex is also noticeable in the spectra of this complex at 930 cm^{-1}. These vibrations of the metal salts generally remain unperturbed upon complexation [31].

3.3 Electronic Absorption Spectra

The ligand (B4AAP) in MeCN shows an absorption bands at 304 nm and 369 nm which are assigned as intraligand charge transfer bands. The UV-vis. spectrum of copper complex in acetonitrile shows three bands which are assigned as an intraligand charge transfer bands (294 nm and 373 nm) and a d-d band ($^2Eg \rightarrow {}^2T_2g$), (702 nm). The d-d band (702 nm) strongly favours octahedral geometry around the metal ion [32]. This is further supported by the magnetic susceptibility value (1.81 B.M.).

The Nickel complex in MeCN solution shows three d-d bands at 886 nm, 697 nm and 553 nm which are assigned as $^3A_2g(F) \rightarrow {}^3T_2g(F)$, $^3A_2g(F) \rightarrow {}^3T_1g(F)$ and $^3A_2g(F) \rightarrow {}^3T_1g(P)$ transitions respectively. The appearance of a band in the near IR region (886 nm) is characteristic for octahedral geometry [33]. This is also confirmed by the magnetic susceptibility value (2.87 B.M).

The Cobalt complex in ethanol shows three absorption bands at 454 nm, 702 nm and 782 nm which are assigned as $^4T_1g(F) \rightarrow {}^4T_2g(F)$, $^4T_1g(F) \rightarrow {}^4A_2g(F)$ and $^4T_1g(F) \rightarrow {}^4T_1g(P)$ transitions respectively. This complex also shows a characteristic band at 782 nm which confirms the octahedral coordination. The magnetic susceptibility value (3.86 B.M.) also confirms this geometry [34].

Vanadyl complex in ethanol solution shows three d-d bands at 839 nm, 670 nm and 491 which are assigned as $^2B_2 \rightarrow {}^2E$, $^2B_2 \rightarrow {}^2B_1$ and $^2B_2 \rightarrow {}^2A_1$ respectively. Square pyramidal geometry [35] is proposed for this system because it shows a band in the 839 nm region ($^2B_2 \rightarrow {}^2E$). This is further confirmed by the ESR spectral data.

3.4 Electrochemical Behavior

The cyclic voltammogram of the copper complex in MeCN solution, recorded at room temperature (Fig. 4), shows a quasi-reversible peak for the couple: copper(II) → copper(III) at Ep_a = +0.55 V with a direct cathodic peak for copper(III) → copper(II) at Ep_c = +0.44 V. Further, it exhibits two irreversible peaks characteristic for copper(II) → copper(I) (Ep_c = - 0.32 V) and copper(I) → copper(0) (Ep_c = - 0.85 V) reduction.

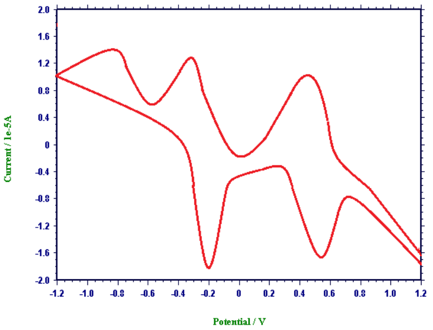


Fig. 4 Cyclic voltammogram of [CuBAAP(DMG)Cl_2] complex in acetonitrile at 300 K (0.1M TBAP). Scan rate 100 mVs^{-1}

In the anodic side, the direct oxidation of copper(0) → copper(II) is observed [36] with a strong stripping peak at Ep_a = - 0.21 V. The cyclic voltammogram of the pure ligand system in acetonitrile solution shows an irreversible reduction peak potential at - 1.52 V, which lies fortuitously outside the range of potentials studied for the complex.

The VO(S4AAPAP) complex in MeCN solution exhibits a cyclic voltammogram typical of VO(II) complexes. The quasi reversible peak at Ep_a = 0.71 V and Ep_c = 0.56 V are attributable to the VO(II)/VO(III) couple. In the negative region, it shows quasi reverisble peaks at Ep_a = -0.62 V and Ep_c = -0.71 V for the couple VO(II)/VO(I). These values do not much deviate from the typical vanadyl complexes such as VO(acen) and VO(salen) [37].

3.5 ESR Spectra

The ESR spectra of the [CuB4AAP(DMG)Cl_2] complex were recorded in DMSO solution at 300 K and 77 K. The spin Hamiltonian parameters for the copper complex are calculated from the spectra. The observed order ($A_{\parallel}$ = 133>$A_{\perp}$ = 55; $g_{\parallel}$ = 2.34>$g_{\perp}$ = 2.07) indicates that the complex is akin to axially elongated octahedral geometry [38, 39].

The ESR parameters and the d-d transition energies were used to evaluate the bonding parameters α^2, β^2 and γ^2 which measure the covalence of the in-plane σ-bonds and the in-plane and out-of-plane π-bonds respectively. The in-plane σ-bonding parameter α^2 was calculated using Kivelson and Neiman expression which is given below:

$$\alpha^2 = -(A_{\parallel}/0.036) + (g_{\parallel} - 2.0023) + 3/7\,(g_{\perp} - 2.0023) + 0.04$$

Orbital reduction factors $K_{\parallel}$ and $K_{\perp}$ were estimated from the simplified expressions:

$$K_{\parallel}^2 = (g_{\parallel} - 2.0023)\Delta E/8\lambda$$
$$K_{\perp}^2 = (g_{\perp} - 2.0023)\Delta E/8\lambda$$

where $K_{\parallel}^2 = \alpha^2\beta^2$; $K_{\perp}^2 = \alpha^2\gamma^2$; $\lambda = 828\ cm^{-1}$ for free ion and E is the electronic transition energy of $^2E_g \rightarrow {}^2T_{2g}$. Significant information about the nature of the bonding in the complex can be derived from the relative magnitudes of $K_{\parallel}$ and $K_{\perp}$. In case of pure σ-bonding $K_{\parallel} = K_{\perp}$, whereas $K_{\parallel} < K_{\perp}$ implies considerable in-plane π-bonding, while for out-of-plane π-bonding $K_{\parallel} > K_{\perp}$. For the present copper complex $K_{\parallel} = K_{\perp} = 0.7254$, together with the α^2 (0.78), β^2 (0.93) and γ^2 (0.93) values, suggesting predominant σ-bonding while the π-bonding is weaker [40].

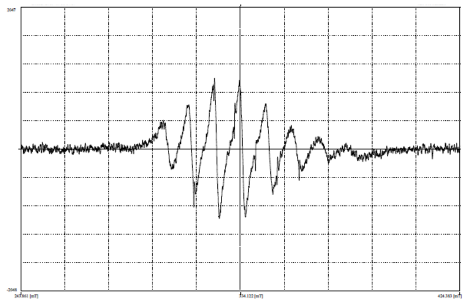


Fig. 5 ESR spectra of [VOB4AAP(DMG)]SO_4 complex in DMSO at 300 K

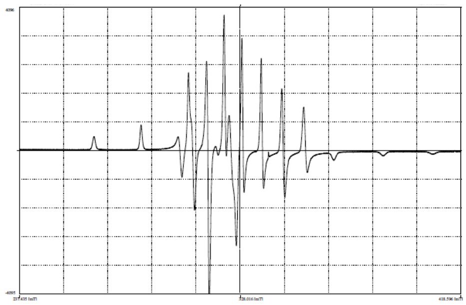


Fig. 6 ESR spectra of [VOB4AAP(DMG)]SO_4 complex in DMSO at 77 K

The isotropic ESR parameters g_0 and A_0 can be calculated from the position and spacing of the resonance lines from the room temperature solution spectrum of the complex. The spectrum is like a typical eight line pattern which shows that a single vanadium is present in the molecule i.e., it is a monomer. In the frozen solid state, the spectrum shows two types of resonance components, one set due to the parallel features and the other set due to the perpendicular features, which indicate axially symmetric anisotropy with well resolved sixteen line hyperfine splitting, characteristic of an interaction between the electron and the vanadium nuclear spin. From the anisotropic spectrum, the anisotropic parameters are calculated. The observed $g_{\parallel}$ = 1.94, $g_{\perp}$ = 1.99, $A_{\parallel}$ = 170 and $A_{\perp}$ = 78 values are almost resemble with that of the square pyramidal geometry [41]. Expressions used for VO(II) axial systems to calculate the various ESR parameters are as follows:

$$g_{\parallel} = 2.0023 - [8\alpha^2\beta^2\lambda/\Delta E\ (x^2 - y^2 \rightarrow xy)]$$
$$A_{\parallel} = P[-4/7\alpha^2 - K + g_{\parallel} - 2.0023 + 3/7\,(g_{\perp} - 2.0023)]$$
$$A_{\perp} = P[-2/7\alpha^2 - K + 11/14\,(g_{\perp} - 2.0023)]$$

where, α^2 and β^2 are the bonding parameters, λ is the spin - orbit coupling constant for the metal ion, K is the isotropic Fermi contact term, P = free

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dipolar term (128×10^{-4} cm^{-1}), $\lambda = 135$ cm^{-1} and E is the electronic transition energy. The lower values of $\alpha^2 = 0.77$ compared to $\beta^2 = 0.89$ indicate that the in-plane σ-bonding is more covalent than the in-plane π-bonding. The ESR spectrum of vanadyl complex, recorded in DMSO solution at 300 K and 77 K is shown in Figs. 5 and 6.

3.6 Biological Activities

Antibacterial activities of the compounds were tested in vitro (50 μg per test) against two Gram-positive *(Staphylococcus aureus and Bacillus subtilis)* and three Gram-negative *(Klebsiella pneumoniae, Escherichia coli and Salmonella typhi)* bacteria by the disc diffusion method using nutrient agar as medium. The minimum inhibitory concentration zone of inhibition against the growth of microrganisms for all the synthesised compounds and control is given in Table 2.

Table 2 The minimum inhibitory concentration of Schiff base, DMG and metal chelates (mg/L)

Compound	*Escherichia coli*	*Salmonella typhi*	*Klebsiella pneumonia*	*Staphylococcus aureus*	*Bacillus subtilis*
DMG	65	60	55	55	60
B4AAP	60	50	65	70	65
[CuB4AAP(DMG)Cl_2]	45	42	50	55	60
[NiB4AAP(DMG)Cl_2]	48	46	45	45	60
[CoB4AAP(DMG)Cl_2]	45	42	50	50	55
[VOB4AAP(DMG)]SO_4	40	35	45	45	40
[ZnB4AAP(DMG)Cl_2]	25	30	35	30	35

From the table, it is clear that the zone of inhibition area is much larger for metal chelates than the ligands. Such increased activity of the metal chelates can be explained on the basis of chelation theory. On chelation, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital. Further, it increases the delocalization of π-electrons over the whole chelate ring and enhances the lipophilicity of the complexes. This increased lipophilicity leads to break-down of the permeability barrier of the cell and thus retards the normal cell processes [42-46].

4. Conclusion

Novel complexes of Cu(II), Ni(II), Co(II), Zn(II) and VO(II) have been prepared using a Schiff base derived from 1-phenyl-2,3-dimethyl-4-imino-benzylidene-pyrazol-5-one and dimethylglyoxime. Electronic absorption and IR spectra of the complexes indicate an octahedral geometry around the central metal ion except VO(II) complex which shows square pyramidal geometry. The monomeric nature of the complexes is confirmed from their magnetic susceptibility. Low conductance data of the chelates support their non-electrolytic nature except vanadyl complex which shows electrolytic in nature due to the presence of sulphate ion outside the coordination sphere. The cyclic voltammogram of the copper complex in MeCN solution shows a quasi-reversible peak for the couple: copper(II) → copper(III) at $Ep_a = +0.55$ V with a direct cathodic peak for copper(III) → copper(II) at $Ep_c = +0.44$ V. Further, it exhibits two irreversible peaks characteristic for copper(II) → copper(I) ($Ep_c = -0.32$ V) and copper(I) → copper(0) ($Ep_c = -0.85$ V) reduction. In the anodic side, the direct oxidation of copper(0) → copper(II) is observed with a strong stripping peak at $Ep_a = -0.21$ V. The VO(S4AAPAP) complex in MeCN solution exhibits a cyclic voltammogram typical of VO(II) complexes. The quasi reversible peak at $Ep_a = 0.71$ V and $Ep_c = 0.56$ V are attributable to the VO(II)/VO(III) couple. In the negative region, it shows quasi reversible peaks at $Ep_a = -0.62$ V and $Ep_c = -0.71$ V for the couple VO(II)/VO(I). The spin Hamiltonian parameters for the copper complex ($A_{\parallel} = 133 > A_{\perp} = 55$; $g_{\parallel} = 2.34 > g_{\perp} = 2.07$) indicates that the complex is akin to axially elongated octahedral geometry. The observed ESR data of vanadyl complex ($g_{\parallel} = 1.94$, $g_{\perp} = 1.99$, $A_{\parallel} = 170$ and $A_{\perp} = 78$) suggest that the complex is resemblance square pyramidal geometry The antimicrobial activity of the ligand and its complexes have been extensively studied on microorganisms such as *Staphylococcus aureus, Klebsiela pneumoniae, Bacillus subtilis, Escherichia coli and Salmonella typhi*. Most of the complexes have higher activity than that of the free ligands.

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