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Synthesis, Structural Characterization, Redox and Antimicrobial Studies of Schiff Base Copper(II), Nickel(II), Cobalt(II), Manganese(II), Zinc(II) and Oxovanadium(II) Complexes Derived from Benzil and 2-Aminobenzyl Alcohol

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Neutral complexes of Cu(II), Ni(II), Co(II), Mn(II), VO(II) and Zn(II) have been synthesized from the Schiff base derived from benzil and 2-aminobenzyl alcohol. The structural features have been arrived from their microanalytical, IR, UV-Vis, ^{1}H NMR, Mass and ESR spectral data. All of the complexes exhibit square-planar geometry except the Mn(II) and VO(II) complexes. The Mn(II) chelate shows an octahedral environment and the VO(II) chelate exists in a square-pyramidal geometry. The monomeric and non-electrolytic nature of the complexes is evidenced by their magnetic susceptibility and low conductance data. The cyclic voltammogram of copper complex in acetonitrile solution shows two quasi reversible peaks for the Cu(II)/Cu(III) and Cu(II)/Cu(I) couples. The X-band ESR spectra of the Cu(II) and VO(II) complexes in DMSO at 300 and 77 K were recorded and their salient features are reported. The biological activity of the metal chelates against the bacteria *Staphylococcus aureus, Bacillus subtilis, Klebsiella pneumoniae, Salmonella typhi, Pseudomonas aeruginosa* and *Shigella flexneri* are also reported. Most of the complexes have higher activity than that of the free Schiff base and the control.

Key words: benzil, 2-aminobenzyl alcohol, Schiff base, ESR spectra, antimicrobial studies

Schiff bases derived from the condensation of diketones with amines represent an important class of chelating agents, the metal complexes of which have been studied widely. During the past decades, there has been a great deal of interest in the synthesis and characterisation of transition metal Schiff base chelates because of their importance as catalysts in many reactions such as carbonylation, hydroformylation, reduction, oxidation, epoxidation and hydrolysis [1–5]. Schiff base complexes are also noted for their significant antimicrobial activities [6,7]. Not only has an upsurge of interest taken place in experimental studies, but also there has been a renewed interest in the structural elucidation of these complexes. A search through the literature reveals that no work has been done on the condensation of benzil with 2-aminobenzyl alcohol [8–14]. As a part of continuing efforts to synthesis and characterise transition

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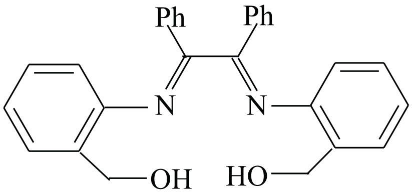
metal chelates using simple Schiff base ligands, in this paper we describe the synthesis, characterisation, electrochemical and antimicrobial studies of transition metal complexes containing tetradentate Schiff base derived from benzil and 2-aminobenzyl alcohol. This ligand system coordinates with the metal ion in a tetradentate manner through the hydroxyl groups and azomethine nitrogen atoms of the Schiff base. The structure of the Schiff base (H_2L) is given in Scheme 1:



Scheme 1. Structure of the Schiff base (H_2L).

EXPERIMENTAL

All the reagents used for the preparation of the ligand and complexes were of Merck products. Spectroscopic grade solvents were used for spectral and cyclic voltammetric measurments. The carbon, hydrogen and nitrogen contents in each sample were performed at RSIC, CDRI, Lucknow. ^1H NMR spectra of the samples were measured in DMSO-d_6 at IICT, Hydrabad. The IR spectra were recorded in KBr pellets using a Perkin-Elmer 783 spectrophotometer. The UV-Vis spectra of the complexes were recorded on a Shimadzu UV-1601 spectrophotometer. The X-band ESR spectra of the copper and vanadyl complexes were recorded in DMSO at 300 K and 77 K on a Varian 112 ESR spectrometer using diphenylpicrylhydrazyl (DPPH) as internal standard at RSIC, IIT, Chennai. Magnetic susceptibility measurements of the complexes were carried out using Gouy balance. Copper sulphate was used as calibrant. Cyclic voltammogram of copper complex was recorded in acetonitrile (1 mmol) solution at 300 K on a BAS CV 50 electrochemical analyμer. The three electrode cell comprised a reference Ag/AgCl, auxillary Pt and the working glassy carbon (0.07 cm^2) electrodes. The molar conductivity was measured on a Systronic conductivity bridge with a dip type cell, using 10^{-4} M solution of complexes in ethanol.

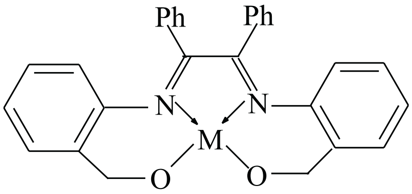
Antimicrobial activity: The *in vitro* biological screening effects of the investigated compounds were tested against the bacteria *S. typhi, S. aureus, K. pneumoniae, B. Subtilis, S. flexneri* and *P. aeruginosa* by the serial dilution method using agar nutrient as the medium. The test solutions were prepared by dissolving the compounds in MeCN and all the blank discs were moistened with the solvent. For disc assays, paper (6 mm) containing the compounds was placed on the surface of the nutrient agar plates previously spread with 0.1 ml of over night cultures of microorganisms. After 36 h incubation at 37°C, the inhibition zones were developed.

Synthesis of Schiff base(H_2L): An ethanolic solution of benzil (2.10 g, 0.01 mol) and 2-aminobenzyl alcohol (2.46 g, 0.02 mol) was boiled under reflux on a water bath for *ca.* 16 h. The resulting solution was concentrated to 5 ml on a water bath and allowed to cool at 0°C for *ca.* 24 h, the pale yellow solid formed was filtered, washed with ethanol and recrystallized in chloroform. Yield: 54%; m.p: 72–73°C.

Syntheses of metal complexes:A solution of 5 mmol of MCl_2 (where M = Cu(II), Ni(II), Co(II), Mn(II) and Zn(II)) and the Schiff base (5 mmol) in ethanol (40 ml) was boiled under reflux for *ca.* 4 h. The resulting solution was concentrated to *ca.* 10 ml and 10 ml of light petroleum (60–80°C) was added. The mixture was cooled at 0°C for *ca.* 12 h and the precipitated complexes were filtered, washed with ethanol and dried *in vacuo*. Vanadyl complex was synthesized by the same procedure but in the presence of 5% aqueous sodium hydroxide solution (5 ml).

RESULTS AND DISCUSSION

The analytical data of the ligand and its complexes agree very well with the general formula ML, while the manganese complex has $MnL\cdot 2H_2O$, where M = Cu(II), Ni(II), Co(II), Zn(II) and VO(II); L = ($C_{28}H_{22}N_2O_2$). The proposed structure of the complexes is given in Scheme 2:



Scheme 2. Structure of the complexes.

Thermal analysis shows that the manganese complex loses two water molecules at *ca.* 170°C, which suggests presence of two molecules of water coordinated to the central metal ion which is further confirmed from its characteristic IR spectrum. The low conductance values of the chelates support the non-electrolytic nature of the metal complexes.

The mass spectra of the ligand and of some of the complexes were recorded and compared for their stoichiometric composition. The molecular ion peak for the ligand was observed at 420 m/z ratio ($C_{28}H_{24}O_2N_2$). For copper complex, the molecular ion peak appeared at 482 m/z ($CuC_{28}H_{22}O_2N_2$) which confirms the stoichiometry of metal complexes as being of the ML type.

The ^1H NMR spectrum of the Schiff base in DMSO-d_6 shows C_6H_5 multiplet at 6.9–7.2 δ range and -CH_2 at 4.6 δ. The peak at 10.8 δ is attributable to the -OH group present in the 2-aminobenzyl alcohol. The absence of this peak, noted in the zinc complex, indicates the loss of the -OH proton due to complexation. There is no appreciable change in all other signals in this complex.

In order to study the binding mode of the Schiff base to the metal in the complexes, the IR spectrum of the free ligand was compared with the spectra of the complexes. The IR spectrum of the ligand shows a weak broad band in the region 3250–3450 cm^{-1} assignable to intramolecular hydrogen bonded -OH groups. The absence of this band, noted in the spectra of the complexes, indicates the deprotonation of the -OH groups on complexation. The ligand shows its characteristic -C=N bands in the region 1640–1620 cm^{-1}, which are also shifted to lower frequencies in the spectra of all the complexes (1600–1580 cm^{-1}). The IR spectra of the metal chelates also show some new bands in the region 480–450 cm^{-1} and 400–350 cm^{-1} which are probably due to the formation of M–O and M–N bonds respectively [15]. The IR spectra of the manganese complex shows a strong broad band in the region 3200–3600 cm^{-1}, confirms the presence of water molecules coordinated to the metal ion. In addition to the other bands, the vanadyl complex shows an additional band at 940 cm^{-1} attributed to the V=O frequency [16].

The electronic spectrum of the ligand in MeCN solution shows absorption at *ca.* 31250 cm^{-1}. The UV-Vis spectrum of copper in MeCN solution displays a broad band $^2B_1g\rightarrow{}^2A_1g$ (11628 cm^{-1}) and a well defined shoulder $^2B_1g\rightarrow{}^2B_2g$ (23529 cm^{-1}), which strongly favour the square planar geometry around the metal ion [17–19]. The broadness of the band can be taken as an indication of distortion from perfect planar symmetry. This is further supported by the magnetic susceptibility value (1.72 B.M.). The nickel complex is diamagnetic suggesting a square planar structure. The electronic spectra of the nickel complex in MeCN shows a d-d band at 15152 cm^{-1} assigned as $^1A_1g\rightarrow{}^1B_1g$ transition, which also indicates square planar geometry [19–20]. Also the cobalt complex in $CHCl_3$ shows a d-d band at 16000 cm^{-1} assigned as $^1A_1g\rightarrow{}^1B_1g$ transition which confirms the square planar coordination [21–23]. Further, the magnetic susceptibility value (3.86 B.M.) also supports the square planar structure of the complex. The vanadyl complex in MeCN solution shows two d-d bands at 18518 cm^{-1} and 11904 cm^{-1}, which are assigned as $^2B_2\rightarrow{}^2A_1$ and $^2B_2\rightarrow{}^2E$ respectively. Square pyramidal geometry [24–26] is proposed for this system because it shows a band in the 11904 cm^{-1} region ($^2B_2\rightarrow{}^2E$). This is further confirmed by the magnetic susceptibility value (1.71 B.M.). The magnetic susceptibility data (5.92 B.M.) of the manganese complex at room temperature is consistent with that of octahedral geometry around the central metal ion.

The ESR spectrum of metal chelates provides information about hyperfine and super hyperfine structures which are important in studying the metal ion environment in complexes, *i.e.*, the geometry, nature of the ligating sites from the Schiff base of the metal and the degree of covalancy of the metal–ligand bonds. The X-band ESR spectrum of the CuL complex, recorded in DMSO at 300 and 77 K, is shown in Fig. 1. The spectrum of the copper complex at 300 K shows one intense absorption band in the high field and is isotropic due to the tumbling motion of the molecules. However, this complex in the frozen state shows four well resolved peaks with low intensities in the low field region and one intense peak in the high field region. The magnetic susceptibility measurements reveal that the copper complex has magnetic moment 1.72 B.M., corresponding to the one unpaired electron, indicating that the complex is mononuclear. This fact was also evident from the absence of a half field signal, observed in the spectrum at 1600 G due to the $m_s = \pm 2$ transitions, ruling out any Cu-Cu interaction [27].

The g tensor values of copper complex can be used to derive the ground state. In square-planar complexes, the unpaired electron lies in the $d_{x^2-y^2}$ orbitals giving ^2B_1g as the ground state with $g_{\shortparallel} > g_{\perp} > 2$, while the unpaired electron lies in the d_{z^2} orbital giving ^2A_1g as the ground state with $g_{\perp} > g_{\shortparallel} > 2$. From the observed values it is clear that $A_{\shortparallel} = 167 > A_{\perp} = 56$; $g_{\shortparallel} = 2.31 > g_{\perp} = 2.07 > 2$ and the ESR parameters of the complexes coincide well with related systems which suggest that the complexes are having square-planar geometry and the systems are axially symmetric [28–30]. Further, this is also supported by the fact that the unpaired electron lies predominantly in the $d_{x^2-y^2}$ orbital. In axial spectra the g-values are related with exchange interaction coupling constant (G) by the expression,

$$G = g_{\shortparallel} - 2/g_{\perp} - 2$$

Figure 1. ESR spectra of CuL complex at 300 K (a) and 77 K (b) in DMSO solution.

According to Hathaway [31], if the value of G is larger than four, exchange interaction is negligible because the local tetragonal axes are aligned parallel or slightly misaligned while the value of G is less than four, exchange interaction is considerable and the local tetragonal axes are misaligned. For present copper complex, the G value is 4.4 which suggests that the local tetragonal axes are aligned parallel or slightly misaligned and consistent with $d_{x^2-y^2}$ ground state.

Electron spin resonance and optical spectra have been used to determine the covalent bonding parameters for the Cu(II) ion in various ligand field environments. The in-plane σ-bonding covalency parameters, α^2 is related to $A_{\parallel}$, $g_{\parallel}$ and $g_{\perp}$ according to the following equation [30,32]

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

If the value of $\alpha^2 = 0.5$, it indicates complete covalent bonding, while the value of $\alpha^2 = 1.0$ suggests complete ionic bonding. The observed value of α^2 (0.69) indicates that the complexes have some covalent character.

The out-of-plane π-bonding (γ^2) and in-plane π-bonding (β^2) parameters are calculated from the following expressions:

$$\beta^2 = (g_{II} - 2.0023)\ E_1 /- 8\lambda\alpha^2;\ \ \gamma^2 = (g_{\perp} - 2.0023)\ E_2 /- 2\lambda\alpha^2.$$

In these equations $\lambda = 828\ \mathrm{cm}^{-1}$ for the free ion and E_1 and E_2 are the electronic transition energies of ${}^2B_{1g} \rightarrow {}^2A_{1g}$ and ${}^2B_{1g} \rightarrow {}^2B_{2g}$ respectively. The observed β^2 (0.78) and γ^2 (1.23) values indicate that there is substantial interaction in the in-plane π-bonding, whereas the out-of-plane π-bonding is completely ionic. This is also confirmed by orbital reduction factors [33] (K_{II} and $K_{\perp}$), which were estimated from the simple relation, $K_{II} = \alpha^2\beta^2$ and $K_{\perp} = \alpha^2\gamma^2$.

Significant information about the nature of bonding in the copper(II) complex can be derived from the relative magnitudes of K_{II} and $K_{\perp}$. In the case of pure σ-bonding $K_{II} \sim K_{\perp}$ *ca.* 0.77, whereas $K_{II} < K_{\perp}$ implies considerable in-plane π-bonding, while for out-of-plane π-bonding $K_{II} > K_{\perp}$. For copper complex the observed order is K_{II} (0.53) < $K_{\perp}$ (0.85) implying the presence of significant in-plane π-bonding.

The ESR spectrum of vanadyl complex, recorded in DMSO solution at 300 and 77 K is shown in Fig. 2. The room temperature spectrum of the complex is typical eight-line pattern which shows that single vanadium is present in the molecule, *i.e.*, it is monomer. In frozen 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, indicate axially symmetric anisotropy with well-resolved sixteen-line hyperfine splitting, characteristic of interaction between the electron and the vanadium nuclear spins [34,35]. The observed parameters $A_{II} = 173 > A_{\perp} = 71$; $g_{II} = 1.98 < g_{\perp} = 2.04$ indicate that the molecule exists in a square-pyramidal geometry which is characteristic for oxovanadium(II) chelates.

The bonding parameters α^2, β^2 and γ^2 were also calculated for this complex by using the following equations [36–38]:

$$\alpha^2 = (2.0023 - g_{II})\ E_1 /8\lambda\beta^2;\ \ \beta^2 = 7/6\ (-A_{II}/p + A_{\perp}/p + g_{II} - 5/14\ g_{\perp} - 9/14\ g_e);$$
$$\gamma^2 = (2.0023 - g_{\perp})\ E_2 /2\lambda\alpha^2.$$

In these equations $P = 128\times10^{-4}\ \mathrm{cm}^{-1}$, $\lambda = 135\ \mathrm{cm}^{-1}$, E_1 and E_2 are the electronic transition energies of ${}^2B_2 \rightarrow {}^2A_1$ and ${}^2B_2 \rightarrow {}^2E$ respectively. The in-plane π-bonding ($\beta^2 = 0.94$) and out-of-plane π-bonding coefficient ($\gamma^2 = 0.90$) values do not deviate much from unity. For most of the complexes, the π-bonding coefficients remain constant and span the region of 0.90 to 1.00. This is consistent with Kivelson's conclusion [38], which suggests that the d_{xy} orbital is essentially non-bonding while π-bonding coefficients remain constant.

Essentially, the delocalization of electrons into the ligand may be gauged from the in-plane σ-bonding coefficient (α^2) values. This follows the σ-donor strength of the ligand and it usually decreases as the covalent bonding increases. The observed

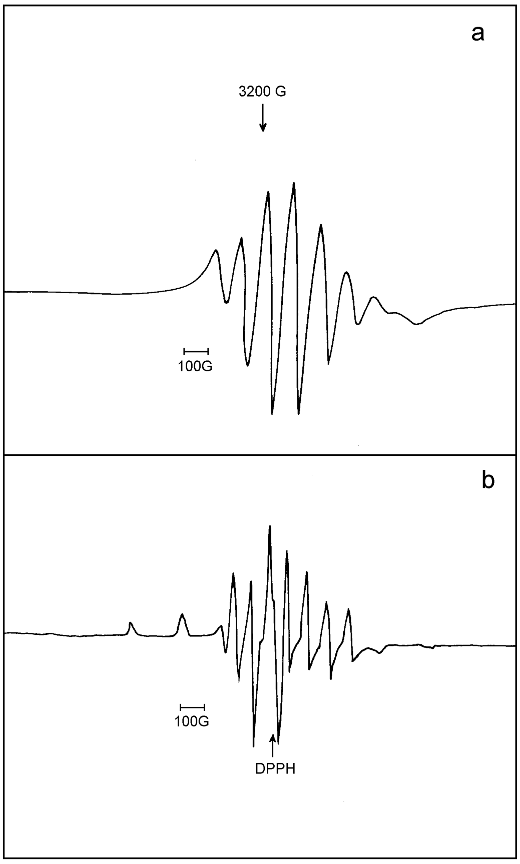


Figure 2. ESR spectra of VOL complex at 300 K (a) and 77 K (b) in DMSO solution.

($\alpha^2 = 0.62$) value indicates that in-plane σ-bonding is significant. The M.O. coefficients also show that the metal ion has some covalent character in the ligand environment.

The cyclic voltammogram of the copper complex (0.01 mol) in MeCN in 0.8 to –1.2 V potential range is shown in Fig. 3. It shows a well defined redox process corresponding to the formation of the couple copper(II)/copper(III) at $Ep_a = 0.46$ V and the associated cathodic peak at $Ep_c = 0.29$ V. This couple is found to be quasi reversible and the ratio of anodic to cathodic peak currents ($Ip_c/Ip_a \sim 1$) is corresponding to simple one-electron process. The complex also shows another quasi reversible peak in the negative region characteristic for copper(II)→copper(I) couple at $Ep_c = -0.67$ V with the associated anodic peak at $Ep_a = -0.28$ V for copper(I)→copper(II) oxidation. The reversibility of the copper(II)/copper(III) couple of the complex was unaffected by varying the scan rates ranging from 25 mVs^{-1} to 100 mVs^{-1} with peak potentials and are reported in Table 1.

Figure 3. Cyclic voltammogram of CuL complex in MeCN solution containing 0.1 M TMAP. Scan rate 100 mVs^{-1}.

Table 1. Redox potential for $[CuL^1]$ complex in MeCN solution containing 0.1 M TMAP at 300 K for the couple Cu(II)/Cu(III).

Scan rate mVs^{-1}	Ep_a (V)	Ep_c (V)	ΔEp	Ip_a (μA)	Ip_c (μA)	Ip_c/Ip_a
25	0.45	0.30	0.15	–52.91	60.06	0.88
50	0.45	0.29	0.14	–58.69	65.21	0.90
75	0.46	0.30	0.14	–45.18	48.62	0.93
100	0.46	0.29	0.13	–47.32	51.43	0.92

The *in vitro* biological screening effects of the investigated compounds were tested against six bacteria: *Staphylococcus aureus, Bacillus subtilis, Klebsiella pneumoniae, Salmonella typhi, Pseudomonas aeruginosa* and *Shigella flexneri* by serial dilution method. The minimum inhibition concentration (MIC) values of the compounds against the growth of microorganisms are summarised in Table 2. A comparative study of the ligands and their complexes (MIC values) indicates that most of the metal chelates exhibit higher antibacterial activity than the free ligand.

Table 2. Antimicrobial activities of transition metal complexes (minimum inhibitory concentration × 10^{-3} M).

Compound	*S. thypi*	*S. aureus*	*K. pneumoniae*	*B. subtilis*	*S. flexneri*	*P. aeruginosa*
$[H_2L]$	7.2	6.4	8.4	5.3	6.8	4.8
[CuL]	4.8	5.1	4.8	4.2	5.1	2.6
[NiL]	5.2	5.4	8.1	4.6	4.7	3.4
[CoL]	3.8	4.2	5.3	4.8	3.8	4.2
$[MnL\cdot(H_2O)_2]$	6.4	4.8	6.4	3.4	5.6	3.6
[ZnL]	3.8	4.5	6.8	4.3	5.4	2.8
[VOL]	5.7	5.2	6.6	3.7	6.2	4.0

Such increased activity of the metal chelates can be explained on the basis of Overtone's concept [39] and the Tweedy's chelation theory [40]. According to Overtone's concept of cell permeability, the lipid membrane that surrounds the cell favours the passage of only lipid-soluble materials due to which liposolubility is an important factor which controls the antimicrobial activity. On chelation, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further, it increases the delocalisation of π-electrons over the whole chelate ring and enhances the lipophilicity of the complexes. This increased lipophilicity enhances the penetration of the complexes into lipid membranes and blocks the metal binding sites in the enzymes of microorganisms. These complexes also disturb the respiration process of the cell and thus block the synthesis of proteins which restrict further growth of the organism. Furthermore, the mode of action of the compounds may involve the formation of a hydrogen bond through the azomethine group with the active centres of cell constituents, resulting in interference with the normal cell process [41].

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