

Synthesis and characterisation of Cu(II), Ni(II), Mn(II), Zn(II) and VO(II) Schiff base complexes derived from *o*-phenylenediamine and acetoacetanilide

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Abstract. Neutral tetradentate N₂O₂ type complexes of Cu(II), Ni(II), Mn(II), Zn(II) and VO(II) have been synthesised using a Schiff base formed by the condensation of *o*-phenylenediamine with acetoacetanilide in alcohol medium. All the complexes were characterised on the basis of their microanalytical data, molar conductance, magnetic susceptibility, IR, UV–Vis ¹H NMR and ESR spectra. IR and UV–Vis spectral data suggest that all the complexes are square-planar except the Mn(II) and VO(II) chelates, which are of octahedral and square pyramidal geometry respectively. The monomeric and neutral nature of the complexes was confirmed by their magnetic susceptibility data and low conductance values. The ESR spectra of copper and vanadyl complexes in DMSO solution at 300 K and 77 K were recorded and their salient features are reported.

Keywords. *o*-Phenylenediamine; acetoacetanilide; Schiff base complexes; electron spin resonance.

1. Introduction

Schiff bases of *o*-phenylenediamine and its complexes have a variety of applications including biological¹, clinical² and analytical³. Earlier work has shown that some drugs showed increased activity when administered as metal chelates rather than as organic compounds^{1,2}, and that the coordinating possibility of *o*-phenylenediamine has been improved by condensing with a variety of carbonyl compounds. A search through literature^{4–14} reveals that no work has been done on the transition metal complexes of the Schiff base derived from *o*-phenylenediamine and acetoacetanilide. In this paper, we report the synthesis of a new type of tetradentate ligand formed by the condensation of *o*-phenylenediamine with acetoacetanilide. This ligand system has both nitrogen and oxygen donor sites. It coordinates with the metal ion in a tetradentate manner through the enolisable carbonyl group of the acetoacetanilide moiety and the azomethine nitrogen atoms of the Schiff base.

The structure of the ligand is shown in chart 1.

*For correspondence

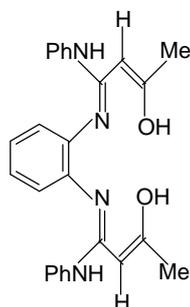


Chart 1.

2. Experimental

Microanalytical data, ^1H NMR spectra of the compounds were measured at the Regional Sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow (RSIC, CDRI). Electronic spectra of the complexes were recorded on a Shimadzu UV-160 spectrophotometer. IR spectra of the samples were recorded on a Perkin–Elmer 783 spectrophotometer as KBr discs. Magnetic susceptibility measurements of the complexes in the solid state were determined using a Gouy balance at room temperature by using copper sulphate as calibrant. Molar conductances of the complexes were measured in ethanol–water at room temperature using a Systronic conductivity bridge type 305. ESR spectra of the complexes were recorded in DMSO solution on a Varian E112 X-band spectrometer at the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology (RSIC, IIT/M), Chennai.

2.1 Synthesis of Schiff base

An ethanolic solution (40 ml) of *o*-phenylenediamine (0.545 g, 0.005 M) was refluxed with acetoacetanilide (1.77 g, 0.01 M) for about 12 h. The volume of the solution was reduced to one third and 10 ml of petroleum ether (60–80°C range) was added with constant stirring. The pale yellow solid acetoacetanilido-*o*-phenylenediamine (AAAPD) formed was filtered and recrystallised from ethanol. Yield: 60% (m.p. 83°C).

2.2 Synthesis of complexes

An ethanolic solution of Schiff base (2.13 g, 0.005 M) was refluxed with MCl_2 (0.005 M) in ethanol for about 6 h. After refluxing, the volume of the solution was reduced to one third and the concentrate cooled at 0°C. The solid complex formed was filtered, washed with ethanol and dried *in vacuo*.

3. Results and discussion

Physical characteristics and microanalytical and magnetic susceptibility data of the complexes are given in table 1. The analytical data of all the complexes correspond to the general formula ML while that of the manganese complex is $\text{MnL}\cdot 2\text{H}_2\text{O}$. Magnetic susceptibility values of the complexes at room temperature are consistent with square planar geometry around the central metal ion except for the Mn(II) and VO(II) complexes

Table 1. Physical characteristics and analytical and magnetic susceptibility data of the complexes.

Compound	Colour	Found (Calcd.) (%)				m_{eff} (BM)
		M	C	H	N	
L	Brown	–	72.8 (73.2)	6.0 (6.1)	12.9 (13.2)	–
[CuL]	Brown	12.6 (13.0)	63.6 (64.0)	4.7 (4.9)	11.2 (11.5)	1.72
[NiL]	Green	11.7 (12.2)	63.4 (63.8)	4.6 (4.9)	10.9 (11.4)	–
[MnL(H ₂ O) ₂]	Brown	10.8 (10.7)	60.2 (60.6)	5.2 (5.4)	10.7 (10.9)	5.62
[ZnL]	Colourless	12.1 (13.4)	63.5 (63.8)	4.7 (4.9)	11.1 (11.4)	–
[VOL]	Pale green	10.7 (10.4)	63.2 (63.6)	4.8 (4.9)	11.5 (11.4)	1.71

L = AAAPD

which show octahedral and square pyramidal geometry respectively. The chelates show no appreciable conductance and this supports their neutral nature. Thermal analysis shows that the manganese complex loses two water molecules at about 170°C, which suggests the presence of two molecules of water coordinated to the central metal ion. This is further confirmed by its characteristic IR spectrum.

3.1 ¹H NMR spectra

The ¹H NMR spectrum of the Schiff base in DMSO shows the following signals: C₆H₅ multiplet at 6.9–7.8 *d* range, –PhNH at 2.49 *d* and =C–CH at 6.3 *d*. The peak at 11.8 *d* is attributed to the enolic –OH group present in the acetoacetanilide moiety. 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.

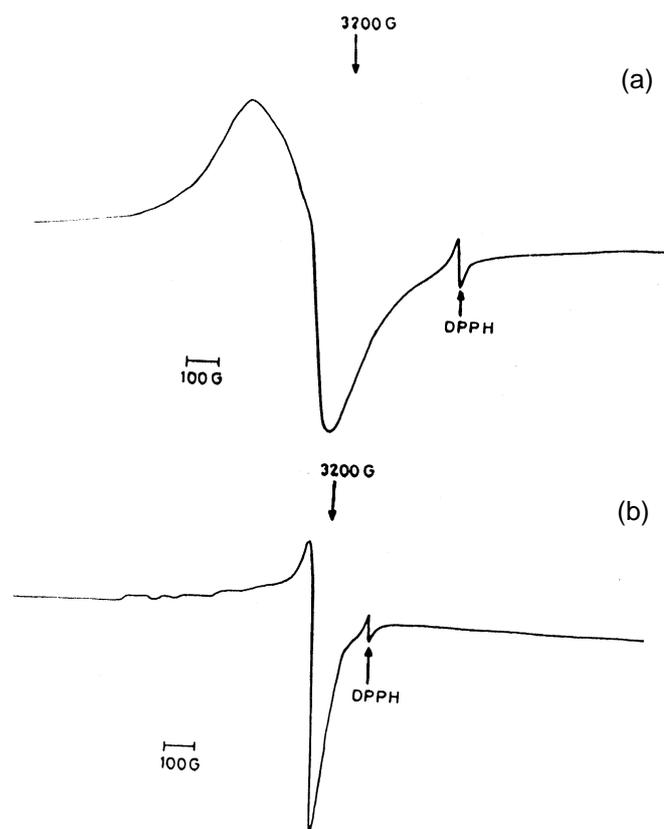
3.2 Infrared spectra

The IR spectra of the complexes are compared with that of the free ligand to determine the changes that might have taken place during the complexation. The band at 1650 cm^{–1} is characteristic of the azomethine nitrogen atom present in the free ligand. The lowering in this frequency region (1600–1580 cm^{–1}), observed in all the complexes, indicates the involvement of the azomethine nitrogen atom in coordination¹⁵. The –OH stretching and bending vibrational frequencies of the acetoacetanilide moiety of the AAAPD appearing in the region 3600–3200 cm^{–1} and 1310 cm^{–1} respectively indicate that the enolic carbonyl group is not involved in the reaction and only the imide carbonyl group participates in the condensation. The disappearance of these two peaks in the spectra of all the complexes indicates that the chelation takes place via the enolic –OH group. Also the ligand and the complexes show an intense peak at 3150 cm^{–1}, which is characteristic of –NH stretching, indicating the existence of a free –NH group. The manganese complex shows a broad band at 3500–3100 cm^{–1} that suggests that water is coordinated to the central metal ion^{15,16}. In addition to other bands, the vanadyl complex shows the characteristic V=O asymmetric stretching frequency at 940 cm^{–1}. These data are well in accordance with those of reported complexes^{16,17}.

Table 2. Electronic absorption spectral data of the Schiff base and the complexes.

Compound	Absorption region (cm ⁻¹)	Band assignment	Geometry
AAAPD	31250 41322	INCT* INCT	–
Cu(AAAPD)	18520 39450 48310	² B _{1g} → ² A _{1g} INCT INCT	Square-planar
Ni(AAAPD)	18800 21650 42190 48780	¹ A _{1g} → ¹ B _{1g} ¹ A _{1g} → ¹ B _{2g} INCT INCT	Square-planar
VO(AAAPD)	12380 21650 40670 47850	² B ₂ → ¹ A ₁ ² B ₂ → ¹ E INCT INCT	Square-pyramidal

*INCT – Intraligand charge transfer band

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

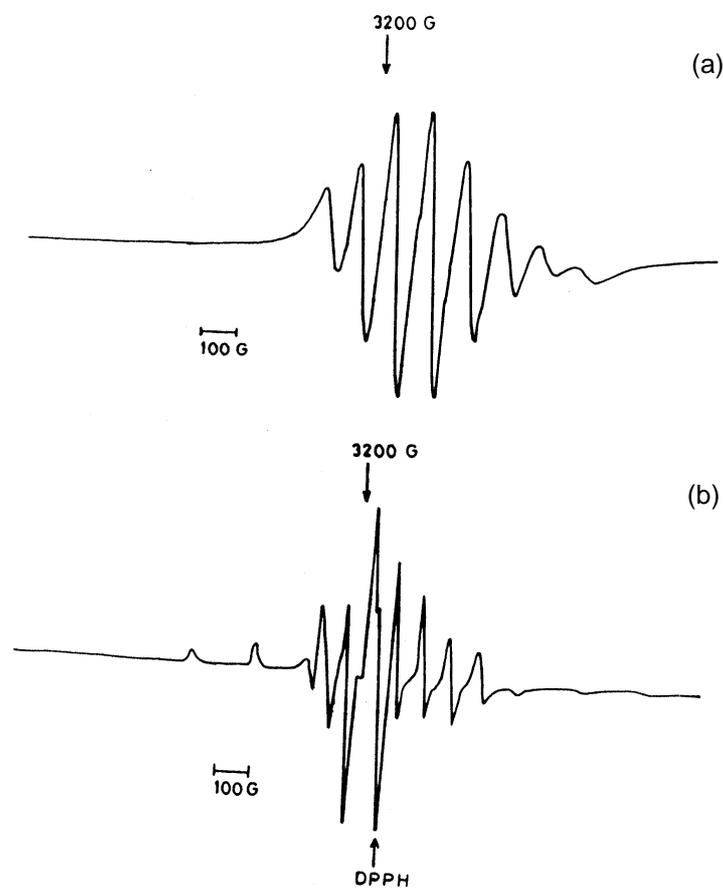


Figure 2. ESR spectra of VO(AAAPD) complex in DMSO solution at (a) 300 and (b) 77 K.

3.3 Electronic absorption spectra

UV-Vis spectra of the AAAPD, Cu(II), Ni(II) and VO(II) complexes were recorded at 300 K using suitable solvents. The solvent, absorption regions, band assignments and proposed geometries of the complexes are given in table 2. These values are comparable with those of the other reported complexes¹⁸⁻²⁴.

3.4 ESR spectroscopy

ESR spectra of Cu(AAAPD) and VO(AAAPD) recorded in DMSO solution at 300 and 77 K are given in figures 1 and 2. The spin Hamiltonian parameters of the complexes were calculated and are summarised in table 3.

The spectrum of the Cu(AAAPD) complex at 300 K shows one intense absorption band in the high field region and is isotropic due to the tumbling motion of the molecules. However, this complex 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. No band

Table 3. Spin hamiltonian parameters of Cu(II) and VO(II) complexes in DMSO at 300 and 77 K.

Complex	$A_{\parallel} \times 10^{-4}$ (cm^{-1})	$A_{\perp} \times 10^{-4}$ (cm^{-1})	$A_{\text{iso}} \times 10^{-4}$ (cm^{-1})	g_{\parallel}	g_{\perp}	g_{iso}	\mathbf{a}^2	\mathbf{b}^2
CuL	153	30	67	2.34	2.08	2.06	0.74	0.78
VOL	175	82	115	1.92	1.97	1.95	0.64	0.92

L = AAAPD

corresponding to $m_s = \pm 2$ transition was observed in the spectrum, ruling out any Cu–Cu interaction. The g tensor values of Cu(II) complex can be used to derive the ground state. In tetragonal and square planar complexes, the unpaired electron lies in the $d_{x^2-y^2}$ orbital giving ${}^2B_{1g}$ as the ground state with the $g_{\parallel} > g_{\perp}$. From the observed values, it is clear that $g_{\parallel} > g_{\perp}$ ($2.34 > 2.08$), which suggests that the complex is square planar. Also it is supported by the fact that the unpaired electron lies predominantly in the $d_{x^2-y^2}$ orbital^{25–31}.

Furthermore, Massacesi *et al*²⁵ reported that g_{\parallel} is 2.4 for copper–oxygen bonds and 2.3 for copper–nitrogen bonds. For our copper complex, $g_{\parallel} = 2.34$, which is between 2.3–2.4 and thus in conformity with the presence of mixed copper–nitrogen and copper–oxygen bonds in these chelates. Molecular orbital coefficients, \mathbf{a}^2 (covalent in-plane \mathbf{s} -bonding) and \mathbf{b}^2 (covalent in-plane \mathbf{p} -bonding), were calculated by using the following equations^{29–32}.

$$\mathbf{a}_{\text{Cu}}^2 = -(A_{\parallel}/0.036) + (g_{\parallel} - 2.0023) + 3/7(g_{\perp} - 2.0023) + 0.04$$

$$\mathbf{b}^2 = (g_{\parallel} - 2.0023)E / -8I\mathbf{a}^2,$$

where E is the electronic transition energy of ${}^2B_{1g} \rightarrow {}^2A_{1g}$. From table 3, it is clear that the in-plane \mathbf{s} -bonding is more covalent than the in-plane \mathbf{p} -bonding. These data are well in accordance with other reported values^{28–30}.

The ESR spectrum of the vanadyl complex (figure 2) was recorded in DMSO solution at 300 and 77 K. The room temperature (300 K) spectrum is 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 indicates axially symmetric anisotropy with well-resolved sixteen-line hyperfine splitting, characteristic of interaction between the electron and the vanadium nuclear spins. The observed g_{\parallel} , g_{\perp} and A_{\parallel} values are well in accordance with that of a molecule which exists in square pyramidal geometry³³.

The molecular orbital coefficients \mathbf{a}^2 and \mathbf{b}^2 were also calculated for the complex by using the following equations³⁴,

$$\mathbf{a}^2 = (2.0023 - g_{\parallel})E/8I\mathbf{b}^2,$$

$$\mathbf{b}^2 = 7/6(-A_{\parallel}/p + A_{\perp}/p + g_{\parallel} - 5/14g_{\perp} - 9/14g_e),$$

where $P = 128 \times 10^{-4} \text{ cm}^{-1}$, $I = 135 \text{ cm}^{-1}$ and E is the electronic transition energy of ${}^2B_2 \rightarrow {}^2E$. The lower value of a^2 compared to b^2 indicates that the in-plane σ -bonding is more covalent than the in-plane p -bonding.

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