



## Synthesis, Physical Characterization and Biological Activity of Some Schiff Base Complexes

R.RAJAVEL\*, M. SENTHIL VADIVU and C. ANITHA

Department of Chemistry,  
Periyar University, Salem-636011, Tamilnadu – India  
*drrajavel@rediffmail.com*

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**Abstract:** Structural modification of organic molecule has considerable biological relevance. Further, coordination of a biomolecules to the metal ions significantly alters the effectiveness of the biomolecules. In view of the antimicrobial activity ligand [*bis*-(2-aminobenzaldehyde)] malonoyl dihydrazone], metal complexes with Cu(II), Ni(II), Zn(II) and oxovanadium(IV) have been synthesized and found to be potential antimicrobial agents. An attempt is also made to correlate the biological activities with geometry of the complexes. The complexes have been characterized by elemental analysis, molar conductance, spectra and cyclicvoltammetric measurements. The structural assessment of the complexes has been carried out based on electronic, infrared and molar conductivity values.

**Keywords:** Biological activity, 2-Aminobenzaldehyde, Malonoyldihydrazide, Oxovanadium(IV)

### Introduction

Malonoyldihydrazide and 2-aminobenzaldehyde compounds are capable to form complexes with transition metal ions in the form Schiff bases. The complexes of copper(II), nickel(II), zinc(II) and oxovanadium(IV) have been prepared and investigated using different chemical techniques, such as; elemental analysis, molar conductance measurements, infrared, electronic spectra and cyclicvoltammetry. The obtained chemical analysis data showed the formation of [M : L] ratio and a square planar geometry was suggested for copper(II), nickel(II) and tetrahedral geometry for zinc(II) complexes and a square pyramidal geometry for oxovanadium(IV) complex. Henri et al<sup>1</sup> have synthesized two new Schiff bases derived from 2,3-diaminopyridine and *o*-vanillin and their transition metal complexes (Cu, Ni, Fe, Zn) and have characterized them by elemental analysis, magnetic susceptibility measurements, IR and NMR. The Schiff bases and most of their metal complexes are reported to have antibacterial activity.

Rajavel and Krishnan<sup>2</sup> have reported the synthesis and characterization of oxovanadium(IV) complexes of the Schiff bases derived by the condensation of 2-aminobenzaldehyde with various diamines as 1,2-diaminoethane, 1,2-diaminopropane, 1,3-diaminopropane and discussed the elemental analysis, electrochemical studies and spectral data of the complexes. Erdal canpolat *et al*<sup>3</sup> have reported the synthesis and characterization of a new 5-bromosalicylidene-*p*-aminoacetophenoneoxime and its complexes with Co(II), Ni(II), Cu(II) and Zn(II) Jian-ning Liu *et al.*<sup>4</sup> have reported synthesis and characterization of metal complexes of Cu(II), Ni(II), Zn(II), Co(II), Mn(II) and Cd(II) with tetradentate Schiff bases. Nair *et al.*<sup>5</sup> have reported synthesis and spectroscopic studies of complexes of Cu, Ni, Fe and Zn. These complexes have been characterized by elemental analysis, electronic, IR and thermal studies.

The present paper aims to prepare, characterize the chemical structure and to study the antibacterial activity of the prepared Schiff base complex derived from malonyldihydrazide and 2-aminobenzaldehyde.

## Experimental

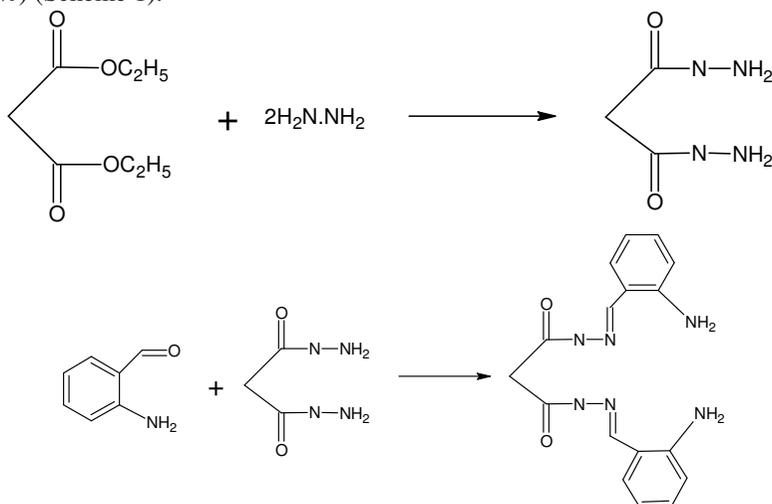
All chemicals used in this work were reagent grade (AR/Aldrich), including  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{ZnSO}_4$ ,  $\text{VO}_4$ , DMSO, DMF, TBAP, acetonitrile, malonyldihydrazide, 2-aminobenzaldehyde and ethanol. Double distilled water was used.

### Synthesis of malonyldihydrazide

Malonyldihydrazide was prepared by reacting the diethylmalonate (1 mole) with hydrazine hydrate (2 moles)

### Synthesis of bis (2-aminobenzaldehyde) malonyldihydrazone

The ligand was prepared by reacting a warm dilute ethanol solution of dihydrazide (0.65 g; 0.5 mole) with 2-aminobenzaldehyde (1.21 g; 1mole). The reaction mixture was refluxed<sup>6</sup> for two hours and suction filtered, washed with ethanol and dried over desiccator. The melting point of the product was found to be 180°C. The colour of the product was yellow (Yield 75%) (Scheme 1).

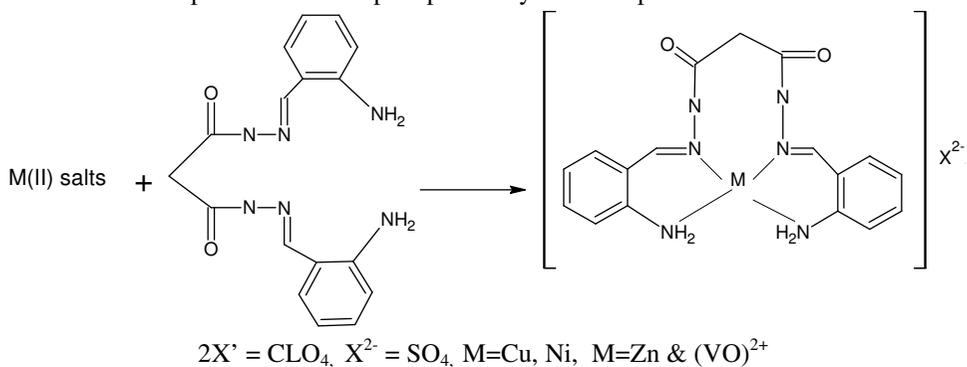


Scheme 1.

*Synthesis of complexes*

The ligand was taken in ethanol and stirred gently for 30 minutes to give a homogeneous suspension. Thio was added to copper(II) perchlorate hexahydrate solution containing trace of acetic acid. The reaction mixture was refluxed for 3 hours. The dark blue product so obtained (Scheme 2) was filtered while hot, washed with ethanol and dried in a desiccator.

The other complexes were also precipitated by a similar procedure in ethanol medium.



**Scheme 2.**

*Bacterial culture*

Different strains of bacteria *E.Coli*, *P.aeruginosa*, *S.aureus* and *Bacillus subtilis* (gram +ve) all strains were collected from clinical sample. The gram positive and gram negative bacteria were isolated from clinical sample and identified using physico-chemical methods. The identity of all the strains was confirmed. Antibiotic sensitivity test was studied by well diffusion method<sup>7</sup>. The bacterial suspension was prepared and added to well. The media with bacteria was poured into well under using suitable techniques. Different weights of the Schiff base and its complexes in DMSO solvent were placed on the surface of the culture and incubated at 37°C for one day. After incubation, the average of inhibition zones was recorded.

*Physico chemical measurements*

The elemental analysis for carbon, hydrogen and nitrogen were performed by microanalytical methods. IR spectra of the ligand and its complexes were carried out by using KBr disc IFS-25 DPUS/ IR spectrometer (Bruker) 1988Y. The electronic absorption was carried out by using a Perkin-Elmer Lambda 4β spectrometer in 1cm-matched silica gel using CHCl<sub>3</sub> as a solvent. The molar conductance measurements were carried out in DMSO using conductivity meter model CM Elico-185. CH instrument model 680 was used for recording the cyclic voltammogram of the complexes.

**Results and Discussion***Physico-chemical characterizations and geometrical configuration of the complexes*

Metal(II) salts react with Schiff base ligand in 1:1 molar ratio in alcoholic medium to afford dark green / blue complexes. The ligand and its complexes are stable at room temperature and are nonhygroscopic. The ligand is soluble in common polar organic solvents, such as ethanol, methanol, and chloroform but partially soluble in hexane. The Schiff base complexes are relatively well soluble in DMF and DMSO. The synthesized ligand and its

complexes were characterized by elemental analysis, spectra, molar conductivity and electrochemical measurements. Apart from this, biological activity of the ligands and its complexes were studied. The geometry of the newly synthesized compounds has been elucidated based on their elemental analysis, molar conductivity and spectral data.

### Elemental Analysis

The stoichiometry of the ligand and its complexes were confirmed by their elemental analysis. The metal / ligand ratio was found to be 1:1 has been arrived at by estimating the metal and nitrogen contents of the complexes. Elemental analysis of ligand and its Cu(II), Ni(II), Zn(II) and VO(IV) complexes show good agreement with the proposed structures of the ligand and its complexes Table 1.

**Table 1.** Analytical and physical data of the compound studied

Compound	Mol. Formula	Mol. Weight	Color	Nitrogen, %		Metal, %	
				Expt	Calcd	Expt	Calcd
Ligand (ambmadh)	(C <sub>17</sub> H <sub>16</sub> N <sub>6</sub> O <sub>2</sub> )	336.34	Pale yellow	24.17	24.98	-	-
Cu(ambmadh)] (ClO <sub>4</sub> ) <sub>2</sub>	[Cu(C <sub>17</sub> H <sub>16</sub> N <sub>6</sub> O <sub>2</sub> )] (ClO <sub>4</sub> ) <sub>2</sub>	598.71	Dark Blue	13.92	14.03	10.42	10.61
[Ni(ambmadh)] (ClO <sub>4</sub> ) <sub>2</sub>	[Ni(C <sub>17</sub> H <sub>16</sub> N <sub>6</sub> O <sub>2</sub> )] (ClO <sub>4</sub> ) <sub>2</sub>	593.86	Dark green	14.01	14.15	9.71	9.88
[Zn (ambmadh)] SO <sub>4</sub>	[Zn(C <sub>17</sub> H <sub>16</sub> N <sub>6</sub> O <sub>2</sub> )] SO <sub>4</sub>	497.77	Brown	16.41	16.88	13.01	13.13
[VO(ambmadh)] SO <sub>4</sub>	[VO(C <sub>17</sub> H <sub>16</sub> N <sub>6</sub> O <sub>2</sub> )] SO <sub>4</sub>	499.30	Dark blue	16.23	16.83	10.07	10.20

### Molar conductance measurements

The molar conductance value (40-50 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>) of the complex which was carried out in DMSO solvent indicates that the complex under study is 1:1 electrolytic nature<sup>8,9</sup>. Further, the low molar conductance of the complexes might arise due to large size of the anionic coordination sphere, which might have low ionic mobility. The values of molar conductance, suggest that complexes are electrolytes, there by showing that the perchlorate/sulphate ion is a counter ion.

### Infrared spectra

The IR spectra provide valuable information regarding the nature of functional group attached to the metal atom. The ligand and metal complexes were characterized mainly using the azomethine and primary amine (-NH<sub>2</sub>) bands. The main infrared bands and their assignments are listed in Table 2. The appearance of a broad strong band in the IR spectra of the ligand in 3400 -3350 cm<sup>-1</sup> is assigned to N-H stretching vibrations of the primary amine group. In the complexes, this band is shifted to lower frequency indicating that the ligand was coordinated to metal ions through the nitrogen atoms of the NH<sub>2</sub> group<sup>10</sup>. The spectrum of the ligand shows two different -C=N bands in the region 1590-1550 cm<sup>-1</sup>, which is shifted to lower frequencies in the spectra of all the complexes (1570-1520 cm<sup>-1</sup>) indicating the involvement of -C=N nitrogen in coordination to the metal ion<sup>11,12</sup>. Assignment of the proposed coordination sites is further supported by the appearance of medium bands at 450-400 cm<sup>-1</sup> which could be attributed to νM-N respectively<sup>13,14</sup>. In addition, the Vanadyl complex shows a band at 940 cm<sup>-1</sup> attributed to V=O frequency<sup>15</sup>.

**Table 2.** Characteristic IR bands ( $\text{cm}^{-1}$ ) of the compounds studied

Compound	NH <sub>2</sub>	C = N	C=O	V=O	ClO <sub>4</sub> <sup>-</sup> / SO <sub>4</sub> <sup>2-</sup>	M-N
Ligand (ambmadh)	3420	1640	1740	-	-	-
[Cu(ambmadh)](ClO <sub>4</sub> ) <sub>2</sub>	3380	1620	1723	-	1090	520
[Ni(ambmadh)](ClO <sub>4</sub> ) <sub>2</sub>	3350	1590	1732	-	1110	480
[Zn(ambmadh)]SO <sub>4</sub>	3390	1600	1730	-	1080	540
[VO(ambmadh)]SO <sub>4</sub>	3380	1610	1736	950	1100	510

### Electronic Spectra

The UV-visible spectrum of the Schiff base ligand and its complexes were recorded in DMSO solution in the range of 200 to 800nm regions and the data are presented in Table 3.

**Table 3.** Absorption Spectral data (nm) of the ligand and its Complexes

Compound	Absorption ( $\lambda_{\text{max}}$ )		
	d-d	$\pi \rightarrow \pi^*$ Benzene/ imino	$n \rightarrow \pi^*$ Azomethine
Ligand (ambmadh)	-	260	370
[Cu(ambmadh)](ClO <sub>4</sub> ) <sub>2</sub>	580	265	320,430
[Ni(ambmadh)](ClO <sub>4</sub> ) <sub>2</sub>	535	250	320,390
[Zn(ambmadh)]SO <sub>4</sub>	480 (LMCT)	240,270	320,440
[VO(ambmadh)]SO <sub>4</sub>	550	240	310,410

The absorption spectrum of free ligand consist of an intense bands centered at 360 nm attributed to  $n \rightarrow \pi^*$  transitions of the azomethine group. Another intense band in higher energy region of the spectra of the free ligand was related to  $\pi \rightarrow \pi^*$  transitions of benzene rings<sup>16</sup>. These transitions are found also in the spectra of the complexes, but they shifted towards lower frequencies, confirming the coordination of the ligand to the metallic ions<sup>17</sup>. Further, the d-d transition of the complexes showed a broad band centered at 550-650 nm suggesting an approximate square planar geometry of the ligand around the metal ion<sup>18</sup>. This is due to electron delocalisation over whole molecule on complexation. Based on these data, a square planar geometry has been assigned to the complexes except VO(IV) complex which has square-pyramidal geometry. These values are comparable with other reported complexes<sup>19,20</sup>.

### Cyclic voltammetry

#### Copper

The cyclic voltammogram of the Cu complex in DMSO scan rate  $100 \text{ mVs}^{-1}$  shows a well-defined redox process corresponding to the formation of Cu(II)/Cu(I) couple at  $E_{\text{p}_a} = 0.53 \text{ V}$  and  $E_{\text{p}_c} = 0.24 \text{ V}$ . This couple is found to be quasi-reversible with  $\Delta E_{\text{p}} = 0.289 \text{ V}$  and the ratio of anodic to cathodic peak currents corresponding to a simple one-electron process<sup>21</sup>.

#### Vanadium

The cyclic voltammogram of the vanadyl complex shows one electron transfer redox peak corresponding to the formation of the VO(IV)/VO(V) and VO(IV)/VO(III) couples<sup>22</sup>. The two peaks are different which indicate the involvement of two electro active species in solution corresponding to VO(V) and VO(III)<sup>23</sup>.

### Nickel

The nickel complex shows two peaks were obtained which are due to Ni(II)-Ni(I) and Ni(I)-Ni(II). For cathodic process of the Ni(II)-Ni(I), the observed peak potential are strongly depends on donor strength of the ligand. The peak separation between the related cathodic and anodic waves indicate a quasi-reversible and reversible redox reactions for Ni(II)/Ni(I) and Ni(I)/Ni(II) systems respectively<sup>24</sup>.

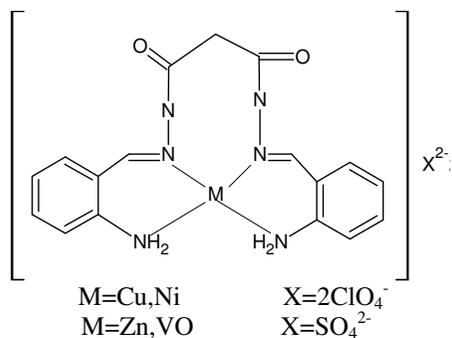
### Zinc

The zinc complexes, the one oxidation and one reduction peak were obtained. This is due to ligand nature. Zn(II) ion does not undergo reduction or oxidation in the given potential range because of invariable oxidation state of Zn is +2.

### Biological activity

The free ligand and its metal complexes were tested against the bacterial species *Staphylococcus Aureus*, *Bacillus subtilis*, *Pseudomonas aeruginosa*, and *Escherichia coli*. Chloramphenicol as a standard antibacterial agent or reference was evaluated for their antibacterial activity and the result was compared with the free ligand and its metal complexes. The comparison of the biological activities of the synthesized compounds and some known antibiotic shows the following results:

1. The free ligand and its metal complexes show positive effect towards *Staphylococcus aureus* more than standard.
2. The free ligand and Ni(II) complex show higher antibacterial effect than that of standard.
3. The copper(II), zinc(II) and oxovanadium(IV) complexes have more biological activity than ligand, Nickel and standard. Such increased activity of the metal chelates can be explained based on chelation theory<sup>25</sup>. 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<sup>26,27</sup>. Further, it increases the delocalization of  $\pi$  electrons over the whole chelate ring and enhances the penetration of the complexes into lipid membranes and blocking of the metal binding sites in the enzymes of microorganisms<sup>28</sup>. These complexes also disturb the respiration process of the cell and thus block the synthesis of proteins, which restricts further growth of the organisms<sup>29</sup>.



## Conclusion

The spectral data show that the Schiff base exist as tetradentate ligand by bonding to the metal ion through the phenolic nitrogen and azomethine nitrogen. The analytical data show the presence of one metal ion per ligand molecule and suggest a mononuclear structure for the complexes. The electronic spectral data is in the favour of square planer geometry for Cu(II), Ni(II) and tetrahedral geometry for Zn(II) complexe, Square pyramidal structure for VO(IV) complexe. On the basis of chelation theory, metal complexes have more biological activity than free ligands.

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