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Research Paper

Preparation, Characterization, ESR study and Antibacterial Studies of Cu(II) Chelates of Schiff bases

Chemistry

KEYWORDS : Schiff base, anthranilic acid, 4-aminoantipyrine, vanillin, furfural, antibacterial activity, metal complexes.

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ABSTRACT

Copper metal complexes find applications in medicine as drugs. The copper metal complexes are a special variety of complexes having nine electrons in the outermost level. They are widely available in the nature and are used in the manufacture of batteries, drugs, enzymatic reactions, insecticides etc. In continuation of our work, in this paper we have tried to study the synthesis, characterization and the antibacterial property of the Schiff bases and their copper complexes. A new series of transition metal complexes of Cu(II) with two bidentate and two tetradentate Schiff base ligands were prepared. The characterization of the Schiff bases and the complexes were done by elemental analysis, molar conductance, infrared, electronic (UV-Vis), electron spin resonance (esr) spectroscopic techniques and thermogravimetric analysis was used to investigate the chemical structure of the prepared ligands and Cu(II) complexes. The infrared spectral studies reveal the involvement of azomethine nitrogen (-C=N) coordination/ carbonyl (-C=O) coordination / carboxylate (-COO-) coordination with the copper (II) ion in the four complexes. Electron Spin Resonance spectroscopy was recorded at 300K (room temperature) and 77K (liquid nitrogen temperature). Quantum mechanical treatment of the esr spectrum was done to evaluate the nature of bonding in the copper (II) complexes. The thermal decomposition of the copper (II) complexes were studied using thermogravimetric analysis in static air with a heating rate of 20°C per minute. Antibacterial screening against bacteria such as staphylococcus aureus, Escherichia coli, bacillus subtilis and pseudomonas aeruginosa were performed using disc diffusion technique. The comparative study of MIC (minimum inhibitory concentration) values of the Schiff base its metal complexes indicate that the copper (II) complexes exhibit greater antibacterial activity than the free ligands. The copper (II) complexes were powdery in texture and hence the XRD was not recorded.

Introduction

Schiff base and its metal complexes have varied applications in biological[1-3], clinical, analytical, corrosion science and pharmacological areas.[4-6]Schiff bases are used as catalysts for certain chemical reactions. Aromatic Schiff bases and their complexes catalyze reactions on oxygenation[7-8] hrdrolysis[9], electro-reduction[10], and decomposition[11]. Schiff bases appear to be important intermediate in a number of enzymatic reactions involving interaction of an enzyme with an amino or a carbonyl group of the substrate [12]. Earlier works done by biochemists[13-14], reported that some drugs showed greater activity, as metal complexes when compared to the organic compounds.[15] The coordinating properties of 4-aminoantipyrine have been modified to give new ligands formed by the reaction with aldehydes, ketones, thiocarbazides and carbazides etc.,[15]

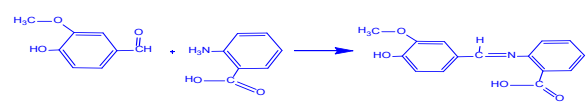
Experimental

Material and methods: All the reagents vanillin, anthranilic acid, 4-aminoantipyrine, o-phenylene diamine, furfural and the metal salts were purchased from Merck and Loba chemie Mumbai, India are used as supplied. The solvents like ethanol, methanol, DMSO etc are purified and dried by standard procedures [7-8]. The microanalytical data of complexes were recorded at Central Electrochemical Research Institute (CECRI) India using vario EL elemental analyzer. IR spectroscopy analyses were recorded on a IR spectroscopy analyses were recorded on Schimadzu FTIR 8400S spectrometer in 4000-200cm^{-1} range using KBr pellet. The UV-Visible spectra were recorded on a Schimadzu UV spectrometer in the wave length range 200-800nm. The thermal analyses were recorded on Universal V4.3A TA Instrument from CECRI, India, with heating rate of 20deg C/min in static air. The ESR spectral analyses were recorded on Bruker instrument at 300 and 77 K from CECRI. The 1H-NMR and 13C-NMR were recorded on a Bruker DPX-300 spectrometer using EtOD as solvent and TMS as internal standard. The molar conductance was measured on ELICO-CM180 using DMSO as the solvent at room temperature. The antibacterial activity was determined with the Disc Diffusion method. Stock solutions were prepared by dissolving the compounds in DMSO and serial dilutions of the compounds were prepared in sterile distilled water to determine the Minimum Inhibition Concentration (MIC).

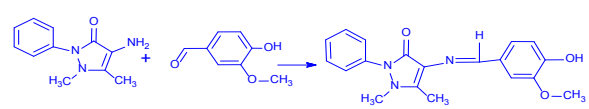
Synthesis of Schiff's bases

The Schiff's bases were prepared by adding equimolar quantities of aldehyde and amine with alcohol as the solvent. The contents were agitated vigorously and refluxed on a water bath for 4-5 hrs. The contents were cooled and poured in to crushed ice. The oily liquid over the water is allowed to stay aside for some time [7], the crystals of the Schiff's base starts to separate. The crystals were washed with sodium bisulphate to remove unreacted aldehydes [7,8]. The crystallization was enhanced by agitating the aqueous solution with a glass rod. The crystals were filtered and recrystallized with THF/Benzene mixture. The scheme for the preparation of the ligands is given in figure-1.

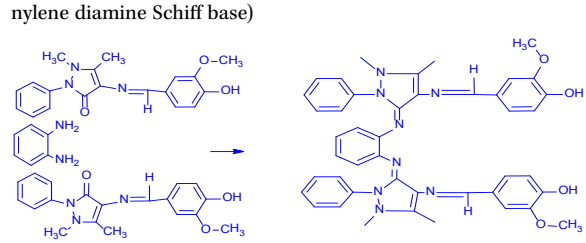
Preparation of ligand VA (Vanillin anthranilic acid Schiff base)



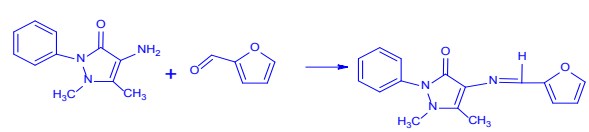
Preparation of ligand AV (4-aminoantipyrine vanillin Schiff base)



Preparation of ligand AVOP (4-aminoantipyrine vanillin o-phenylene diamine Schiff base)



Preparation of ligand AFOP (4-aminoantipyrine furfural o-phenylene diamine Schiff base)



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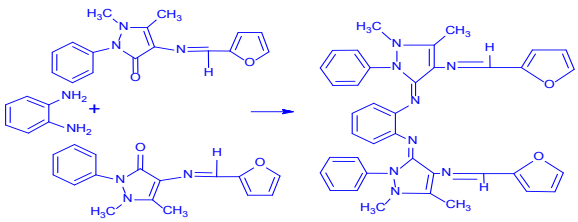

Figure-1. Preparation of Schiff's base ligands.
Synthesis of Schiff base complexes

The Schiff base ligand is dissolved in 50ml hot ethanol. The hot alcoholic solution of the metal salt (CuSO4.5H2O) was slowly added to the alcoholic solution of the ligand with constant stirring and refluxed over a water bath for 4-5 hrs. The hot solution was reduced to one third its volume and allowed to cool for crystallization. The precipitate obtained was washed with double distilled water and hot ethanol. The molar ratio of metal: ligand was maintained as 1:2 for the preparation of [Cu(VA)2(H2O)2] and [Cu(AV)2(H2O)2]SO4. The molar ratio of the metal: ligand used for preparing [Cu(AVOP)] SO4 and [Cu(AFOP)] SO4 is 1:1.

Antibacterial activity

The antibacterial activity was determined with the Disc Diffusion method [18,19]. Stock solutions were prepared by dissolving the compounds DMSO and serial dilutions of the compounds were prepared in sterile distilled water to determine the Minimum Inhibition Concentration (MIC). The nutrient agar medium was poured into Petri plates. A suspension of the tested microorganism (0.5 ml) was spread over the solid nutrient agar plates with the help of a spreader. Fifty micro-litres of the stock solutions was applied on the 10mm diameter sterile disc. After evaporating the solvent, the discs were placed on the inoculated plates. The Petri plates were placed at low temperature for two hours to allow the diffusion of the chemical and then incubated at a suitable optimum temperature (29+/- 2 C) for 30-36 hours. The diameter of the inhibition zones was measured in millimeters. The biological screening effects of the complexes were, tested against the bacteria *Staphylococcus aureus, Escherichia coli, Bacillus subtilis* and *Pseudomonas aeruginosa.*

Results and Discussion

CHNS and molar conductance measurements

The CHNS analyses of the Schiff base and metal complexes are summarized in the table 1.

Table 1-Analytical data and physical properties of the synthesized ligand and complexes.

Compound(Empirical formula) Colour	m.p (°C)	M.Wt/ Yield %	Elemental analyses Found (Calcd),%					Λ_m(Ohm^{-1}cm^{2}mol^{-1})
			C	H	N	S	Metal	
$Cu(VA)_2(H_2O)_2$]/ Green	170	639.55/ 70	55.2 (56.3)	4.63 (4.378)	4.348 (4.378)		9.936 (9.8)	1.88
$C_{19}H_{19}N_3O_3$= AV (Yellow)	167	337.302/86	66.422 (67.66)	5.8 (5.6)	12.642 (12.45)	0 0	0 0	- -
$[Cu(AV)_2(H_2O)_2]SO_4$ (Green)	186	869.5/66	52.248 (52.411)	4.891 (4.872)	9.665 (9.655)	3.986 (3.678)	7.48 (7.304)	118
$C_{44}H_{42}N_8O_4$= AVOP (Dark Yellow)	210	746.876/72	70.521 (70.759)	4.983 (5.668)	14.997 (15.003)	0 0		- -
[Cu(AVOP)] SO_4 (Brown)	195	906.488/75	57.937 (58.3)	4.231 (4.67)	11.932 (12.362)	3.269 (3.537)	7.264 (7.01)	102
$C_{38}H_{34}N_8O_2$= AFOP (Brown)	160	634.82/62	70.939 (71.831)	5.247 (5.356)	18.951 (17.643)	0 0	- -	
[Cu(AFOP)] SO_4 (Brown)	157	794.35/60	56.826 (57.457)	3.968 (4.314)	13.863 (14.106)	4.125 (4.036)	7.903 (8.00)	108

The molar conductivity values of the copper complexes reveal the presence of ions outside the coordination sphere. In Cu(VA)2(H2O)2] complex the conductivity value is 1.88 Ohm-1cm2mol-1. The low value suggests that the copper complex is neutral in charge. The two positive charges present in Cu^{+2} is neutralized by the two COO- ions supplied by the VA ligand [10-12]. In the remaining copper (II) complexes the coordination sphere has two positive charges electrically balanced by the presence of $SO4^{-2}$ ions outside the coordination sphere.

Infrared spectral analyses

The infrared spectroscopic data is given in table 2. In the ligand VA and its $[Cu(VA)_2(H2O)_2]$ complex, it is seen that the –OH phenolic group does not undergo any change on co-ordination, where as the frequency for the –C=O, -C=N and –COO- shifts to lower frequencies indicating the participation of oxygen of COO- group and azomethine –C=N nitrogen in coordination [9-12]. The presence of two coordinated water molecules is supported by the bands for –OH at 3443cm-1 and bands for M-O at 870 cm-1. In the ligand AV and the [Cu(AV)2(H2O)2]SO4 copper complex the phenolic –OH frequency does not change. The frequency for –C=O and –C=N shifts to lower frequency and new bands for M-O and M-N are found indicating the participation of –C=O in the five member ring and nitrogen in the azomethine group in coordination with copper metal ion. In the ligand AVOP and its copper complex [Cu(AVOP)] SO4 the phenolic –OH is present but the frequency for azomethince group undergoes a shift in frequency. In the ligand AFOP and its copper complex [Cu(AFOP)] SO4 the azomethine group undergoes a shift in frequency and the remaining absorption are not altered. This shows that the coordinating sites for the [Cu(AVOP)] SO4 and [Cu(AFOP)] SO4 complex are through the four azomethine groups in the ligand.

Table 2- Characteristic infrared absorption frequencies in cm^{-1} of Schiff base ligand and copper complexes

Compound	ν(OH) water	ν(OH) Phenolic	νcm^{-1} (C=O)	νcm^{-1} (C=N)	νcm^{-1} COO	νM-O coordinated water	ν M-O	ν M-N
$C_{15}H_{13}NO_4$=VA		3239	1668	1585	1481			
$[Cu(VA)_2(H_2O)_2]$	3443	3122	1598	1553	1459	870	711	
$C_{10}H_{10}N_2O_2$		3064	1624	1579				
$[Cu(AV)_2(H_2O)_2]$ SO_4	3117	3122	1607	1559	1458	702		451.36
$C_{44}H_{42}N_8O_4$=AVOP		3107.34		1650,1565				
[Cu(AVOP)] SO_4		3063.06		1514				445.57
$C_{38}H_{34}N_8O_2$=AFOP				1650 to 1565				
[Cu(AFOP)] SO_4				1625, 1523.15				445.57

Electronic absorption spectral analyses

The electronic absorption data is used for analyzing the structure of the complexes. Based on the electronic absorption spectral data the copper complexes of VA and AV ligands is said to have octahedral geometry with tetragonal distortion and the remaining two copper complexes are said to possess square planar geometry [13-15].

Table 3- Electronic absorption spectral data for the Schiff base ligand and the copper metal complexes in ethanol

Compound	Absorption nm/(cm^{-1})	Band assignment	Geometry
$C_{15}H_{13}NO_4$=VA	260 (38461) and 315 (31746)	π→π*, n- π* transitions.	
$[Cu(VA)_2(H_2O)_2]$	757.5(13200),533.9(18730)and 415(24096)	$^2A_1g \rightarrow {}^2B_1g$ ($dz^2 \rightarrow dx^2\text{-}y^2$) $^2B_2g \rightarrow {}^2B_1g$ ($dxy \rightarrow dx^2\text{-}y^2$) $^2Eg \rightarrow {}^2B_1g$ ($dxz, dyz \rightarrow dx^2\text{-}y^2$)	Octahedral
$C_{19}H_{19}N_3O_3$	260(38461)and 315(31746)	π→π* , n- π* transitions.$^6A_1g \rightarrow {}^4A_1g$	
$[Cu(AV)_2(H_2O)_2]$ SO_4	748(13368),537(18621) and 418(23923)	$^2A_1g \rightarrow {}^2B_1g$ ($dz^2 \rightarrow dx^2\text{-}y^2$) $^2B_2g \rightarrow {}^2B_1g$ ($dxy \rightarrow dx^2\text{-}y^2$) $^2Eg \rightarrow {}^2B_1g$ ($dxz, dyz \rightarrow dx^2\text{-}y^2$)	Octahedral
$C_{44}H_{42}N_8O_4$ = AVOP	272 (36764) and 305 (32868)	π→π*, n- π* ILCT	
[Cu(AVOP)] SO_4	320 (31250) ν_1, 352 (28409) ν_2 and 660 (15151.5) ν_3	ν_1 and ν_2 are ILCT $\nu_{3=} {}^2B_1 \rightarrow {}^2A_1g$	Square planar
$C_{38}H_{34}N_8O_2$ = AFOP	262(38167) and 319(31347)	π→π*, n- π* transitions.	
[Cu(AFOP)] SO_4	330(30303),358(27932) and 425(15797)	ν_1 and ν_2 are INCT $\nu_{3=} {}^2B_1 \rightarrow {}^2A_1g$	Square planar

NMR spectral analyses

The 1H NMR data for the Schiff ligand is given in table 4. The NMR data is used for identifying the structure of the ligands [2,4,18-21]. The various 1H NMR absorption regions are given in table 4, the table 5 gives the specific 13C-NMR regions of absorption that takes part in ligation with the copper (II) metal ion.

Table 4-1H NMR chemical shift of ligand

Type of protons	δ(VA Ligand)	δ (AV ligand)	δ (AVOP Ligand)	δ (AFOP Ligand)
-O-CH_3	3.85	3.85	3.85	
-CH_2	2.44	2.44	2.44, 3.10	2.40, 3.19
-CH_2	3.10	3.10	3.10	
-OH	5.35	5.35	5.35	
Ar-H	6.90, 7.35, 7.54, 7.66, 7.80,8.10, 8.22	6.93,7.37, 7.51	6.90, 7.37, 7.51	6.53, 6.90, 7.35, 7.44
-N=CH	8.38	9.49	8.15, 8.48	7.75, 7.82
-COOH	11.08			

Table-5 13C-NMR spectrum of the ligands

Compound	**-COOH**	**-CH=N-**	**-C-N-**
$C_{15}H_{13}NO_4$=VA	166.73	160.17	151.08
$C_{19}H_{19}N_3O_3$= AV		163.21	110.37
$C_{44}H_{42}N_8O_4$= AVOP		163.60	108.81
$C_{38}H_{34}N_8O_2$= AFOP		163.6	108.81

Electron spin resonance (esr) spectral analyses

The esr spectra of copper complex provide important information in studying the structure of complex. The esr spectra of the Cu(II) complex are recorded at room temperature (300K) and at liquid nitrogen temperature (77K). The spectrum of copper complex has a single intense absorption band in the high field region and the molecule is isotropic due to the tumbling motion of the molecule. When the complex is frozen to liquid nitrogen temperature, four well resolved peaks in the low field region are obtained. This shows the presence of an octahedral geometry for the copper complex. The various parameters for the copper complexes such as exchange interaction G, spin-orbit coupling constant $^{\lambda}$, covalency parameter α^2, In-plane π- bonding parameter β^2, Orbital reduction factor $K_{\parallel}$, $K_{\perp}$, K^2 were evaluated [22-26].

The values of the calculated esr parameters are given in table 6 and table 7.

Table 6 – Experimental values in g units for copper complexes

Compound	$g_{\parallel}$	$g_{\perp}$	$\lvert g \rvert$	$A_{\parallel cm^{-1}}$	$A_{\perp}$	$\lvert A \rvert$
$[Cu(VA)_2(H_2O)_2]$	2.288	2.0428	2.1245	0.1226	2.0428	
$[Cu(AV)_2(H_2O)_2]SO_4$	2.302	2.048	2.1327	0.12696	2.048	0.7218
[Cu(AVOP)] SO_4	2.2312	2.0346	2.1001	0.01755	2.0346	0.7249
[Cu(AFOP)] SO_4	2.2895	2.0478	2.1284	0.01587	2.0478	

Table 7 – Calculated ESR parameters copper complexes

Compound	G	λ cm^{-1}	α^2	β^2	$K_{\parallel}$	$K_{\perp}$	K^2
$[Cu(VA)_2(H_2O)_2]$	7.054	-14021	0.72319	0.7872	0.8078	0.589	0.8838
$[Cu(AV)_2(H_2O)_2]$ SO4	6.558	-14254	0.7547	0.8014	0.8425	0.5136	0.8856
[Cu(AVOP)] SO_4	7.0866	-15909	0.721	0.7262	0.5236	0.2955	0.332
[Cu(AFOP)] SO_4	6.31208	-16811	0.7515	0.9345	0.743	0.4709	0.6776

Thermal analyses

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Thermal analysis is used to find the decomposition pattern of the copper (II) complexes, to find the water of hydration and the residue formed [19-21].

Thermo gravimetric analysis of complexes

The complexes were found to be thermally stable. The first stage decomposition corresponds to the loss of water from the complex. The removal of the ligands occurs during the second and third stages, leaving a residue.

Table 8- Thermo gravimetric analyses of complexes

Compound	Temp.Range (°C)	Stage	Weight loss (%)/Residue	
			Found	Calculated
	55.61	I	2.84	2.81
	55.61-152.12	II	16.68	16.57
	152.12-407.67 Above 407.67	III	69.38 11.10(Residue)	68.18
	234.86	I	3.04	2.81
	234.86-555.57	II	83.14	84.5
	Above 555.57	IV	12.79(Residue)	
[Cu(AVOP)] SO_4	Above 193-522	I	8.389(Residue)	8.39(Residue)
[Cu(AFOP)] SO_4	218-579	I	8.389(Residue)	8.39(Residue)

Antibacterial activity

The antibacterial study for the complexes was performed on *staphylococcus aureus, Escherichia coli, Bacillus subtilis* and *Pseudomonos aeruginosa.* The toxicity of the complexes was, found to be better than the ligand owing to the theory of Tweedy [26-28]. This is probably due to the greater lipophilic nature of the complexes. Such increased activity of the metal chelates can, be explained based on Overtone's concept and chelation theory. According to Overtone's concept of cell permeability the lipid membrane that surrounds the cell favors the passage of lipid soluble materials due to which liposolubility is an important factor which controls the antimicrobial activity.

Table 6 - Antibacterial activity data for the ligands and their copper metal complexes

Compound	S.aureus	E.coli	B.subtilis	P.aeruginosa	Inference Anti bacterial activity
$C_{15}H_{13}NO_4$	4	3	2	2	+
$[Cu(VA)_2(H_2O)_2]$	-	-	15	15	+++
$C_{19}H_{19}N_3O_3$	4	3	3	2	+
$[Cu(AV)_2(H_2O)_2]Cl_2$	4	3	14	17	++++
$C_{44}H_{42}N_8O_4$	3	6	2	6	+
$[Cu^{+2}(AVOP)]$ SO_4	2	6	3	9	+
$C_{38}H_{34}N_8O_2$	7	6	5	4	+
$[Cu^{+2}(AFOP)]$ SO_4	12	13	13	14	+++

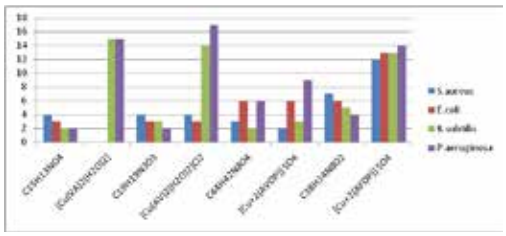

Figure-5. Antibacterial activity data for the ligands and their copper metal complexes

3D modeling of copper complex using Chembio draw software

The 3D modeling of copper complex was drawn using Chembiodraw software**29.** (Figure.4.14) the actual and optimal bond length in nanometer was calculated. The table 4.7 gives the values of the actual and optimal bond length, which are in agreement with each other.

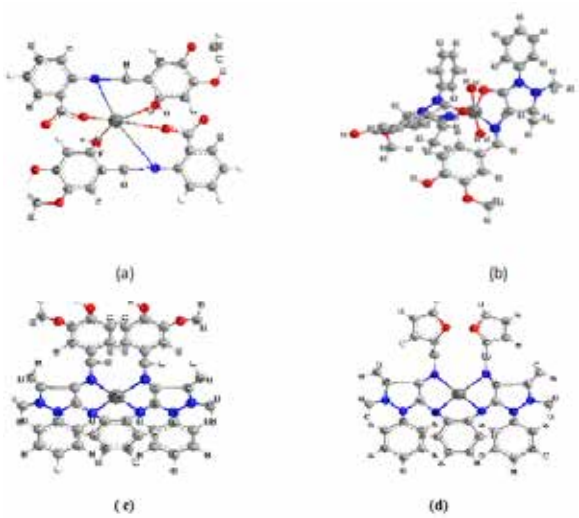

Figure.6 3D Structure of (a)$[Cu(VA)_2(H_2O)_2]$ (b) $[Cu(AV)_2(H_2O)_2]$ SO_4 (c) $[Cu(AVOP)]SO_4$ $[Cu(AFOP)]$ SO_4 complexes

Conclusion

In this work we have reported the co-ordination chemistry of copper complexes derived Schiff base ligand VA, AV, AVOP and AFOP with copper (II) metal. Copper (II) forms distorted octahedral complexes with VA and AV ligands as shown in figure 7(a) and (b). Whereas copper (II) forms square planar complexes with AVOP and AFOP ligands as shown in figure-7(c) and 7(d). The copper complex of VA is neutral in charge and the remaining complexes are charged with one sulphate ($SO4^{-2}$) ion outside the coordination sphere.

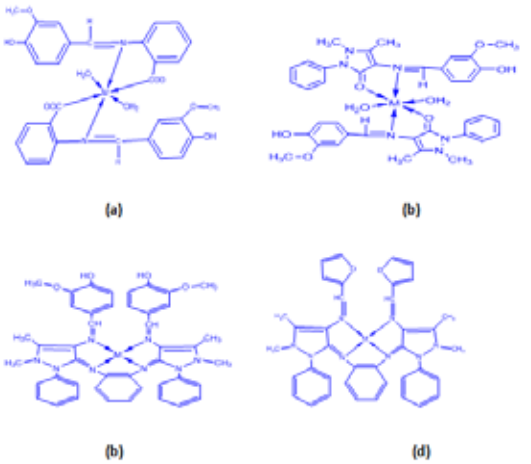

Figure-7. Structure of (a)$[Cu(VA)_2(H_2O)_2]$ complex, (b) $[Cu(AV)_2(H_2O)_2]^{2+}$, (c) [Cu(AVOP)] SO_4 , (d) [Cu(AFOP)] SO4 complex

REFERENCE

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