

Synthesis And Characterization Of Cu (Ii) And Zn(Ii) Complexes With Schiff Base Derived From 3-Aminocoumarin And 4-Acetyl Resorcinol

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ABSTRACT

Schiff base metal complexes achieved great attention in research focus because of their industrial, antifungal, antibacterial, anticancer and herbicidal application. Novel Schiff base mixed ligand complexes of Cu(II) and Zn(II) were prepared from 3-AC and 4-AR by template synthesis. Both complexes were characterized by elemental and metal ion analyses, IR and UV-Vis spectroscopy, magnetic susceptibility data and conductance measurements.

Analytical data of the mixed ligand complexes shows a M:L ratio of 1:2 and 1:1 for copper and Zinc complexes respectively. Based on these data, an octahedral geometry for Cu(II) complex and a tetrahedral geometry for the Zn(II) complex was proposed. In the Cu(II) complex, the mixed ligand acts as an ON donor and in the Zn(II) complex, it acts as an ONO donor.

Key words:

Mixed ligand complexes; 3-aminocoumarin (3-AC); 4-acetylresorcinol (4-AR) and Schiff base

1. INTRODUCTION

Coumarins, or benzo- α -pyrones, are a very large and important family of compounds. Their defining structure consists of fused pyrone and benzene rings, with the pyrone carbonyl group at position 2 (Wagner, 2009). Coumarin is a widely occurring secondary metabolite that occurs naturally in several plant families and essential oils. It has been used in flavoring food and in cosmetic products as a fragrant (Aslam, *et al.*, 2010, Dighe, *et al.* 2010)

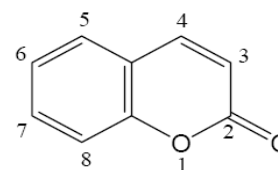


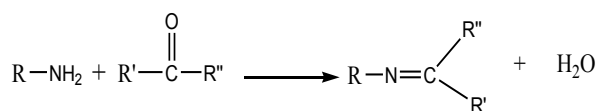
Fig. 1: Structure of Coumarin (2H-chromen-2-one)

Many substituted coumarins and their derivatives have been developed synthetically which are known to exhibit a wide spectrum of pharmacological activities, such as, antimicrobial, antifungal, anticoagulant, anti-inflammatory, antioxidant, analgesic etc (Seyed M. R., 2011, Singh, I. *et al.*, 2010, Kasabe, *et al.*, 2010)

Aminocoumarins which contain an amino group bonded to the benzene nucleus are widely investigated, whereas those containing amino group in α -pyrone ring have received great attention in recent years. From the group of aminocoumarins, 3-aminocoumarin and its derivatives are not well studied (Mayekar, *et al.*, 2010). The 3-aminocoumarin moiety can be recognized in the molecular structure of several natural antibiotics, such as novobiocin, chlorobiocin, coumermycin, etc. These antibiotics and their derivatives are in the research focus (Bistra, *et al.*, 2010)

Acylation of resorcinol is a very important reaction leading to the formation of 2,4-dihydroxy acetophenone also known as resoacetophenone (4-acetyl resorcinol) and 2,4-dihydroxy-5-acetyl acetophenone (reso-di-acetophenone). 4-acetyl resorcinol (4-AR) finds wide applications as an intermediate in the manufacture of pharmaceuticals, perfumes, fine chemicals and leukotriene antagonists (Yadav and Joshi, 2002)

The condensation of primary amines with aldehydes and ketones give imines. Imines that contain an aryl group bound to the nitrogen or to the carbon atom are called Schiff bases, since their synthesis was first reported by Schiff (Shalin, *et al.*, 2009)



A large number of Schiff bases and their complexes are of significant interest and attention because of their biological activity including anti-tumor, antibacterial, fungicidal, anti-carcinogenic and catalytic activity (Srivastava, *et al.*, 2011). They are capable of forming coordinate bonds with many of metal ions through either/both azomethine nitrogen and phenolic oxygen. Schiff bases are generally bi-, tri- or polydentate ligands capable of forming very stable complexes

with transition metals. Some are used as liquid crystals (Arulmurugan, 2010).

The pharmacological activity of Schiff bases (containing ON and ONO donor atoms) of 3-amino coumarin derived by condensation with salicylaldehyde, acetylacetone and ortho-nitrobenzaldehyde and their metal complexes are reported by Shyamala *et al.* (Shyamala *et al.*, 2010)

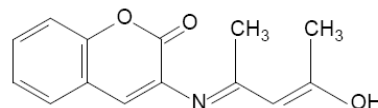


Fig. 2: Proposed structure of the ligand N-acetylacetonyl-3-aminocoumarin

The ONNO donor Schiff bases of 4-acetyl resorcinol with orthophenylene diamine and sulphanilamide have been reported by Venkatesh P. This study shows better activity of the Cu^{2+} and Zn^{2+} metal complexes of sulphanilamide Schiff base which might be due to its pharmacophore sulphanilamide and its potency is further enhanced by the metal coordination Venkatesh, 2011).

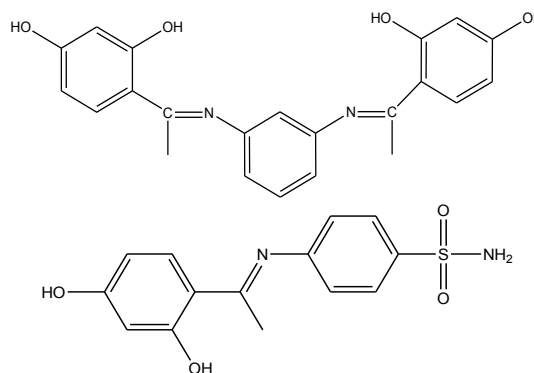


Fig. 3: Schiff bases derived from 4-acetyl resorcinol with orthophenylene diamine and sulphanilamide

Most of the 3d transition metal ions exhibit vital roles in biological systems. They are called metalloproteins (Rosette, 2002). Literature survey reveals that a number of OO, ONN and ONO donor sequences resulted in the formation of polynuclear metal chelates (Pulimamidi, 2011).

Since coumarin moiety, ON donating ligands as well as 4-acetyl resorcinol and their metal ions influence and enhance biological activity, (Sohrab, 2009), the present investigation attempts at synthesizing and characterizing metal complexes with Schiff base derived from 3-aminocoumarin and 4-acetyl resorcinol) with the aim to obtain more potent biologically active compounds and their metal complexes.

2. EXPERIMENTAL

Materials and methods

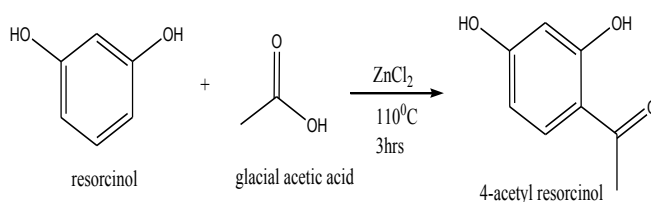
All the chemicals, reagents and solvents were A.R. grade purchased from Sigma-Aldrich Fluka, BDH, Merck, Riedel-de Haën, Scharlau and ACS, ISO. Solvents such as ethanol and methanol were distilled for further purification.

IR spectra were recorded using Perkin-Elmer FT-IR spectrophotometer in the range of 4000-450 cm^{-1} . ^1H and ^{13}C NMR were recorded in CDCl_3 by using Bruker 400 ultra shielded NMR. The magnetic susceptibility of the complexes was measured using MSB-AUTO, Sherwood magnetic balance. Elemental analysis of CHN was done by using Exter Analytical CE 440 elemental analyzer. Molar conductivities of the complexes were recorded at room temperature using HANNA Instrument EC 214 conductivity meter. The metal estimation was done using BUCKER Scientific 210 VGB atomic absorption spectrophotometer. The electronic spectrum of Zn complex was recorded in the UV and visible region (200-2500 nm) by Cary 5E UV-VIS NIR spectrophotometer and for other complexes it was carried out in the range of 200-900 nm by SPECTRONIC GENESYTM 2PC UV-Visible spectrophotometer. Melting or decomposition point was determined by Stuart SMP3 digital melting point apparatus.

Synthesis

Synthesis of 4-acetyl resorcinol (4-AR) or 2,4-dihydroxy-acetophenone (Baluja, 2006)

Anhydrous zinc chloride (16.5 g) was dissolved in 15.8 mL glacial acetic acid. Resorcinol (11.0 g) was added and the mixture was heated at 110 $^{\circ}\text{C}$ for 3 h. The resulting solution was cooled to room temperature and then poured over crushed ice. The product was filtered and washed with 30% HCl to remove excess zinc chloride. The product was recrystallized from methanol, dried and weighed. Yield: 8.8 g (80%), m.p: 144 $^{\circ}\text{C}$.



Scheme 1: Synthesis of 4-acetylresorcinol

Synthesis of 3-aminocoumarin (3-AC) (Maddi, 2007)

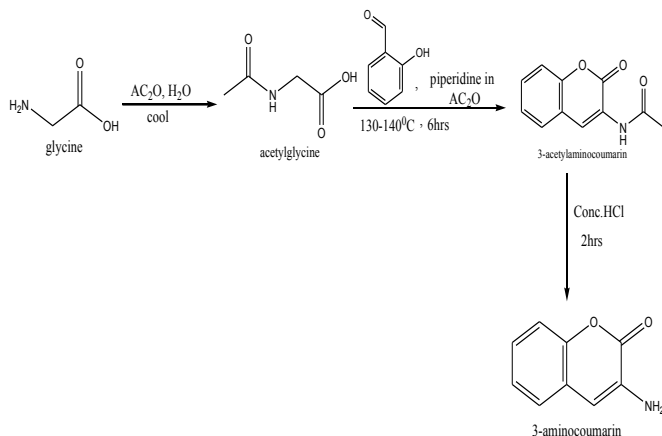
3-aminocoumarin can be prepared in three steps. These are: i) acylation of glycine to form acetylglycine, ii) synthesis of 3-acetylaminocoumarin by reacting acetylglycine, salicylaldehyde & piperidine in acetic anhydride, iii) hydrolysis of 3-acetylaminocoumarin to form 3-aminocoumarin.

a. Preparation of acetylglycine

Acetylglycine was synthesized by adding acetic anhydride (14.5 g, 0.14 mol) to a solution of glycine (5.0 g, 0.06 mol) in water (75 mL). The reaction mixture was stirred for 20 min. at room temperature, and cooled in a refrigerator overnight. Acetylglycine which separated as white crystals was filtered, washed with cold water and dried at 100 $^{\circ}\text{C}$. Yield: 4.2 g (84%), m.p: 206-208 $^{\circ}\text{C}$.

b. Synthesis of 3-Acetylaminocoumarin

3-Acetylaminocoumarin was prepared by heating a mixture of acetyl glycine (5.0 g, 0.043 mol), salicylaldehyde (12.2 g, 0.1 mol) and a drop of piperidine in acetic anhydride (5 mL, 0.049 mol) at 130-140°C for 6 h. The reaction mixture was cooled, diluted with 10 ml of water, and further refluxed for 30 min. The gummy mass thus obtained after removal of water under reduced pressure was repeatedly washed with ether to remove adhering traces of piperidine and acetyl glycine. The crude product when crystallized from ethanol furnished the product as a crystalline solid. Yield: 2 g (40%), m.p: 200-203°C.



Scheme 2: Synthesis of 3-aminocoumarin

c. Hydrolysis of 3-Acetylaminocoumarin

3-Aminocoumarin was prepared by treating a solution of 3-acetylaminocoumarin (5 g, 0.024 mol) in hot ethanol (25 mL) with concentrated hydrochloric acid (5 mL) and the resulting mixture was refluxed for 2 h. The reaction mixture was cooled diluted with water, neutralized with aqueous saturated sodium bicarbonate and kept overnight. The solid thus separated was filtered. Further purification by crystallization from ethanol gave the product, a creamish crystalline solid, Yield: 3.5 g (70%), m.p: 127°C. It was characterized by ¹H NMR.

¹H NMR: 4.3ppm (s, NH₂), 6.76ppm (s, CH), 7.20-7.40ppm (m, CH). These results are concurrent with the reported data.

Synthesis of Schiff base ligand

The preparation of the ligand was attempted by the following method. The 3-aminocoumarin (0.50 g, 0.0031 mol) was dissolved in methanol (20 mL) and heated for few minute. Then, resoacetophenone (0.47 g, 0.0031 mol) was added to the hot alcoholic solution of 3-aminocoumarin. The mixture was refluxed over water bath for more than 8 h. The solution was cooled overnight and needle like crystals were obtained. TLC, melting point and NMR spectroscopy data of the product revealed that it was 3-aminocoumarin, and the Schiff base condensation did not take place. So, an alternate template method synthesis was carried out.

Synthesis of metal complexes

Template synthesis: The metal complexes were synthesized by template method. To a solution of 4-acetylresorcinol (5.62 g, 0.037 mol) in hot methanol (20 mL), solution of metal ion (0.02 mol each) was added. The resulting mixture was refluxed on a water bath for about half an hour. After 30min. of refluxing, 3-aminocoumarin (6 g, 0.037 mol) was added. The pH of solution was adjusted

to 7 with alcoholic ammonia solution (1:1) and refluxed further for about 8-18 h over water bath. The solid obtained was filtered, washed with methanol, and air dried. Yield: 2.64 g (42%) and 2.3 g (46.2%) for Cu(II) and Zn(II) respectively.

3. RESULT AND DISCUSSION

In the course of synthesis, it was found that 3-aminocoumarin and 4-acetyl resorcinol condensed to give Schiff base of mixed ligands by template method only in the zinc and copper complexes. Cr(III), Fe(III) and Ni(II) ions did not form any complexes with the Schiff base of mixed ligands. Both metal complexes obtained were colored and stable to air and moisture at room temperature. Cu(II)

complex is soluble in common organic solvents such as DMF, DMSO, and acetonitrile and sparingly soluble in acetone, chloroform, methanol, dioxane and water. But the zinc complex is soluble only in DMF and acetonitrile and sparingly soluble in other solvents. The observed molar conductance value of zinc complex (44 $\mu\text{S}/\text{cm}$ in table 1) in 10^{-3} M DMF solution suggests the non-electrolytic nature of this complex. The complexes do not show sharp melting points. They decompose at temperatures above 300°C (Table 1). The analytical data reveals M:L ratio of 1:1 and 1:2 for Zn(II) and Cu(II) mixed ligand complexes respectively (Table 1). The data has good agreement with the suggested structure of the complexes.

Table 1: Elemental analysis and some physical characteristics of ligands and complexes

Compounds Empirical formula	Molecular Weight (g/mol)	color	m.p/ dec. pt ($^{\circ}\text{C}$)	Yield (%)	Found (calculated) %				Conductivity ($\mu\text{S}/\text{cm}$)
					C	H	N	M	
3-aminocoumarin $\text{C}_9\text{H}_7\text{NO}_2$	161	creamish	131	70	(67.07)	(8.70)	(8.70)		-
4-acetyl resorcinol $\text{C}_8\text{H}_8\text{O}_3$	152	orange	144	80	63.46 (63.53)	4.81 (4.46)	-		-
Zn(L)Cl $\text{ZnC}_{17}\text{H}_{12}\text{O}_4\text{Cl}$	394.9	yellow	> 303	46.2	52.33 (52.65)	3.46 (3.05)	3.42 (3.55)	16.56 (16.97)	44
$\text{Cu}(\text{L})_2(\text{NH}_3)\text{Cl}$ $\text{CuC}_{34}\text{H}_{27}\text{NO}_8\text{Cl}$	704	Dark brown	> 300	42	58.47 (57.95)	2.40 (3.83)	6.16 (5.97)	9.02 (9.30)	92.6

Infrared spectra

The characteristic infrared frequencies of ligand and metal complexes are listed in Table 2 and 3. The IR spectrum of 3-aminocoumarin shows a doublet at 3428 cm^{-1} and 3313 cm^{-1} assignable to asymmetric and symmetric ν_{NH_2} respectively. The strong band located at 1706 cm^{-1} was assigned to $\nu_{\text{C=O}}$ of

coumarin moiety. Lowering of this peak from the expected value of 1729 cm^{-1} for unsubstituted coumarin may be due to conjugation between C=O and the NH_2 group at $\text{C}3^{12}$. Slight broadening of the $\nu_{\text{N-H}}$ can also be accounted to this H-bonding. The peak at 1589 cm^{-1} is due to rocking frequency of $\delta_{\text{N-H}}$ and $\delta_{\text{C-H}}$. The weak band located at



1407 cm^{-1} is assigned to $\nu_{\text{C-N}}$. Infrared spectrum of the 4-acetyl resorcinol shows two broad bands at 3573 cm^{-1} and at 3301 cm^{-1} that may be attributed to H-bonded two phenolic OH stretching frequencies ($\nu_{\text{O-H}}$) (Silverstein, 1981). In addition there are three strong bands at 1631 cm^{-1} , 1607 cm^{-1} and 1206 cm^{-1} which are assigned to the $\nu_{\text{C=O}}$, $\nu_{\text{C=C}}$ and $\nu_{\text{C-O}}$ respectively.

In Cu(II) complex, a medium broad band centered at 3450 cm^{-1} can be assigned to $\nu_{\text{O-H}}$ of phenol. The $\nu_{\text{N-H}}$ for coordinated ammonia molecule is observed near the same region as a broad band centered at 3330 cm^{-1} . Zn(II) complex shows a medium broad band in the region 3500-3300 cm^{-1} which is assigned to $\nu_{\text{O-H}}$ stretching frequency. The broad nature of the band suggests presence of intra or/and intermolecular H-bonding. The band at 3301 cm^{-1} observed due to $\nu_{\text{O-H}}$ in 4-AR disappeared in both copper and zinc complexes indicating deprotonation of OH and coordination between metal ion and oxygen of phenol. The Zn(II) and Cu(II) complexes exhibit bands at 1669 cm^{-1} and 1746 cm^{-1} respectively which are assigned to $\nu_{\text{C=O}}$ moiety of the coumarin (William, 1982). This carbonyl stretching is located at higher frequency in Cu(II) complex indicating its non participation in coordination to the metal ion (Abou-Melha & Faruk, 2008). It also accounts for the disappearance of H-bonding between C=O and NH_2 that shifts $\nu_{\text{N-H}}$ of 3-AC to lower frequency in comparison to unsubstituted coumarin. The band located at

1631 cm^{-1} which was assigned to acetyl carbonyl group of 4-acetyl resorcinol also disappeared in both the mixed ligand complexes. This confirms that the condensation reaction has taken place and Schiff base has formed. The band observed as a shoulder at 1630 cm^{-1} in Cu(II) complex can be assigned to the bending mode of NH_3 of ammonia (Hosseini and Maryam, 2008). New bands at 1606 cm^{-1} in Zn(II) complex and at 1610 cm^{-1} in Cu(II) complex are assigned to $\nu_{\text{C=N}}$ stretch. The azomethine stretching frequency in free Schiff bases are normally observed around 1630-1620 cm^{-1} (Nakamoto, 1987). This band is seen shifted to lower frequency indicating the involvement of azomethine nitrogen in coordination to metal²⁸. It is also deducible that mixed ligand Schiff base complex has formed. The phenolic $\nu_{\text{C-O}}$ stretching is seen to have shifted to higher frequency by 17-27 cm^{-1} in both the complexes showing coordination of the metal to the ligand through oxygen of phenol.

A medium band around 1031 cm^{-1} in Zn(II) complex and 1050 cm^{-1} in Cu(II) complex is characteristic of $\nu_{\text{O-C-O}}$ corresponding to cyclic grouping of 3-aminocoumarin. Some new bands identified in the complexes at 458 and 412 cm^{-1} have been assigned to stretching frequency of metal chlorine bonds ($\nu_{\text{M-Cl}}$). New bands at 593 and 622 cm^{-1} in Zn(II) complex and at 451 and 476 cm^{-1} in Cu(II) complex are assigned to $\nu_{\text{M-N}}$ and $\nu_{\text{M-O}}$ respectively (Nakamoto, 1987).

Table 2: Important IR absorption frequencies (in cm^{-1}) of 3-AC, 4-AR and mixed ligand Schiff base complexes

No.	Compound	$\nu(\text{N-H})$	$\nu(\text{O-H})$ phenolic	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{C-O})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$	$\nu(\text{M-Cl})$
1	3-AC	3428 (asy) 3313(sym)	-	1705 s	-	1170 $\nu(\text{C-O-C})$	-	-	
2	4-AR	-	3573 w, br, 3301 s, br	1631sh		1206 s			
3	Zn(L)Cl	-	3353 m, br	1669 sh (coumarin)	1606 s	1243 w	622 w	593 m	490 w
4	$\text{Cu(L)}_2(\text{NH}_3)\text{Cl}$	3330 s, br	3450 s, br	1746 s (coumarin)	1610 s	1223 s	476 m	451m	412 w

s= strong, br = broad, m = medium, w = weak, sh = shoulder, asy= asymmetric, sym= symmetric

Electronic spectra and Magnetic moments

In both 3-aminocoumarin and 4-acetylresorcinol, absorption bands observed at 323 nm and 318 nm respectively are assigned to $n \rightarrow \pi^*$ transition of carbonyl group. Similarly, the $\pi \rightarrow \pi^*$ transition band of benzene ring was observed at 242 nm for 3-aminocoumarin and at 230 nm and 270 nm for 4-acetylresorcinol.

Copper(II) complex of mixed ligand Schiff base shows a broad absorption band at 460 nm (21739 cm^{-1}) which can be assigned to d-d transition corresponding to ${}^2T_{2g} \leftarrow {}^2E_g$. An intense band was observed around 390 nm which is characteristic of charge transfer transition.

As expected for a d^{10} electronic configuration, the electronic spectrum of zinc(II) mixed ligand complex does not show any d-d transition. The observed bands are due to the ligand and charge transfer transitions. The bands at 325 nm (30769 cm^{-1}) and 286 nm (34965 cm^{-1}) are assigned to $n \rightarrow \pi^*$ transition of azomethine (Bagihallia, 2009) and to $\pi \rightarrow \pi^*$ transition of benzene ring respectively. The other band located at 473 nm ($21,142 \text{ cm}^{-1}$), is assigned to charge transfer transition. The yellow color of the complex may be conjured as having arisen from this absorption in the visible region (Ronald C. Denney and Roy, 1987)

The magnetic moment of complexes is given in table 4. The observed magnetic moment for copper mixed ligand was 2.05 BM. This experimental value agrees with expected magnetic moments value for one unpaired electron (1.75-2.2 BM) in octahedral geometry. The observed magnetic moment value is significantly larger than the spin only value showing the orbital contribution to the magnetic moment. Zn(II) mixed ligand is a diamagnetic complex and has zero magnetic moment (Miesler, 1987, Kingston, 2011, Housecroft and Sharpe, 2007)

Table 3: Electronic spectra and magnetic moment data

Compounds	Transitions (nm)			μ_{eff} (BM)
	d-d / CT	$\pi \rightarrow \pi^*$ / benzene	$n \rightarrow \pi^*$ / carb. / azom.	
3-AC		242	270 (carb.)	-
4-AR	318	230	323 (carb.)	-
Zn(L)Cl	473 (CT)	-	325 (azom.)	DM
Cu(L) ₂ (NH ₃)Cl	460, 390			2.05

carb. = carbonyl, azom. = azomethine, DM = diamagnetic

4. CONCLUSION

From the results obtained for copper(II) and zinc(II) mixed ligand complexes, it is clear that Schiff base of mixed ligands has formed through the template method of synthesis. The ligand acts as bidentate ON donor in Cu(II) complex, coordinating to the metal through oxygen of phenol and azomethine nitrogen of Schiff base of the mixed ligand. It acts as a tridentate ONO donor in Zn(II) complex, coordinating to the metal through oxygen of phenol, azomethine nitrogen and carbonyl oxygen of coumarin. Based on elemental and metal ion analyses, IR, and electronic spectral data, magnetic susceptibility and conductance data, an octahedral geometry for the Cu(II) complex and a tetrahedral geometry for Zn(II) complex was suggested. The proposed structures are given in Figure 4.

Extension of this work can be carried out to synthesize a single crystal and thereby crystal structures can be determined. Also biological activity of these complexes can be evaluated as the complexes contain the biologically active coumarin moiety. Additional data as thermal analysis, x-ray crystallography and

ESR spectral study (for Cu²⁺ complex) may also be conducted.

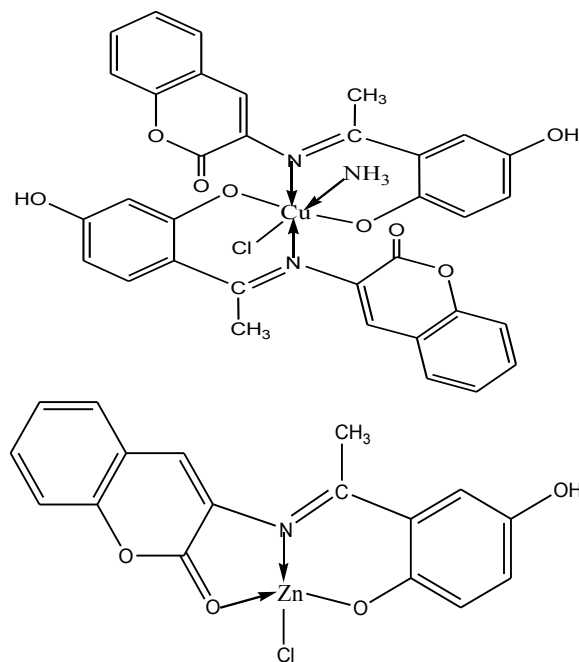


Fig. 4: Suggested structure of Cu²⁺ and Zn²⁺ mixed ligand Schiff base complexes

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