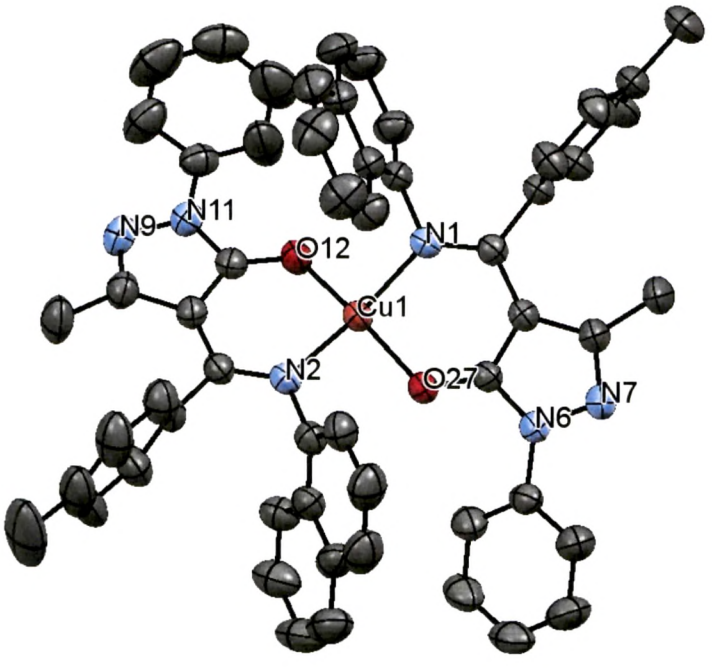
Chapter – 2



Synthesis, characterization and catalytic activities of copper(II) complexes of pyrazolone-based Schiff base ligands

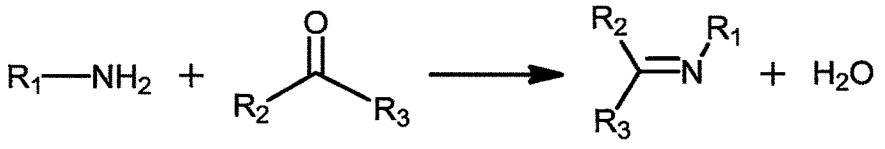
2.1. Introduction

Schiff bases (imines) constitute one of the most widely used families of organic compounds, not only as synthetic intermediates but also in coordination chemistry and their chemistry is essential material in organic textbooks [1]. Schiff base ligands are easily synthesized and form complexes with almost all metal ions. Coordination complexes of Schiff bases have been extensively studied due to their attractive chemical and photophysical properties. A large number of Schiff bases and their complexes are of significant interest and attention because of their biological activity including anti-tumour, antibacterial, fungicidal and anti-carcinogenic properties [2] and their applications in homogeneous and heterogeneous catalysis [3]. The present chapter has been focused on the synthesis of metal complexes of Schiff bases of pyrazolone and their catalytic applications.

Figure 2.1. Hugo Schiff, 24 April 1915 [2*g*].

The condensation of primary amines with aldehydes and ketones give imines (Scheme 2.1). 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 Hugo (Ugo)

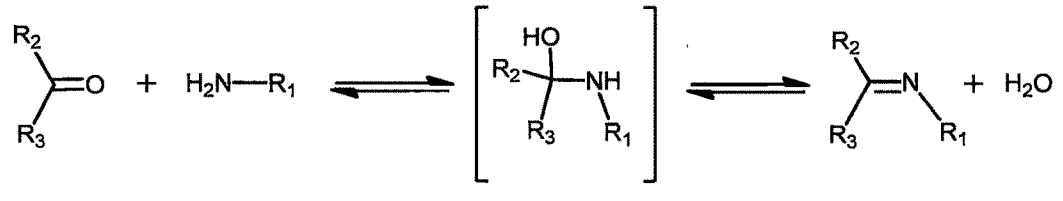
Schiff (*see* Figure 2.1). In 1864 Schiff studied the reaction of aniline with aldehydes, including acetaldehyde, valeraldehyde, benzaldehyde, and cinnamaldehyde, and he discovered that imines were formed. The first brief paper was entitled "A New Series of Organic Bases" ("Eine neue Reihe organischer Basen") [4].



Scheme 2.1. Schiff base formation.

Schiff bases or imines also known as azomethines are represented by the general formula ($R_2R_3C{=}NR_1$). The substituents R_2 and R_3 may be alkyl, aryl, heteroaryl, hydrogen. The substituent at the *N*-imino (C=N) may be alkyl, aryl, heteroaryl, hydrogen or metallo (usually Si, Al, B. Sn). Schiff bases having aryl substituents are substantially more stable and more readily synthesized, while those which contain alkyl substituents are relatively unstable. Schiff bases of aliphatic aldehydes are relatively unstable and readily polymerizable, while those of aromatic aldehydes having effective conjugation are more stable. The physical properties and reactivity of imines are and continue to be studied by more than a hundred years

The most common method for preparing imines is the original reaction discovered by Schiff [4, 5]. Basically it consists in the reaction of an aldehyde (respectively a ketone) with a primary amine and elimination of one water molecule (Scheme 2.2). This reaction can be accelerated by acid catalysis and is generally carried out by refluxing a mixture of a carbonyl compound and an amine, in a Dean Stark apparatus in order to remove the water. This removal is important as the conversion of aminal into the imine is reversible.



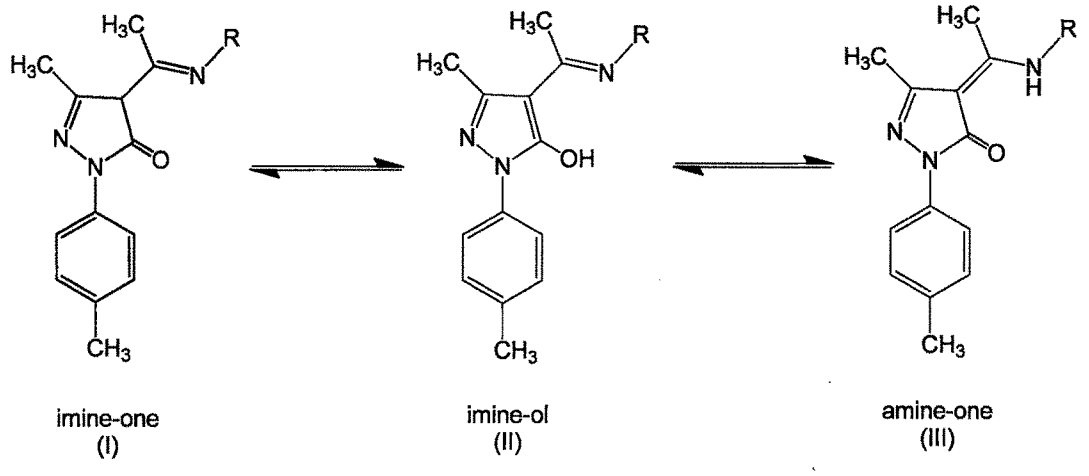
Scheme 2.2. Schiff base reaction for the preparation of imines.

Aliphatic ketones react with amines more slowly than aldehydes to form imines, therefore, higher reaction temperatures and longer reaction time are required. Acid catalysts and water removal from the reaction mixture can significantly increase the reaction yields, which can reach 80%–95% values. Aromatic ketones are less reactive than aliphatic ones and require harsh conditions to be converted into imines.

2.1.1. Schiff bases of 4-acylpyrazolones and their metal complex

4-ayclpyrazolones are an important class of β-diketones and widely used in the formation of coordination complexes with various metal ions [6]. The chemistry of 4-acylpyrazolone has been discussed in the Chapter 1. In this Chapter we have focused our attention on the Schiff bases derived from the 4-acylpyrazolones.

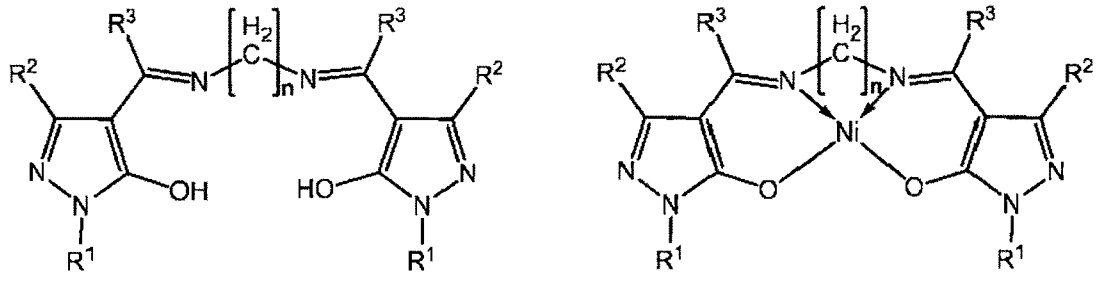
4-acylpyrazolones upon reaction with the corresponding primary amines form Schiff bases [7]. The Schiff bases of 4-acylpyrazolones can exist in three tautomeric forms; (I) imine-one, (II) imine-ol and (III) amine-one (Scheme 2.3). Jadeja *et al* extensively studied the tautomeric forms of Schiff bases of 4-acylpyrazolones and reported that amine-one form exist in the solid state, while imine-one and imine-ol forms exist in the solutions [7].



Scheme 2.3. Tautomeric forms of Schiff base of 4-acylpyrazolone ligands.

Various Schiff bases of 4-acylpyrazolones have been synthesized and studied by many researchers. It is difficult to cover all the literature reports on the Schiff bases of 4-acylpyrazolones and their metal complexes in this chapter. However, we have included some of the literatures having various types of Schiff bases of 4-

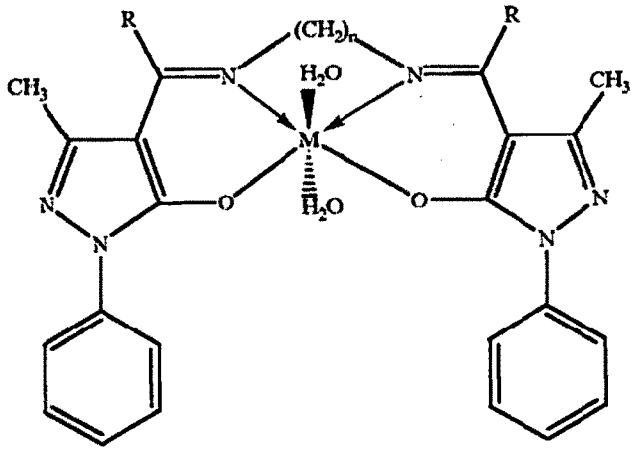
acylpyrazolones and their metal complexes. Cour *et al* [8] synthesized a series of tetradentate Schiff bases by the reaction between 4-acylpyrazolones and aliphatic diamines (n = 2 or 3). Ni(II) complexes of synthesized Schiff bases were synthesized. A general structure for the synthesized compounds is shown in Figure 2.2.



n = 2 or 3
R^1 = Me or Ph
R^2 = Me or Ph
R^3 = Ph, *p*-ClC_6H_4, p-MeC_6H_4, *p*-$O_2NC_6H_4$

Figure 2.2. General structure of tetradentate Schiff base ligands and their Ni(II) complexes.

A series of bis-(4-acylpyrazolone)diimmine Schiff bases was synthesized by Fabio *et al* [9]. Zn(II) and Cd(II) complexes of these Schiff bases were synthesized and characterized by various instrumental techniques. These complexes possess a six-coordinate metal environment (*see* Figure 2.3).



n = 2, 3, 4
R = C_6H_5, $CH_2C(CH_3)_3$, $CH(C_6H_5)_3$

Figure 2.3. General structure of metal complexes of bis-(4-acylpyrazolone)diimmine Schiff bases.

Yang *et al* synthesized a Schiff base by the condensation of isoniazide with corresponding 4-acylpyrazolone. The lanthanum (Eu and La) complex having general formula $Ln(HL)_3 \cdot 3.5H_2O$ was synthesized and characterized by single crystal XRD (*see* Figure 2.4). X-ray diffraction analysis showed that the coordination polyhedron of the Eu complex is a tricapped trigonal prism. Anti tumour activities of these complexes were also studied [10].

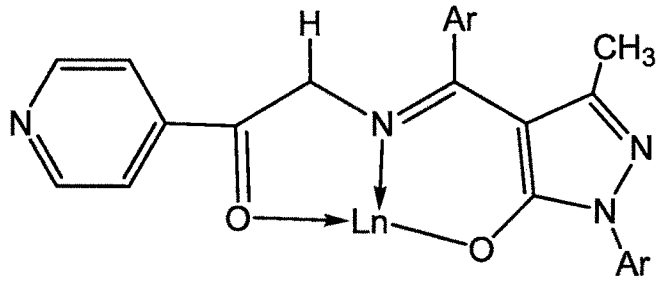


Figure 2.4. Structure of Lanthanum complex.

Schiff base ligand (BHMP) was synthesized by the condensation of 4-(1-phenyl-methyliden)- 3-methyl-l-phenyl-pyrazol-5-one and benzoylhydrazide in boiling methanol [11]. Oxo-rhenium complexes of the type $ReO(L)_2$ containing donar type O-N-O was synthesized and characterized by X-ray analysis (*see* Figure 2.5).

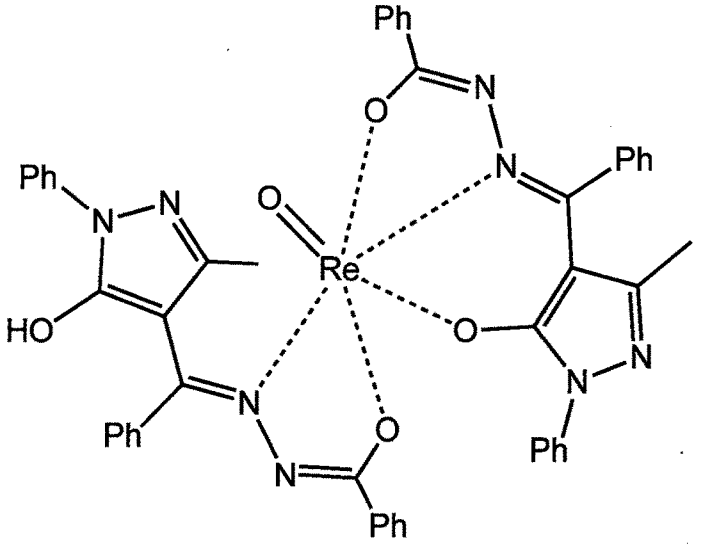


Figure 2.5. Structure of $ReO(BHMP)_2$ complex.

Jadeja *et al* reported the synthesis of Schiff bases of 4-[{(aryl)imino}ethyl]-3-methyl-1-(4'-methylphenyl)-2-pyrazolin-5-one by condensing with various aniline derivatives [7]. The Cu(II) complexes of these Schiff bases were synthesized and

characterized by various spectroscopic and analytical techniques. The complexes exist in octahedral geometries (*see* Figure 2.6).

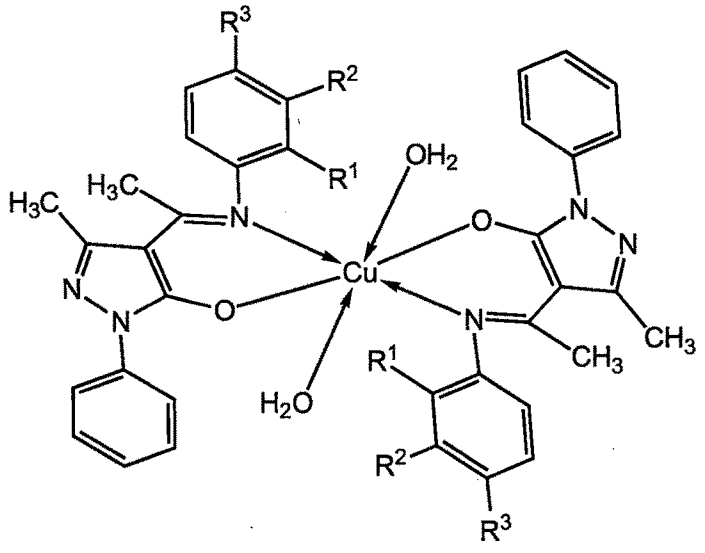


Figure 2.6. General structure of Cu(II) complexes.

The synthesis of mixed-ligand Cu(II) complex of *N*-(1-phenyl-3-methyl-4-benzylidene5-pyrazolone) *p*-nitrobezoylhydrazide and pyridine was reported by Jia *et al* [12]. In the mixed-ligand complex, the coordination geometry around the tetra-coordinated Cu(II) ion is square-planar composed of two oxygen atoms and one nitrogen atom of Schiff base and one nitrogen atom of pyridine (*see* Figure 2.7).

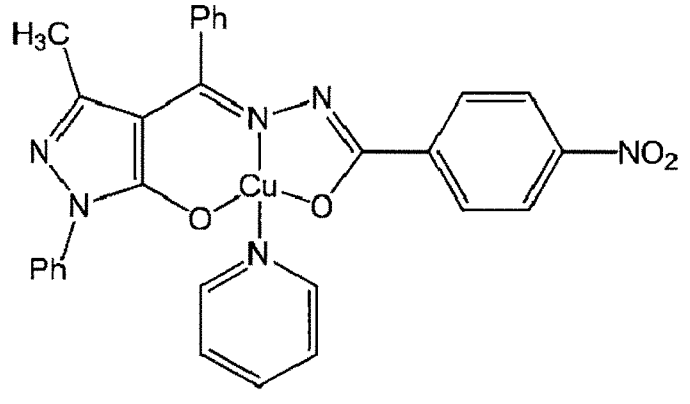


Figure 2.7. Structure of mixed ligand Cu(II) complex.

The crystal structure of Bis{1-n-hexyl-3-methyl-4-[1-(phenylimino)propyl]-1H-pyrazol-5-olato}copper(II), having square planer geometry was reported [13*a*]. O and N atoms of the Schiff base coordinate with metal centre to form two six member

chelate rings (*see* Figure 2.8 A). Belmar et al also reported pyrazolone based nitridomanganese(V) complexes [13*b*]. Single crystal XRD study was also carried out to confirm the proposed geometry of the synthesized complex (*see* Figure 2.8 B).

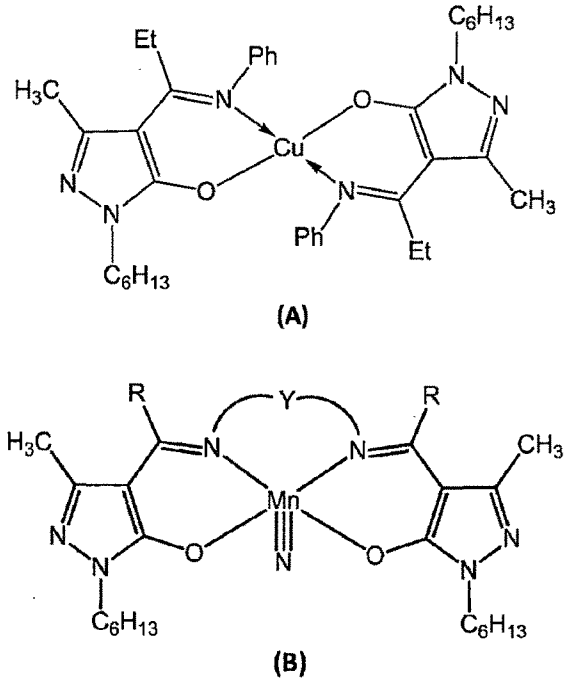


Figure 2.8. (A) Structure of Cu(II) complex and (B) structure of nitridomanganese(V) complex.

A series of Schiff bases was synthesized by the condensation of 4-acyl-3-methyl-1-phenyl-2-pyrazolin-5-one and 4-aminoantipyrine (*see* Figure 2.9). Nitrosyl complexes of Schiff base with molybdenum were also synthesized [14].

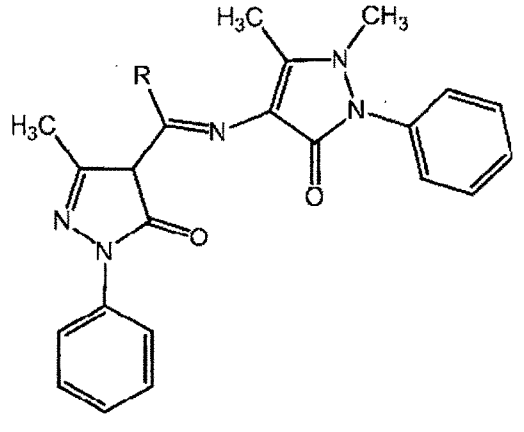


Figure 2.9. Structure of Schiff base of 4-acylpyrazolone and 4-aminoantipyrine.

A Schiff base derived from diethenetriamine 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone was reported by Yang *et al* [15]. Zn(II) and Ni(II) complexes of this new Schiff base were synthesized and single crystal structure X-ray analysis of Ni(II) complex was also carried out (*see* Figure 2.10).

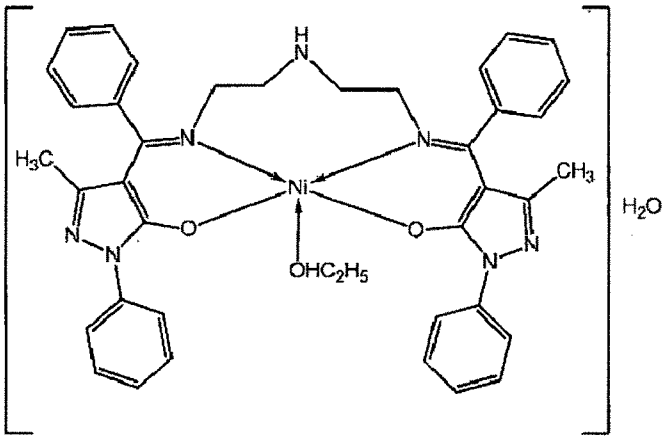
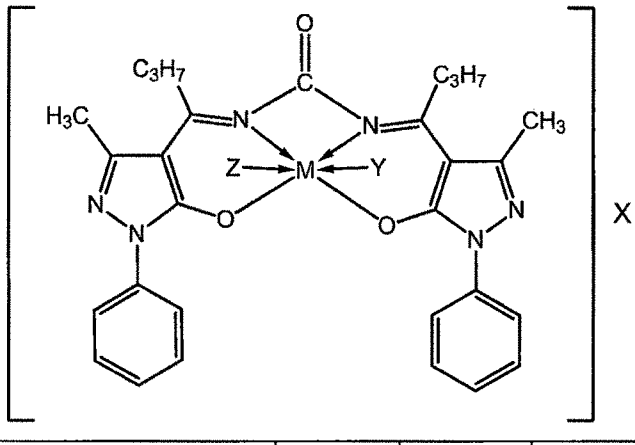


Figure 2.10. Structure of Ni(II) complex.

The tetradentate ONNO donor Schiff base ligand was derived from 4-butyryl-1,3-diphenyl-2-pyrozolin-5-one and urea [16*a*]. Oxovanadium(IV), Cr(III), Fe(III), Fe(II), Ni(II), Cu(II), Zn(II) and UO_2(VI) complexes of Schiff base ligand were also synthesized (*see* Figure 2.11).



M	Z	Y	X
OV(IV)	–	H_2O	
Cr(III), Fe(III)	H_2O	H_2O	NO_2
Fe(II), Ni(II), Cu(II), Zn(II)	H_2O	H_2O	–
UO_2(IV)	–	–	H_2O

Figure 2.11. Suggested general structure of metal chelates.

A series of tridentate pyrazolone-based thio-Schiff bases and were synthesized by the interaction of 4-acylpyrazolones with thiosemicarbazide in an ethanolic medium [16*b*]. Copper Schiff-base complexes, [Cu(L)(H_2O)], have been prepared by the interaction of the aqueous solution of copper sulfate pentahydrate with hot ethanolic solution of thio-Schiff base ligands (*see* Figure 2.12). Jadeja *et al* also reported the Cu(II) complexes of Schiff bases derived from the condensation of 4-toluoylpyrazolones and substituted aniline derivatives [16*c*].

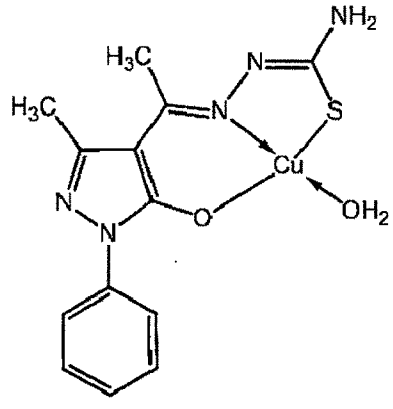


Figure 2.12. Structure of the Cu(II) complex.

A pyrazolone containing zinc Schiff base complex was synthesized and its absorption and fluorescent properties modulated by Ag^+ ions were investigated [17]. The complex exhibits a mononuclear structure with the Zn^{2+} centre coordinated by two imine nitrogen atoms, two benzoyl oxygen atoms, and two pyrazolone oxygen atoms in a distorted octahedral geometry (*see* Figure 2.13).

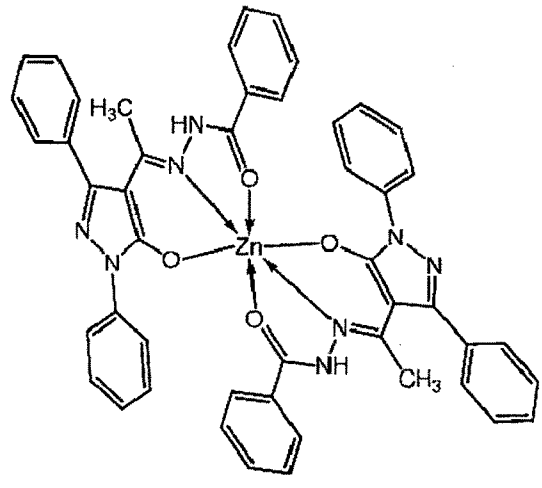


Figure 2.13. Structure of Zn(II) complex.

Tridentate pyrazolone-based Schiff bases were synthesized by the interaction of 4-acyl/aroyl pyrazolones with 2-Amino Phenol [18]. Binuclear copper Schiff base complexes were synthesized by the interaction of the aqueous solution of copper acetate monohydrate with hot ethanolic solution of the appropriate ligand (*see* Figure 2.14).

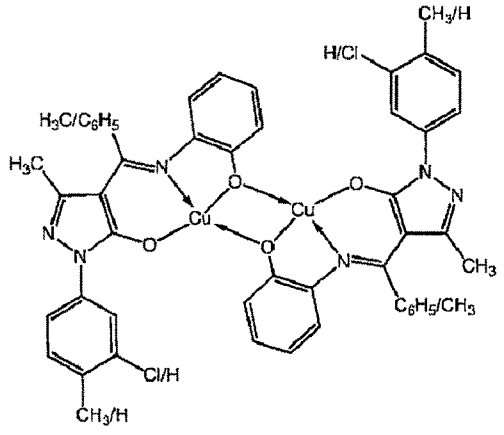


Figure 2.14. Structure of binuclear Cu(II) complex.

A series of binuclear magnesium benzylalkoxide complexes with NNO-tridentate pyrazolone Schiff base ligands was reported by Lin *et al* [19]. The complexes having general formula $[LnMg(\mu\text{-}QBn)]_2$ were characterized by various spectroscopic techniques and single crystal XRD. X-ray analysis reveals that they are binuclear bridging through benzylalkoxy oxygen atoms with penta-coordinated metal centres (*see* Figure 2.15).

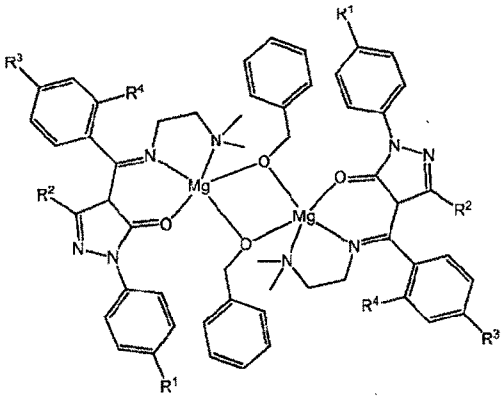


Figure 2.15. Structure of binuclear magnesium complex.

Five new metal complexes $[Zn(HL^1)(OAc)(CH_3CH_2OH)]$ **1**, $[Cd_2(HL^1)_2(OAc)_2(CH_3CH_2OH)_2]$ **2**, $[Cu(L^1)_6]$ **3**, $\{[Zn(L^2)(CH_3OH)]\cdot(CH_3OH)\}_n$ **4** and $[Cu(L^3)]_n$ **5** of polydentate pyrazolone-based Schiff base ligands (*see* Figure 2.16) were reported and characterized by single crystal XRD. The different structures of complexes and the different coordination modes of ligands in these complexes indicate that the metal atoms with different coordination geometries have a great influence on the structure of products. The substituents at the 4-position also affect the structure of the resulting complexes [20].

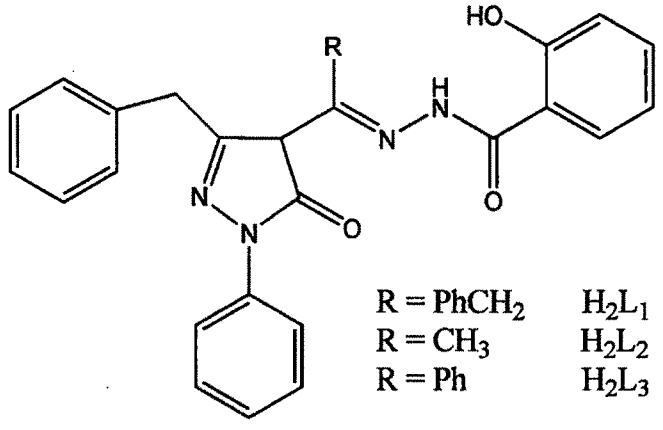


Figure 2.16. General structure of the ligands.

2.1.2. Objective and methodology for the present work

The interest in the coordination chemistry of pyrazolone Schiff bases and their various applications has increased greatly in the last decade [7-21]. However, very less attention has been paid on the use of pyrazolone Schiff base complexes as catalyst for the organic transformations. Only a few reports are available in the literatures for the use of pyrazolone Schiff base complexes as catalysts. Wu *et al* synthesized Cu(II), Ni(II) and Co(II) complexes of pyrazolone Schiff bases and used them for the norbornene and styrene polymerization [22]. Lü *et al* synthesized monuclear and trinuclear Zn(II) complexes based on the asymmetrical bis-pyrazolone-Schiff-base ligand precursors and used these complexes for the ring-opening copolymerization of CHO and MA [23].

In this chapter we have synthesized the copper(II) complexes of Schiff bases derived from the condensation of 4-acylpyrazolones and primary amines. Single crystal X-ray analysis of one of the Cu(II) complex was also carried out. Synthesized

Cu(II) complexes were used as the homogeneous catalysts for the solvent free oxidation of benzyl alcohol and styrene using H_2O_2 as an oxidant.

2.2. Experimental

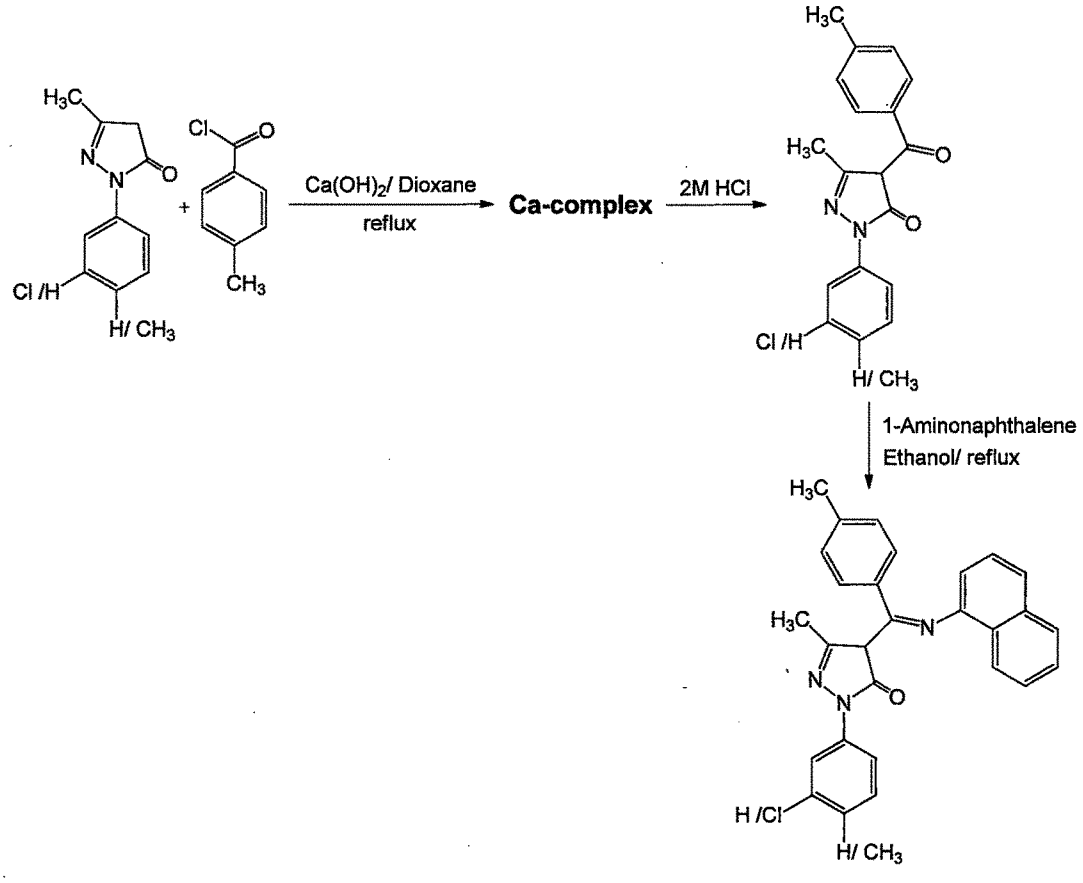
2.2.1. Materials and physical measurements

All reagents and solvents were purchased from commercial sources and were further purified by the standard methods, if necessary [24]. Pyrazolone derivatives were obtained from Nutan Dye Chem. Sachin, Surat. Copper acetate and naphthylamine were purchased from Loba Chem., Mumbai. Benzyl alcohol, styrene, hexane and 30% aqueous H_2O_2 were purchased from Merck and used as received.

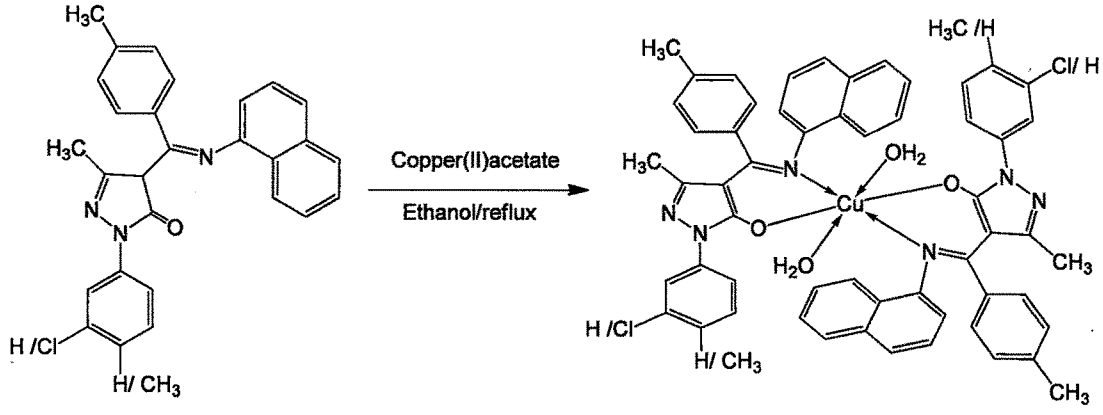
Infrared (IR) spectra were recorded on a Perkin Elmer Fourier transform IR (FT-IR) spectrum RX 1 spectrometer as KBr pellets. ^{1}H NMR spectra of ligands were recorded with AV 400 MHz Bruker FT-NMR instruments. Mass spectra of the ligands were recorded on Trace GC ultra DSQ II. Elemental analysis of C, H and N were determined using a Perkin Elmer series-II 2400 elemental analyzer. X-ray intensity data for L^1, L^2 and L^3 were collected on Bruker CCD area-detector diffractometer equipped with graphite monochromated MoKα radiation (λ = 0.71073Å). X-ray intensity data for $[Cu(L^1)_2]$ were collected on on a Xcalibur, Eos, Gemini diffractometer equipped with a graphite monochromated Cu Kα radiation (λ = 1.54184). Electronic spectra were recorded on a Perkin Elmer Lambda 35 UV-Vis spectrometer. EPR spectra of complexes were recorded on X-band instrument at EPR laboratory, SAIF, IIT, Bombay, at room temperature and liquid nitrogen temperature. ESI-mass spectra were recorded on Waters Q-ToF micromass. A simultaneous TG/DTA was carried out on a SII EXSTAR6000 TG/DTA 6300. The experiments were performed in N_2 at a heating rate of 10 °C min^{-1} in the temperature range 25–750 °C using a platinum pan. Purity of the ligands and their complexes were tasted by thin layer chromatography. Gravimetric and volumetric analysis were performed for the determination of copper after decomposition of complexes in nitric acid.

2.2.2. Synthesis of 4-acylpyrazolones [PMP (1), PTPMP (2) and MCPMP (3)]

PMP, PTPMP and MCPMP were synthesized according to the method reported previously in Chapter 1.



Scheme 2.4. Synthesis of Schiff base ligands of 4-acylpyrazolones.



Scheme 2.5. Synthesis of copper(II) complexes of Schiff base ligands of 4-acylpyrazolones.

2.2.3. Synthesis of Schiff base ligands

The synthesis of Schiff base ligands is shown in Scheme 2.4. PMP (10 mmol) was dissolved in minimum amount of absolute ethanol. To this solution, a solution of 1-aminonaphthalene (10 mmol) in 20ml was added drop wise. The reaction mixture was refluxed for 12 hours. After cooling a microcrystalline yellow compound was separated. The compound was filtered and washed with water and then with ethanol and dried in vacuum. The suitable crystals for single crystal X-ray study were grown in acetonitrile.

Ligand L^1: Yield: 3.5g, 84%, m.p: 184 °C, ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.67(s, 3H), 2.33(s, 3H), 6.85(d, 1H), 7.12 (d, 2H), 7.15(m, 5H), 7.20(m, 1H)7.43 (m, 2H), 7.54(m, 1H), 7.61(m, 1H), 7.64(d, 1H), 7.84(d, 1H), 8.0(m, 2H), 8.26(d, 1H), 13.3(s, 1H); IR spectra (KBr, cm^{-1}): 2923, 1589, 1485, 1266, 898, 768; ESI-MS *m/z*: 417.08 M^+ (calculated = 417.18).

Ligand L^2: Yield: 3.4g, 79%, m.p: 161°C, ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.66(s, 3H), 2.33(s, 3H), 2.38(s, 3H), 6.84(d, 1H), 7.16(m, 5H), 7.28(t, 2H), 7.56(t, 1H), 7.62 (m, 2H), 7.73(d, 1H), 7.84(d, 1H), 7.93(d, 2H), 8.26(d, 1H), 13.31(s, 1H); IR spectra (KBr, cm^{-1}): 2919, 1592, 1486, 1208, 945, 781; ESI-MS *m/z*: 431.1 M^+ (calculated = 431.19).

Ligand L^3: Yield: 3.2g, 71%, m.p: 146 °C, ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.66(s, 3H), 2.33(s, 3H), 6.86(d, 1H), 7.14(m, 5H), 7.18(m, 1H), 7.36(t, 1H), 7.57(m, 1H), 7.64(m, 2H), 7.85(d, 1H), 8.05(m, 1H), 8.18(t, 1H), 8.24(d, 1H), 13.19(s, 1H); IR spectra (KBr, cm^{-1}): 2922, 1585, 1480, 1268, 1209, 967, 778; ESI-MS *m/z*: 451.1 M^+ (calculated = 451.14).

2.2.4. Synthesis of Cu(II) complexes

All the Cu(II) complexes of Schiff bases were prepared by the following method (*see* Scheme 2.5). The metal salt (2 mmol) was dissolved in minimum amount of water and the solution was added to a hot ethanolic solution of the corresponding Schiff base (4 mmol). After the complete addition small amount of Na-acetate was added and the reaction mixture was refluxed for 4 hours. A crystalline solid was formed which was filtered, washed with hot distilled water and then from ethanol and dried under vacuum.

2.2.5. Catalytic reactions

2.2.5.1. Oxidation of benzyl alcohol

Catalytic oxidation of benzyl alcohol was carried out in a 50 mL round bottom flask fitted with a water circulated condenser using copper(II) complexes $[Cu(L^{1-2})_2(H_2O)_2]$ of 4-acylpyrazolone ligands as a catalyst. In a typical reaction, benzyl alcohol, catalyst and 30% H_2O_2 were intensively stirred at the 90 °C temperature for the whole duration of the reaction. After completion of the reaction, reaction mixture was concentrated on rotary evaporator. Hexane was added to the system, and the organic phase was separated. By this simple procedure, isolation of the carbonyl product in the organic phase was achieved.

2.2.5.2. Oxidation of styrene

Catalytic oxidation of styrene was carried out in a 50 mL round bottom flask fitted with a water circulated condenser using copper(II) complexes $[Cu(L^{1-2})_2(H_2O)_2]$ of 4-acylpyrazolone ligands as a catalyst. In a typical reaction, styrene, catalyst and 30% H_2O_2 were intensively stirred at the 80 °C temperature for the whole duration of the reaction. After completion of the reaction, reaction mixture was concentrated on rotary evaporator. Hexane was added to the system, and the organic phase was separated. By this simple procedure, isolation of the carbonyl product in the organic phase was achieved.

2.3. Results and discussion

The synthesized ligands were characterized by FT-IR, ^1H NMR, Mass spectra and single crystal X-ray analysis. All spectral data are agreed with the Schiff base ligand structures. The Cu(II) complexes having the general composition $[Cu(L)_2(H_2O)_2]$ have been synthesized by a general procedure based on the mixing of an aqueous solution of copper acetate with an ethanolic solution of the ligand in 1:2 molar ratio and isolation of final precipitate by filtration. The complexes are stable to air and moisture without any kind of decomposition also after several months. The complexes are insoluble in water, but soluble in acetonitrile, DMF and DMSO. All the complexes were characterized by elemental analyses, FT-IR, Mass spectrometry, TG-DTA, EPR and UV-Visible spectroscopic techniques. The single crystal structure

of Complex **1** was investigated using X-ray analysis. Analytical data of the synthesized complexes were given in Table 2.1.

Table 2.1. Analytical data of Cu(II) Complexes.

Complex	Molecular Formula	Color	Yield (%)	Elemental analysis			
				%C	%H	%N	% Cu
1	$C_{60}H_{56}CuN_6O_4$	Brown	67	71.97 (72.12)	5.15 (5.19)	9.12 (9.01)	6.8 (6.81)
2	$C_{58}H_{52}CuN_6O_4$	Brown	60	71.82 (72.52)	5.38 (5.46)	8.78 (8.75)	6.58 (6.62)
3	$C_{56}H_{46}Cl_2CuN_6O_4$	Dark brown	64	66.23 (67.16)	4.16 (4.63)	8.39 (8.39)	6.33 (6.35)

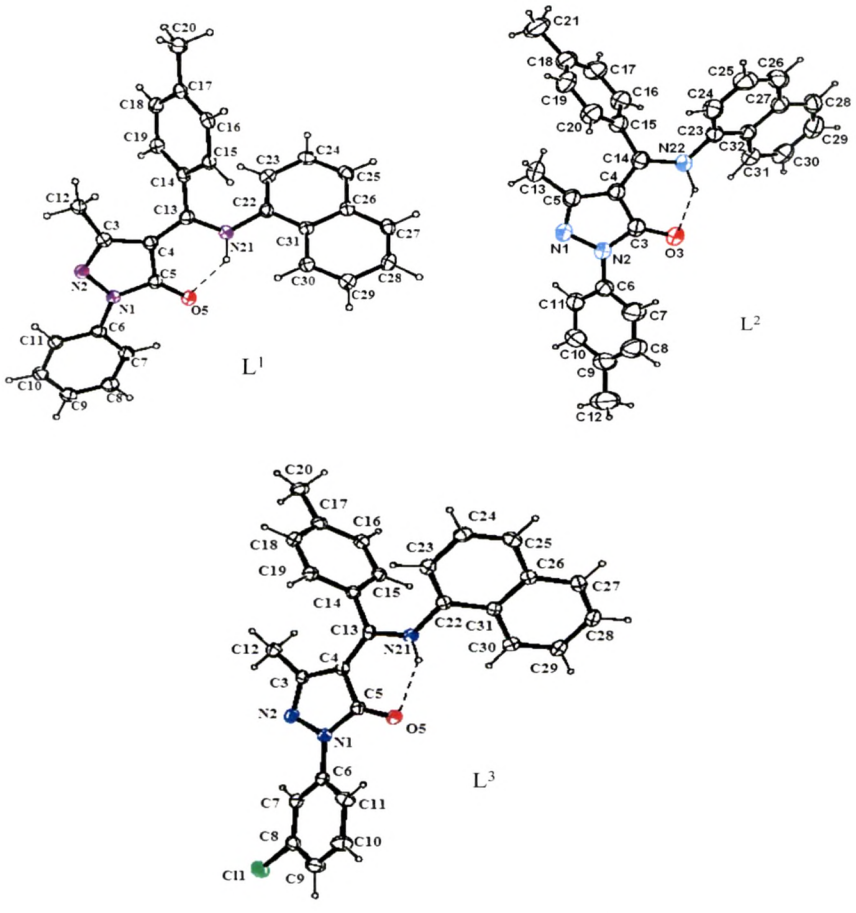


Figure 2.17. ORTEP views of ligands L^1, L^2 and L^3.

Table 2.2. Summary of crystallographic data for the ligands L^1, L^2 and L^3.

	L^1	L^2	L^3
Empirical formula	$C_{28}H_{23}N_3O$	$C_{29}H_{25}N_3O$	$C_{28}H_{22}N_3OCl$
Formula weight	417.49	431.52	451.94
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	*Pbca*	*P*-1	*P*-1
a (Å)	15.518(3)	7.0212(5)	7.0658(12)
b (Å)	15.158(3)	11.2828(6)	10.8912(18)
c (Å)	18.110(4)	15.8177(10)	15.837(3)
α (°)	90	71.306(5)	70.928(3)
β (°)	90	80.636(5)	81.102(3)
γ (°)	90	84.692(5)	86.555(3)
V(Å^3)	4260.0(15)	1170.04(13)	1137.9(3)
Z	8	2	2
$\rho_{calcd.}$(g cm^{-3})	1.302	1.225	1.319
Abs coeff, μ(cm^{-1})	0.080	0.075	0.194
F(000)	1760	456	472
No. of parameters refined	381	399	386
Final R	0.0489	0.0601	0.0521
wR(F^2)	0.1132	0.1256	0.1369
Goodness-of-fit	1.004	0.956	1.001
CCDC	817985	854557	817983

2.3.1. Crystal structure study

2.3.1.1. Crystal structures of Ligands L^1, L^2 and L^3

The crystallographic data for ligands were summarized in Table 2.2. X-ray intensity data were collected on Bruker CCD area-detector diffractometer equipped with graphite monochromated MoKα radiation (λ = 0.71073Å). *ORTEP* views of the ligands were illustrated in Figure 2.17. The structures were solved by direct methods using *SHELXS97* [25]. All non-hydrogen atoms of the molecule were located in the best E-map. Full-matrix least-squares refinement was carried out using *SHELXL97* [25]. All hydrogen atoms were included as idealized atoms riding on the respective carbon atoms with C-H bond lengths appropriate to the carbon atom hybridization. Atomic scattering factors were taken from International Tables for X-ray Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4). Single crystal data reveals that all the Schiff base ligands are present in amine-one [12] form in the solid state. Selected bond lengths and bond angles were presented in the Table 2.3 and Table 2.4.

Table 2.3. Selected bond lengths and bond angles in the ligands.

	Ligand L^1	Ligand L^2	Ligand L^3
Bond distances (Å) with esd's in parentheses			
N1-N2	1.406(2)	1.404(2)	1.401(2)
N1-C5	1.375(3)	1.374(3)	1.382(3)
N1-C6	1.414(2)	1.411(3)	1.413(2)
N2-C3	1.306(3)	1.308(3)	1.311(2)
C3-C4	1.439(3)	1.445(3)	1.436(3)
C3-C12	1.490(3)	1.491(3)	1.498(2)
C5-O1	1.254(2)	1.252(3)	1.247(2)
C4-C13	1.389(3)	1.394(3)	1.406(3)
N21-C13	1.339(3)	1.345(3)	1.329(2)
N21-C22	1.426(3)	1.427(3)	1.425(3)

Examination of non bonded contacts reveals intramolecular hydrogen bonding in ligands. Hydrogen bonding data for one of the ligand are summarized in Table 2.5.

The packing of molecules in the unit cell is further stabilized by π-π stacking interactions in ligand L^2 (Figure 2.18). Summary of π-π stacking interaction is given in Table 2.6.

Table 2.4. Selected bond lengths and bond angles in the ligands.

	Ligand L^1	Ligand L^2	Ligand L^3
Bond angles (°) with esd's in parentheses			
N2-N1-C5	111.7(1)	111.8(2)	112.1(2)
N2-N1-C6	118.4(1)	118.7(2)	119.5(2)
C5-N1-C6	129.9(2)	129.2(2)	128.4(2)
N1-N2-C3	106.7(2)	106.7(2)	106.3(2)
C3-C4-C5	104.9(2)	105.0(2)	105.4(2)
N1-C5-O1	126.3(2)	125.6(2)	126.1(2)
C4-C5-O1	128.8(2)	129.3(2)	129.4(2)
C13-N21-C22	127.6(2)	127.3(2)	128.5(2)

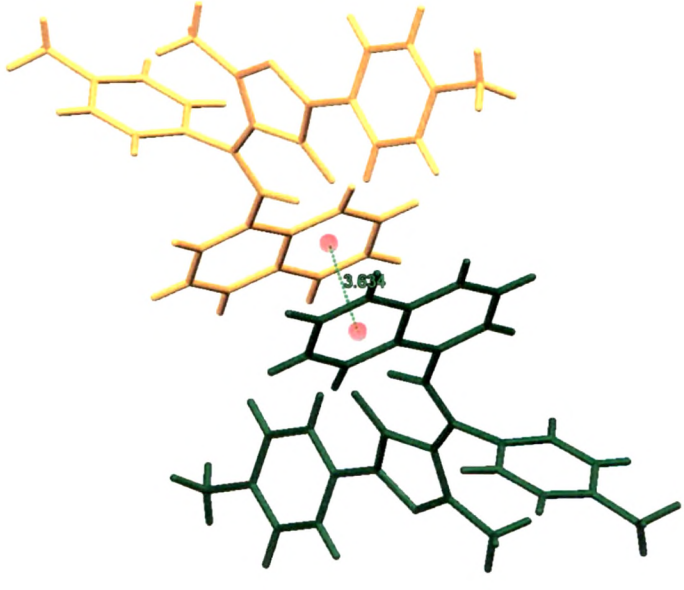


Figure 2.18. π-π stacking interaction in ligand L^2, different colors showing different layers of molecule.

Table 2.5. Hydrogen–bonding geometry in ligand L^2 (e.s.d.'s in parentheses). Cg1, Cg2, Cg3 and Cg4 denote the centroid of the N1-C5, C6-C11, C15-C20 and C27-C32 rings respectively.

D–H...A	D–H(Å)	H...A(Å)	D...A(Å)	D–H...A(°)
N22-H22...O3	1.04(3)	1.81(3)	2.701(3)	142(2)
C24-H24...Cg1^{i}	0.97(2)	2.88(2)	3.534(3)	125(2)
C29-H29...Cg2^{ii}	1.04(3)	2.53(3)	3.521(3)	159(2)
C21-H213...Cg3^{iii}	0.89(4)	3.11(5)	3.761(5)	132(4)
C12-H121...Cg4^{iv}	0.93(4)	2.87(5)	3.690(6)	147(4)
Symmetry code :	**(i) -1+ x, y, z**		**(ii) 2- x, 1-y, 1-z**	
	(iii) 1- x, 2-y, -z		**(iv) 1+ x, -1 + y, z**	

Table 2.6. Geometry of π-π interactions. CgI...CgJ represents the distance between the ring centroids; CgI...P, the perpendicular distance of the centroid of one ring from the plane of the other. α is the dihedral angle between the planes of rings I and J; β is the angle between normal to the centroid of ring I and the line joining ring centroids; Δ is the displacement of the centroid of rings J relative to the intersection point of the normal to the centroid of ring I and the least-squares plane of ring J. Cg4 denotes the centroid of the C27-C32 ring.

CgI	CgJ	CgI...CgJ(Å)	CgI...P(Å)	α(°)	β(°)	Δ(Å)
4	4^{ii}	3.634(2)	3.444	0.03	18.64	1.15
Symmetry code : (i) 1-x, 1-y, 1-z						

2.3.1.2. Crystal structure of Complex $[Cu(L^1)_2]$

The complex **1** was dissolved in acetonitrile and heated till the solution become clear and then it was allowed to crystallize at RT. Dark brown crystals of

single crystal X-ray diffraction quality were obtained within a week. The crystal used for data collection was of dimensions 0.3 × 0.2 × 0.2 mm^3. The crystal structure of the complex was solved by single-crystal XRD in the space group *P-1* of the triclinic system and refined to give formula $[Cu(L^1)_2](CH_3CN)$. Data collection parameters and refinement results are summarized in Table 2.7. Single crystal data reveal that the two *N,O*-chelating pyrazolone-Schiff base ligands are coordinated to copper centre creating distorted square planer geometry. Thus both the ligands form two six member chelate rings with the copper metal centre (*see* Figure 2.19). Interestingly, in the crystal structure of the complex **1**, coordinated water molecules were eliminated and one acetonitrile molecule has appeared in the crystal lattice. The elimination of weakly coordinated water molecules has taken place due to the heating of acetonitrile solution of complex **1**, which we used for obtaining X-ray diffraction quality single crystals by slow evaporation of the solution. However, FT-IR, TG-DTA and elemental analyses of the crude complex shows the coordination of two water molecules in the complex. Both the ligands are in *anti* conformation to each other, coordinated nitrogen atoms and oxygen atoms of both the ligands are *trans* to each other. The bite angles O1-Cu1-N21 and O2-Cu1-N52 are 95.70(7) and 94.93(7), respectively.

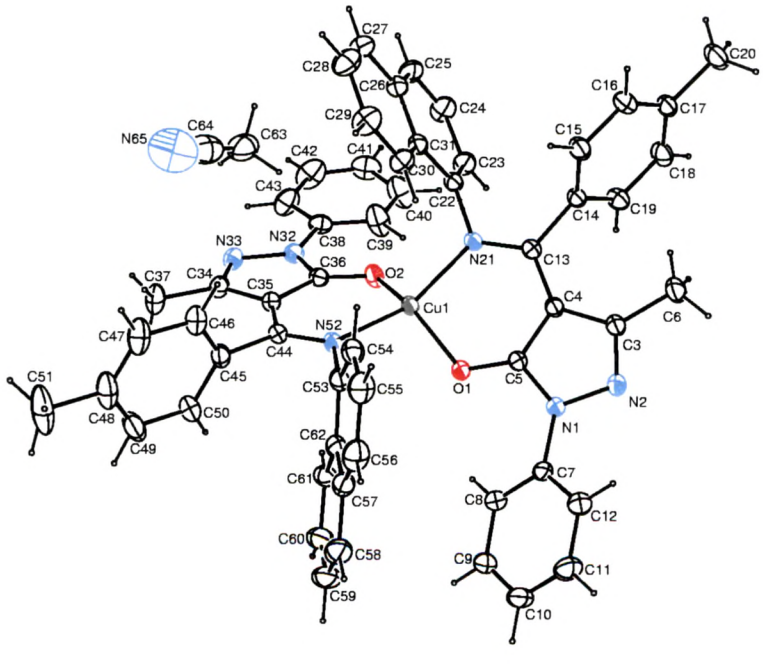


Figure 2.19. ORTEP view of complex **1** with displacement ellipsoids drawn at 50% probability level.

Table 2.7. Crystal structure data and structure refinement details for complex **1**.

Complex 1	$[Cu(L^1)_2](CH_3CN)$
Empirical formula	$C_{56}H_{44}N_6O_2Cu \cdot CH_3CN$
Formula weight	937.57
Crystal color and size (mm)	Brown, 0.3 × 0.2 × 0.2
Crystal system	Triclinic
Space group	*P-1*
a (Å)	12.9460(5)
b (Å)	13.9454(5)
c (Å)	13.9454(5)
α (°)	68.737(4)
β (°)	67.769(4)
γ (°)	68.977(4)
V (Å^3)	2391.32(16)
Z	2
ρ_{calc} (mg/mm^3)	1.302
F (000)	978.0
Radiation	CuKα (λ = 1.54184)
θ range for data collection	3.11 < θ < 65.00
Index ranges	-14 ≤ h ≤ 15, -16 ≤ k ≤ 15, -18 ≤ l ≤ 17
Reflections collected/ unique	15791/ 8108
Refinement method	Full-matrix least square on F^2
Final R	0.0431
Goodness of Fit on F^2	1.032
Final residual electron density (eÅ^{-3})	-0.263 < Δρ < 0.370
CCDC	1007668

The Cu^{II} has a distorted $\{O_2N_2\}$ square planer environment with six different bond lengths. Selected bond lengths and bond angles are listed in Table 2.8. The bond lengths of Cu1-O1 and Cu1-O2 are found to be 1.9045(14) and 1.9113(15), respectively, while the bond lengths of Cu1-N21 and Cu1-N52 are found to be 1.9838(16) and 1.9758(16), respectively. It is clear from the data that bond lengths of Cu-N bonds are greater than the bond lengths for Cu-O bonds in the complex. After the complexation with Cu^{II} the bond lengths O1-C5 and O2-C36 of the ligands were increased from 1.254(2) to 1.275(2) and 1.278(2), respectively. The bond lengths N21-C13 and N52-C44 of the ligands were decreased from 1.339(3) to 1.315(3) and 1.320(3), respectively. The bond lengths N21-C22 and N52-C44 of the ligands were increased from 1.426(3) to 1.447(3) and 1.440(3), respectively.

Table 2.8. Selected bond lengths and bond angles.

Cu1-O1	1.9045(14)	**O2-C36**	1.278(2)
Cu1-O2	1.9113(15)	**N21-C13**	1.315(3)
Cu1-N21	1.9838(16)	**N52-C44**	1.320(3)
Cu1-N52	1.9758(16)	**N21-C22**	1.447(3)
O1-C5	1.275(2)	**N52-C44**	1.440(3)
O1-Cu1-O2	142.87(7)	**Cu1-O2-C36**	122.1(2)
N21-Cu-N52	149.32(8)	**Cu1-N21-C13**	125.7(1)
O1-Cu1-N21	95.70(7)	**Cu1-N52-C44**	126.3(4)
O1-Cu1-N52	93.92(7)	**C13-N21-C22**	119.1(2)
O2-Cu1-N52	94.93(7)	**C44-N52-C53**	118.9(2)
O2-Cu1-N21	94.77(7)	**Cu1-N21-C22**	115.1(1)
Cu1-O1-C5	121.7(1)	**Cu1-N52-C53**	114.6(1)

The bond angles C13-N21-C22 and C44-N52-C53 of ligands were decreased from 127.6(2) to 119.1(2) and 118.9(2), respectively, after complexation with copper(II). The bond angle N21-Cu1-N52 (142.87(7)) is greater than the bond angle O1-Cu-O2 (149.32(8)). Ligands L^1 exists in the amine-one form in solid state and in complex it exists in imine-ol form (*see* Figure 2.20).

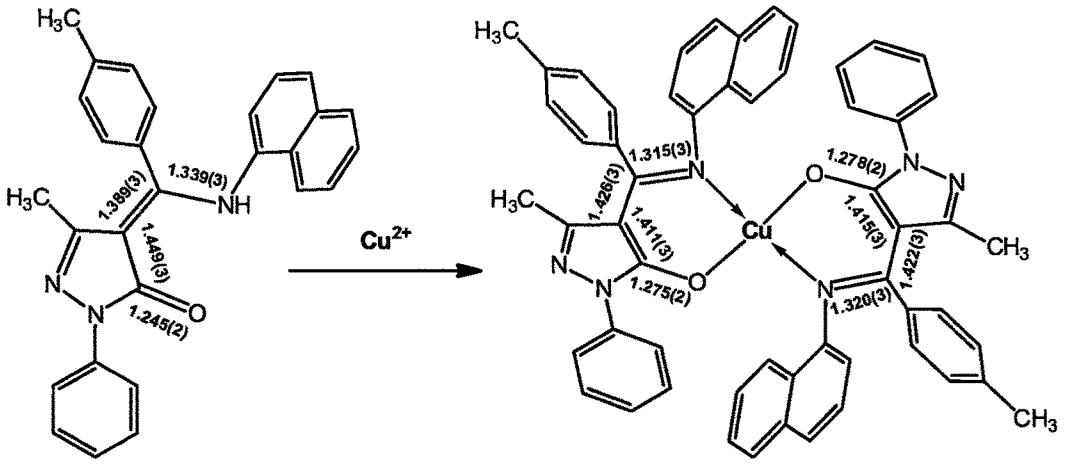


Figure 2.20. Bond distances of L^1, before and after complexation with Cu(II).

2.3.2. ^{1}H NMR study of the ligands

The synthesized ligands were characterized by the ^{1}H NMR spectra in $CDCl_3$. All the spectra are in good agreement with the proposed structure of the ligands.

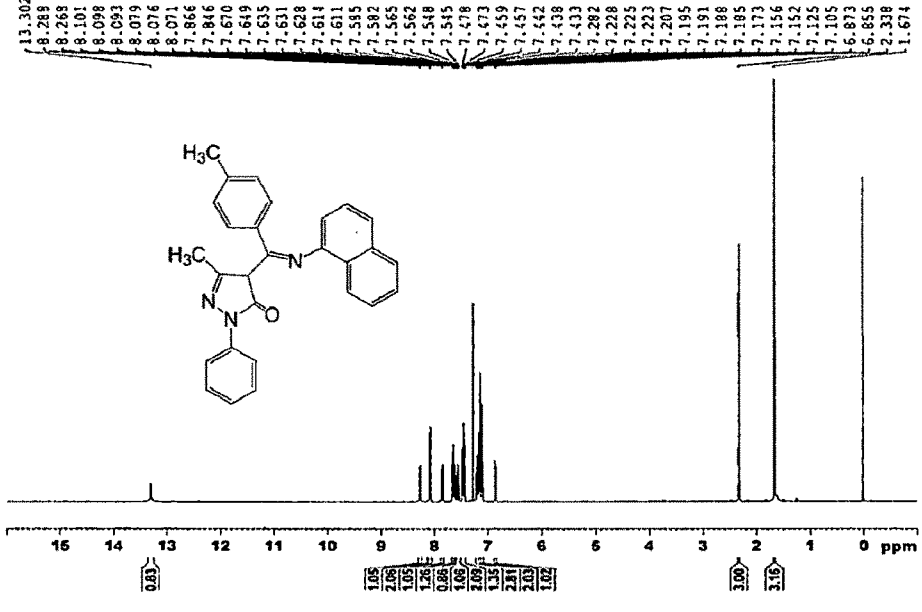


Figure 2.21. ^{1}H NMR spectrum of the ligand L^1.

In the spectra of ligands L^1, L^2 and L^3 two, three and two singlet appeared for the methyl proton, respectively. Due to the aryl protons of naphthalene and two phenyl rings doublets, overlapped doublet and multiplet were observed in the region 6.8-8.3 δ. All the ligands are showing singlets at 13.3, 13.31 and 13.19 δ correspond to the -NH proton, which shows all the ligands exist in the amine-one form in the solution state in non-polar solvents. ^{1}H NMR spectrum of the ligand L^1 is illustrated in the Figure 2.21.

2.3.3. FT-IR spectral studies

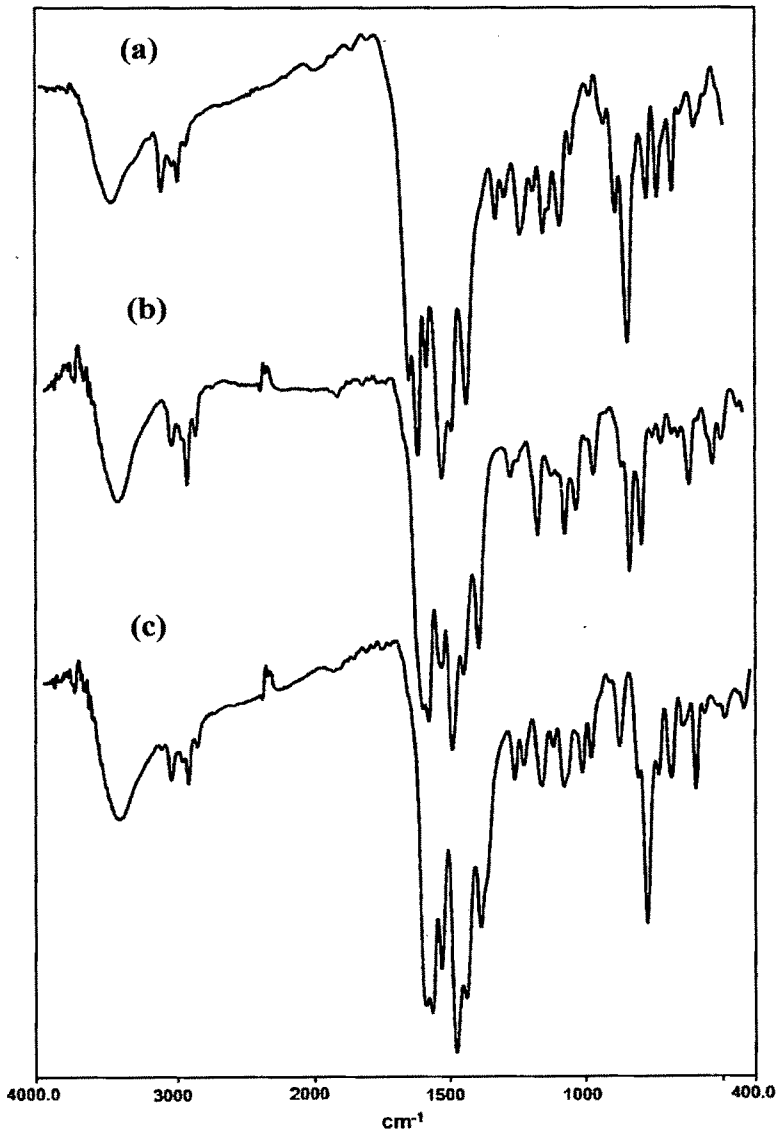


Figure 2.22. IR spectra of (*a*) complex $[Cu(L^1)_2(H_2O)_2]$, (*b*) complex $[Cu(L^2)_2(H_2O)_2]$ and (*c*) complex $[Cu(L^3)_2(H_2O)_2]$.

FT-IR spectra of ligands exhibits the bands within the range 1580-1590 cm^{-1} which can be assign to $\upsilon_{C=N}$ (cyclic). All the complexes shows absorption in 1560-1570 cm^{-1} shifted to lower wavelength which is due to the interaction with metal ion. The complexes show the absorption within 3420-3450 cm^{-1} which can be assigned to the coordinated water molecules. The complexes show bands within the range 585-595 cm^{-1} and 470-490 cm^{-1} due to the υ_{M-N} and υ_{M-O}. FT-IR spectra of the Cu(II) complexes is depicted in the Figure 2.22.

2.3.4. Mass spectral studies

The mass spectra of Schiff base ligands were in good agreement with the proposed structures. Schiff base L^1 shows molecular ion peak at *m/z*= 417.08 with a relative intensity near to 70% which is equal to its molecular mass (Figure 2.23). The other peaks appeared in the mass spectrum (abundance range 1-100%) are attributed to the fragmentation of ligand molecule obtained from the rupture of different bonds inside the molecule.

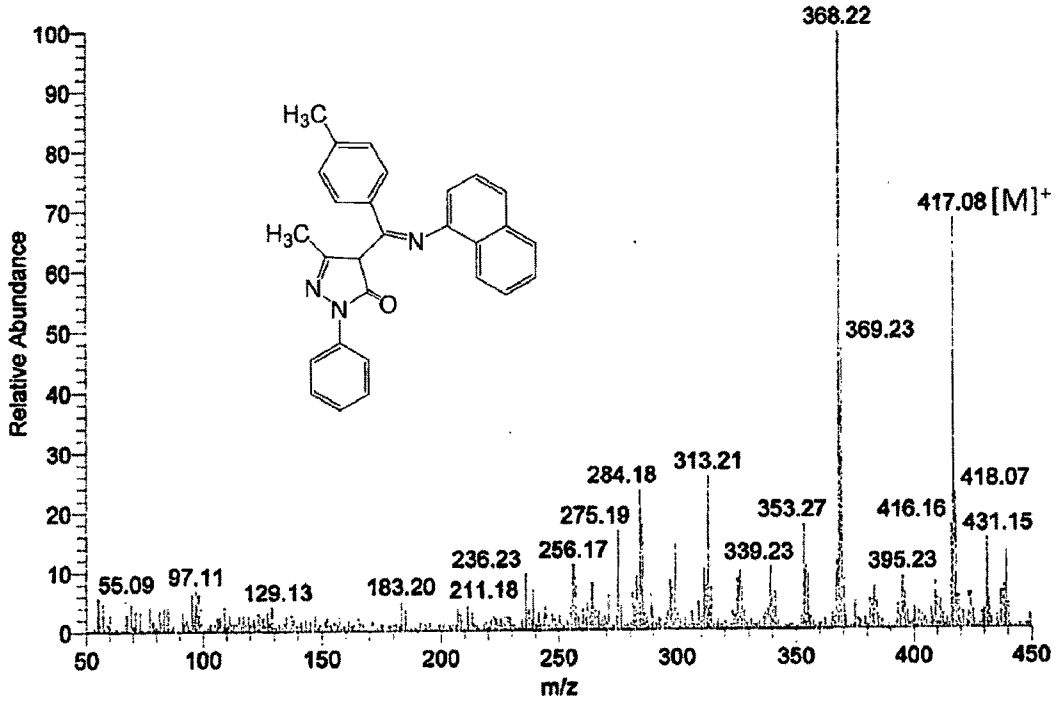


Figure 2.23. ESI-MS of the ligand L^1.

ESI-Mass spectra of complexes $[Cu(L^2)_2(H_2O)_2]$ and $[Cu(L^3)_2(H_2O)_2]$ were recorded. Complex $[Cu(L^2)_2(H_2O)_2]$ shows molecular ion peak *m/z*= 925.6 $[M+H]^+$,

926.6[M+2H]$^+$ and base peak at m/z= 432.3. The base peak is attributed to the ligand L^2 (M^++1). Complex $[Cu(L^3)_2(H_2O)_2]$ shows molecular ion peak m/z= 967.5 $[M+2H]^+$ and base peak at m/z= 452.2. The base peak is attributed to the ligand L^3 $[M+H]^+$. Mass spectra of both the complexes are well agreed with the proposed structures of the complexes. Fragmentation of weakly coordinated water molecule/ion in ESI mass spectra is not unlikely. To confirm the presence of weakly coordinating H_2O molecules in the complexes, we carried out thermogravimetric analyses of complexes. Mass spectrum of the complex $[Cu(L^2)(H_2O)]$ is depicted in the Figure 2.24.

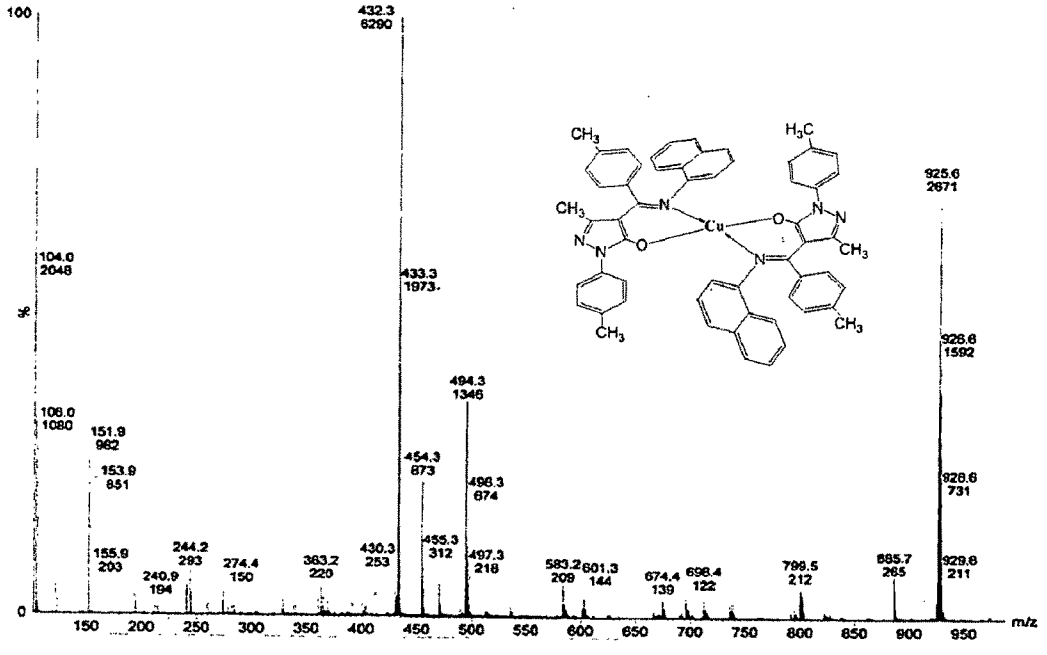


Figure 2.24. ESI-MS of the complex $[Cu(L^2)(H_2O)]$.

2.3.5. Electronic spectral studies

Electronic spectra of all the complexes were recorded in DMF. For octahedral Cu(II) complexes, the expected transition is $^2B_{1g} \rightarrow {}^2A_{1g}$ with respective absorption at 500–700 nm. Due to Jahn–Teller (J-T) distortions, Cu(II) complexes give a broad absorption between 600 and 700nm. All the complexes under this study exhibit a broad band in the region of 590–680 nm (Figure 2.25). Absorption coefficients were found to be 863, 832 and 859 (in nm) for the complexes $[Cu(L^1)_2(H_2O)_2]$, $[Cu(L^2)_2(H_2O)_2]$ and $[Cu(L^3)_2(H_2O)_2]$, respectively. The electronic spectral data are summarised in Table 2.9.

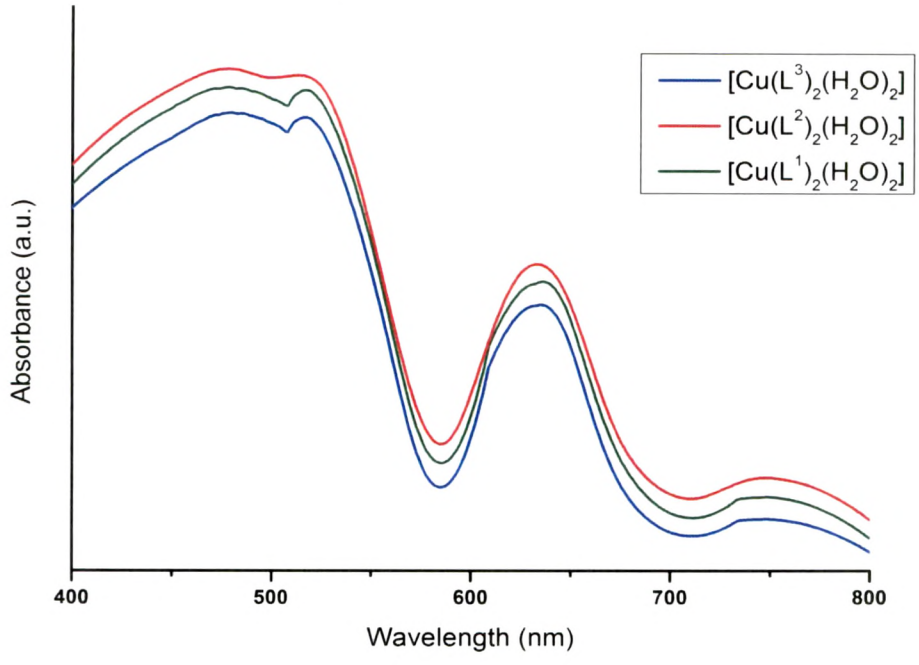


Figure 2.25. UV-Vis spectra of Cu(II) complexes.

Table 2.9. UV-Vis data of the complexes **1-3**.

Cu(II) complexes	UV-Vis data (in nm)
Complex $[Cu(L^1)_2(H_2O)_2]$	462 (LMCT), 623 ($d \rightarrow d$), 727 ($d \rightarrow d$)
Complex $[Cu(L^2)_2(H_2O)_2]$	471 (LMCT), 618 ($d \rightarrow d$), 725 ($d \rightarrow d$)
Complex $[Cu(L^3)_2(H_2O)_2]$	485 (LMCT), 624 ($d \rightarrow d$), 729 ($d \rightarrow d$)

2.3.6. EPR spectral studies

The full range (3200 – 2000 G) X-band EPR spectra for the copper complexes (frozen liquid state and room temperature solid state) were recorded. The EPR spectrum of the complex **2** in liquid nitrogen temperature is shown in Figure 2.26. The EPR spectrum of the metal complex provides information about hyperfine and super hyperfine structures, which is important in the study of the metal-ion environment in

the complexes, i.e., the geometry, the nature of the ligating sites from the ligand of the metal, and the degree of covalency of the metal-ligand bonds.

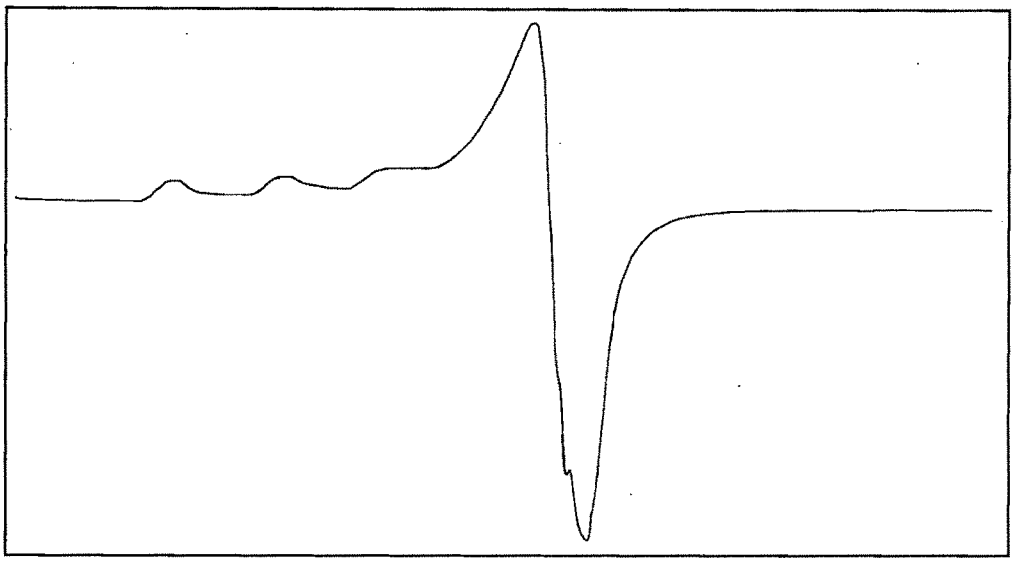


Figure 2.26. EPR spectrum of complex $[Cu(L^2)_2(H_2O)_2]$ at liquid nitrogen temperature.

The EPR spectra of all the complexes shows typical four line pattern which suggest that single copper is present in the molecule, i.e. it is mononuclear. X-band EPR spectra were recorded in DMF for all the complexes. The *g*-values and *A*-values were computed from the spectra using TCNE free- radical as *g* marker. EPR spectral data are included in Table 2.10.

Table 2.10. EPR spectral data of the Cu(II) complexes.

Complex	$g_{\parallel}$	$g_{\perp}$	g_{av}	$A_{\parallel}$	$A_{\perp}$	A_{av}
$[Cu(L^1)_2(H_2O)_2]$	2.307	2.336	2.326	140	11.6	38.9
$[Cu(L^2)_2(H_2O)_2]$	2.319	2.371	2.354	77.5	28	7.16
$[Cu(L^3)_2(H_2O)_2]$	2.319	2.343	2.335	150	8.3	44.4

2.3.7. Thermogravimetric analysis

The synthesized copper complexes were found to be air stable and have higher thermal stability. The thermal study was carried out using the thermogravimetric technique with a heating rate of 10 °C min^{-1}. The experimental results (Table 2.11) revealed that the degradation occurred in multiple stages. Up to 200 °C mass loss is not observed indicating the absence of lattice water molecule in the complexes. The complexes slowly started to decompose within the range of 200-350 °C, corresponds to the loss of coordinated water molecules. In the temperature range 350-600 °C degradation due to pyrolysis of the ligand molecule is observed. In the temperature range 600–800 °C the mass loss is due to the pyrolysis of another ligand molecule. The final product of the thermal decomposition CuO was determined by elemental analysis. TG-DTA thermograms of the complexes $[Cu(L^1)_2(H_2O)_2]$, $[Cu(L^2)_2(H_2O)_2]$ and $[Cu(L^3)_2(H_2O)_2]$ are depicted in the Figure 2.27.

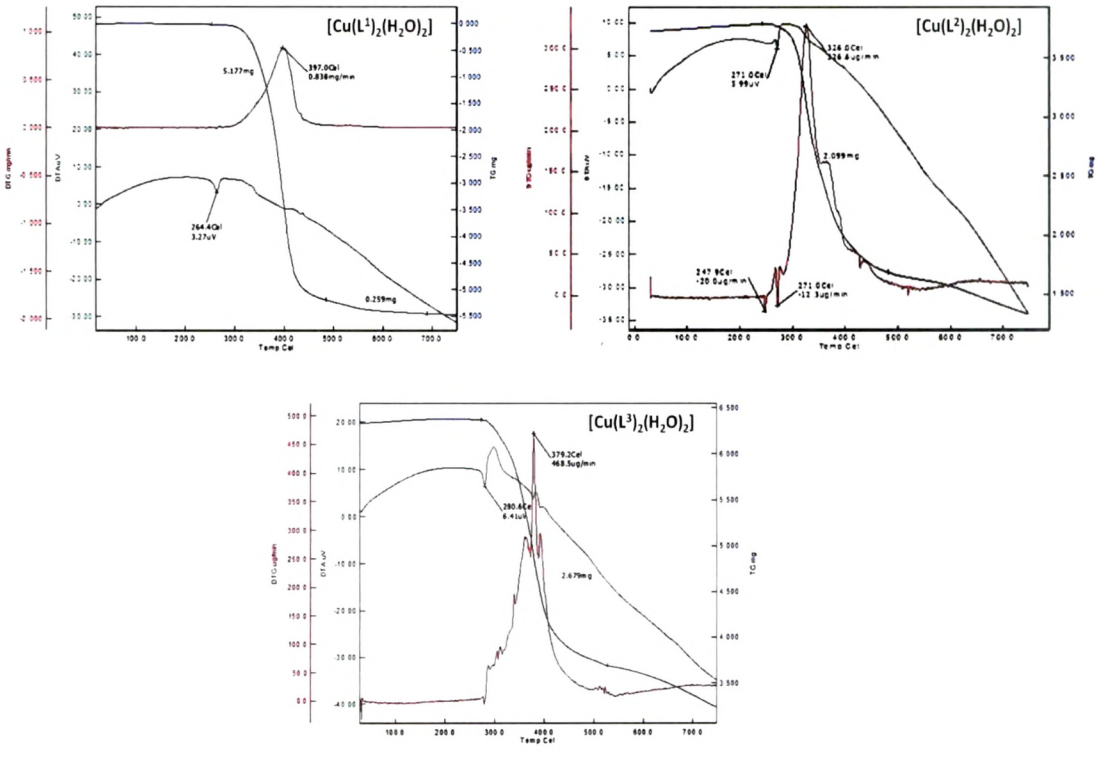


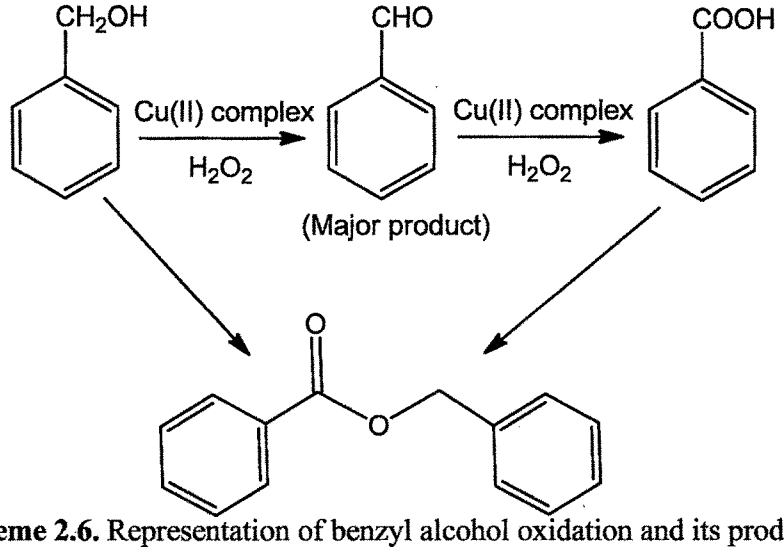
Figure 2.27. TG-DTA and DTG thermograms of copper complexes.

Table 2.11. Thermal analysis data of Cu(II) complexes.

Complexes	TGA range (^{0}C)	DTA	DTG	Mass loss(%) obs.(calcd.)	Assignments
$[Cu(L^1)_2(H_2O)_2]$	200-350	264	391	3.85(3.86)	Loss of two coordinated water molecules
	350-600			44.65(44.66)	Loss of one L^1 ligand
	600-800			8.53	Remaining CuO residue
$[Cu(L^2)_2(H_2O)_2]$	200-350	271	326	3.93(3.90)	Loss of two coordinated water molecules
	350-600			45.2(45.25)	Loss of one L^2 ligand
	600-800			(8.63)	Remaining CuO residue
$[Cu(L^3)_2(H_2O)_2]$	200-350	280	379	3.70(3.70)	Loss of two coordinated water molecules
	350-600			44.98(44.98)	Loss of one L^3 ligand
	600-800			(8.18)	Remaining CuO residue

2.3.8. Catalytic activity studies

2.3.8.1. Oxidation of benzyl alcohol using Cu(II) complexes



Scheme 2.6. Representation of benzyl alcohol oxidation and its products.

The oxidation of benzyl alcohol, catalyzed by Cu(II) complexes was carried out using H_2O_2 as an oxidant to give benzaldehyde, benzoic acid and benzyl benzoate as products. The formation of all these products is represented by Scheme 2.6. These are common products and have been identified by others as well [26].

The oxidation of benzyl alcohols was carried out in solvent free condition. The reaction conditions were adopted from the part-1 of the chapter-1. Thus, the optimum condition for the maximum % conversion as well as selectivity for the oxidation of benzyl alcohol to benzaldehyde is reaction temperature (90 °C), benzyl alcohol (10 mmol), 30% H_2O_2 (30 mmol), catalyst amount (0.045 mmol) and reaction time (24 h) The progress of the reaction was monitored by GC-MS analysis and products formed in the reactions were matched with those reported in the literature.

Table 2.12. Catalytic activity of Cu(II) complexes towards the oxidation of benzyl alcohol.

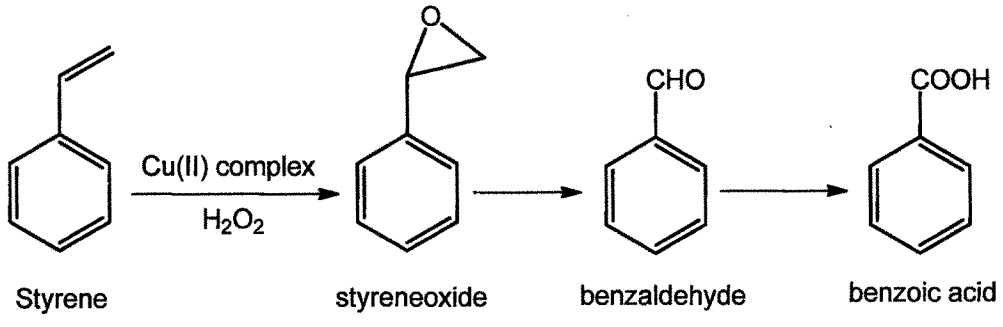
Complex	Substrate	Product	%Conversion of benzyl alcohol	%Selectivity of benzaldehyde	TON
$[Cu(L^1)_2(H_2O)_2]$	Benzyl alcohol	Benzaldehyde	80	90	229
$[Cu(L^2)_2(H_2O)_2]$	Benzyl alcohol	Benzaldehyde	86	87	240
$[Cu(L^3)_2(H_2O)_2]$	Benzyl alcohol	Benzaldehyde	83	89	246

The objective of the present study was to compare the reactivity of synthesized copper complexes for the oxidation of benzyl alcohol. Thus, all three complexes were used as a catalyst for the oxidation of benzyl alcohol under the same reaction conditions. From the reaction data (Table 2.12) we could observe that the complex $[Cu(L^2)_2(H_2O)_2]$ shows 86% conversion in compare to complexes $[Cu(L^1)_2(H_2O)_2]$ and $[Cu(L^3)_2(H_2O)_2]$ which show 80% and 83% conversion. The complex $[Cu(L^1)_2(H_2O)_2]$ shows 90% selectivity for the benzaldehyde, while the complex

$[Cu(L^2)_2(H_2O)_2]$ and $[Cu(L^3)_2(H_2O)_2]$ shows 87% and 89% selectivity for the benzaldehyde.

2.3.8.2. Oxidation of styrene using Cu(II) complexes

The oxidation of styrene, catalyzed by Cu(II) complexes was carried out using H_2O_2 as an oxidant to give benzaldehyde, styreneoxide and benzoic acid as products. The formation of all these products is represented by Scheme 2.7. These are common products and have been identified by others as well [27]. However, benzaldehyde was characterized as the major oxidation product in the present case. The oxidation of benzyl alcohols was carried out in solvent free condition. The reaction conditions were adopted from the part-1 of the chapter-1. In the present case, styrene (10 mmol), 30% H_2O_2 (30 mmol) and catalyst (20 mg) were taken in a 50 ml round-bottom flask and the reaction mixture was heated at 80 °C for 24 h. After completion of the reaction the products were extracted in the hexane. % Conversion, % selectivity and turn-over number are presented in the Table 2.13. Complexes $[Cu(L^1)_2(H_2O)_2]$, $[Cu(L^2)_2(H_2O)_2]$ and $[Cu(L^3)_2(H_2O)_2]$ are showing 37, 59 and 41% conversion, respectively.



Scheme 2.7. Representation of styrene oxidation and its products.

The complexes $[Cu(L^1)_2(H_2O)_2]$, $[Cu(L^2)_2(H_2O)_2]$ and $[Cu(L^3)_2(H_2O)_2]$ show 100, 90 and 97% selectivity for the benzaldehyde. The results reveals that complex $[Cu(L^2)_2(H_2O)_2]$ shows better conversion of styrene as compare to other two complexes, but shows only 90% selectivity for benzaldehyde. Whereas, complex $[Cu(L^1)_2(H_2O)_2]$ less conversion of styrene, but shows 100% selectivity for the benzaldehyde.

Table 2.13. Catalytic activity of Cu(II) complexes towards the oxidation of styrene.

Complex	Substrate	Product	% Conversion of styrene	% Selectivity of benzaldehyde	TON
$[Cu(L^1)_2(H_2O)_2]$	Styrene	Benzaldehyde	37	100	118
$[Cu(L^2)_2(H_2O)_2]$	Styrene	Benzaldehyde	59	90	189
$[Cu(L^3)_2(H_2O)_2]$	Styrene	Benzaldehyde	41	97	137

2.4. Conclusions

In summary, three new Schiff bases of 4-acylpyrazolone were synthesized and characterized by various spectroscopic and analytical techniques. The structures of the synthesized Schiff bases were determined by single-crystal X-ray diffraction and found to be exists in amine-one form in the solid state. These Schiff bases were used to synthesize three new copper complexes, which were characterized by spectroscopic and analytical techniques. The evidences from FT-IR, TG-DT analysis, elemental analysis and UV-Vis spectroscopy suggested a distorted octahedral environment around the copper through coordination of two *N,O*-chelating Schiff bases ligands and two coordinated water molecule. The single crystal X-ray analysis of complex 1 reveals that after heating the acetonitrile solution of complex **1**, coordinated water molecules got eliminated and one acetonitrile molecule was entered in the crystal lattice. Thus, after crystallization the geometry of the complex changes from an octahedral geometry to square planer geometry. The synthesized Cu(II) complexes were used as homogeneous catalysts for the solvent free oxidation of styrene and benzyl alcohol. The complexes were found to be successful in the oxidation of styrene and benzyl alcohol to benzaldehyde under mild reaction conditions.

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Synthesis and crystal structure of a series of pyrazolone based Schiff base ligands and DNA binding studies of their copper complexes

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ABSTRACT

PMP (5-methyl-4-(4-methyl-benzoyl)-2-phenyl-2,4-dihydro-pyrazol-3-one), PTPMP (5-methyl-4-(4-methyl-benzoyl)-2-p-tolyl-2,4-dihydro-pyrazol-3-one) and MCPMP (2-(3-Chloro-phenyl)-5-methyl-4-(4-methyl-benzoyl))-2,4-dihydro-pyrazol-3-one) were synthesized and used for the synthesis of Schiff base ligands. Schiff base ligands were characterized by FT-IR, ^{1}H NMR, Mass and single crystal X-ray analysis. Cu(II) complexes of synthesized ligands were prepared and characterized by elemental analysis, FT-IR, TGA–DTA, UV–Visible, ESI mass and ESR spectroscopy. On the basis of analytical and spectroscopic techniques, distorted octahedral geometry of the complexes was proposed. The interaction of Cu(II) complexes with CT-DNA was investigated by Absorption titration, Viscosity and fluorescence spectroscopy. Results suggest that the synthesized complexes bind to DNA via an intercalative mode and can quench the fluorescence intensity of EB bound to DNA.

1. Introduction

Pyrazolone and its derivatives form an important class of compounds and have attracted considerable scientific and applied interest. Pyrazolones especially, Acylpyrazolones are an interesting class of β-diketone compounds which are widely used as solvent extractions of metal ions, laser working materials and NMR shift-reagents [1–3]. The 4-acyl-pyrazolone derivatives are broadly used in many fields, especially in biological, clinical and analytical applications [4–7].

The interest in the coordination chemistry of pyrazolones has increased greatly in the last decade [8]. Due to the presence of two oxygen donor atoms and facile keto–enol tautomerism, they easily coordinate with metal ions after deprotonation of the enolic hydrogen and provide stable metal complexes with six-membered chelate rings. Pyrazolones are used in analytical chemistry for the determination and isolation of almost all metal ions due to their high extracting ability, intense color of the complex extracts and low solubility of the complex in some solvents [9].

The well-known Cu(II) ion forms a series of coordination compounds with well defined structures. It plays an important role in the numerous biological processes that involve electron transfer reactions or the activation of some anti-tumor substances [10]. In addition, 4-acyl pyrazolones can form a variety of Schiff bases and are reported to be superior reagents in biological, clinical and analytical applications [11,12]. Investigations on copper complexes to probe nucleic acids are becoming more prominent in the research area of bioinorganic chemistry [13–15]. Studies pertaining to DNA cleavage by synthetic reagents are of considerable interest because of their utility tools in molecular biology. This has resulted in the development of both sequence specific DNA cleavers [16] and DNA foot printing agents [17].

In our previous work, a series of Schiff base of 4-acylpyrazolone derivatives and their transition metal complexes have been reported [18,19]. In this paper, our group has focused much on synthesizing new Schiff bases of 4-acyl pyrazolone derivatives (see Scheme 1), studying on their crystal structures, synthesis of their transition metal complexes and also studying their DNA binding activities. In this present paper we are reporting the binding studies of Cu(II) complexes with CT-DNA by UV–Visible, fluorescence spectroscopy and viscosity measurements.

2. Experimental

2.1. Materials and physical measurements

All reagents and solvents were purchased from commercial sources and were further purified by the standard methods, if necessary [20]. Pyrazolones were obtained from Nutan Dye Chem. Sachin, Surat. Copper acetate and naphthylamine were purchased from Loba Chem., Mumbai. Disodium salt of calf thymus DNA (highly polymerized), purchased from Sigma, was stored at 4 °C and used as received. The stock solution of DNA was prepared by

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