



SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL STUDIES OF N'-((5-CHLORO-3-METHYL-1-PHENYL-1H-PYRAZOL-4YL) METHYLENE SCHIFF'S BASE LIGANDS AND THEIR TRANSITION METAL COMPLEXES

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ABSTRACT:

Divalent transition metal complexes of Co, Ni and Cu with substituted N'-((5-chloro-3-methyl-1-phenyl-1H-pyrazol-4yl) methylene Schiff's base ligands have been synthesized and characterized by elemental analyses, FT-IR, UV-Vis, ¹H NMR, ¹³C NMR, mass spectra, molar conductance and thermal gravimetric analysis. The Job's continuous variation method spectrophotometrically and elemental analysis results in data show the stoichiometry of synthesized complexes as 1:2[M: L] ratio. The IR spectral data suggest that this ligand behaves as monobasic bidentate ligands with NO donor atoms toward the metal ion. The complexes have been assigned a square planar geometry around the metal ion. The metal complexes have significant antibacterial and antifungal activity comparable with the parent ligand. The antioxidant activities of these complexes were determined by DPPH and hydrogen peroxide (H₂O₂) scavenging activity. The Cu complexes have a more promising antioxidant activity than their free parent ligand.

KEYWORDS- Schiff's base ligands, divalent metal complexes, antibacterial, antifungal, and antioxidant activity.

INTRODUCTION-

Schiff bases are condensation products of primary amines with carbonyl compounds and they were first reported by Schiff¹ in 1864. The common structural feature of these compounds is the azomethine group with a general formula RHC=N-R1, where R and R1 are alkyls, aryl, cycloalkyl, or heterocyclic groups which may be variously substituted. These compounds are also known as anils, imines, or azomethines. Schiff bases are generally excellent chelating agents^{ii-iv} especially when a functional group like -OH or -SH is present close to the azomethine group to form five or six-membered rings with the metal ion. The versatility of Schiff base ligands and biological, analytical, and industrial applications of their complexes make further investigations in this area highly desirable,^{v-vi} Schiff bases resulting from aromatic aldehydes ortho-substituted with a hydroxyl group have initially aroused the

researchers' interest because of their ability to act as bidentate ligands for transitional metal ions^{vii-viii} Schiff bases have been reported for their biological properties, like, antibacterial, antifungal activities^{ix-xi} Their metal complexes have been widely studied because they have anticancer and herbicidal applications^{xii-xiii} They serve as models for biologically important species. Schiff bases derived from pyrazole-4-carbaldehyde shows antimicrobial and anti-inflammatory agents.

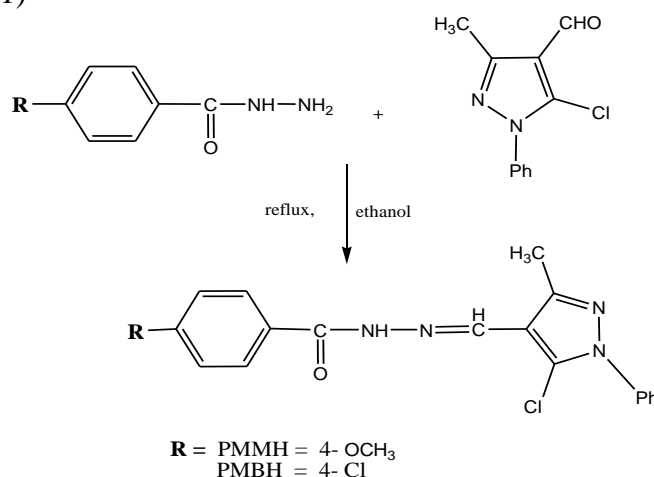
This paper presented here, 5-chloro pyrazole-4-carbaldehyde Schiff's base ligand was synthesized by condensation of 5-chloro-3-methyl-1-phenyl-pyrazole-4-carbaldehyde with different substituted amines. Its coordination behavior with divalent Co (II), Ni (II), and Cu (II) ions was studied and the synthesized compounds were screened for their evaluation of the biological activity.

Material and Methods

The elemental contents were carried out on Thermo- scientific (FLASH 2000) analyzer. The IR spectrum was recorded on Perkin Elmer - Spectrum RX-IFTIR spectrometer. The UV-Vis spectrum was taken on a Shimadzu UV-1800 spectrophotometer. The ¹H & ¹³C NMR spectral data were recorded on Bruker Advance NEO, 500 MHz NMR spectrometer. The mass spectrum was carried out on Waters micro mass Q-TOF. The stoichiometry ratio of complexes is determined by Job's method. Magnetic susceptibility carried on Sherwood scientific Cambridge UK. Thermogravimetric studies were carried out in the temperature range RT-650 °C on a TGA 55, TA instrument, USA. The molar conductance was carried out on CM model ELICO, 162 conductivity cells.

Synthesis and characterization of Ligands

The synthesis of ligands is similar to the previous literature method^{xiv-xv} the following ligand has been prepared earlier by D. Kaushik et al. and is taken from reference^{xvi}. The ethanolic solution of 5-chloro-3-methyl-1-phenyl pyrazole-4-carbaldehyde (0.01 mmol) was added dropwise into the ethanolic solution of 4-methoxybenzohydrazide (0.1mol) for **PMMH** and 4-chlorobenzohydrazide (0.1mol) for **PMBH**. Add 10% NaOH was added and reflux with stirring for 3 hrs. The reaction progress was monitored by TLC. Solid Precipitated compound was filtered, washed, and recrystallized from ethanol. It was dried into the vacuum desiccator. (Scheme 1)



Scheme1. Synthesis of ligands (PMMH and PMBH)

PMMH

Yield 88.4 % ; m. p. 203°C; White solid; Anal. Calcd for C₁₉H₁₇ClN₄O₂, Calcd. (%):C, 61.87; H, 4.65; N, 15.19. Found (%): C, 61.36; H, 4.72; N, 14.90. FT-IR (cm⁻¹): 1609(C=O), 1572(C=N), 1461, 1253, 1181(N-N), 1033, 950, 839, 761, 695, 502. ¹H NMR (500 MHz, DMSO-d₆, δ ppm):11.66 (s, 1H, -NH), 8.47 (s, 1H, N=C-H), 7.91-7.93 (d, 2H, Ar-H), 7.49-7.61 (m, 5H, Ph, Ar-H), 7.06-7.07 (d, 2H, Ar-H), 3.84 (s, 3H,-OCH₃), 3.4 (s, 3H,-OCH₃). ¹³C NMR (125 MHz, DMSO-d₆, δ ppm): 183.98, 162.02, 161.88, 148.24, 139.18, 137.20, 136.42, 132.57, 129.19, 128.55 127.0, 125.14, 125.32, 124.38, 113.6, 113.22, 55.33, 14.25. Mass (ESI) [M⁺] = 369.2 amu.

PMBH

Yield 85 % ; m. p. 211°C; yellow solid; Anal. Calcd for C₁₈H₁₇Cl₂N₄O₂ Calcd. (%): C, 57.92; H, 3.78; N, 15.09. Found (%): C, 57.76; H, 3.92; N, 15.21. FT-IR (cm⁻¹): 1611(C=O), 1565(C=N), 1494, 1353, 1144(N-N) 1094, 1012, 845, 690, 538. ¹H NMR (500 MHz, DMSO-d₆, δ ppm): 11.83 (s, 1H, -NH), 8.47 (s, 1H, N=C-H), 7.95-7.96 (d, 2H, Ar-H), 7.56-7.62 (m, 5H, Ph, Ar-H), 7.49-7.52 (d, 2H, Ar-H), 2.50 (s, 3H,-CH₃). ¹³C NMR (125 MHz, DMSO-d₆, δ ppm): 161.46, 148.29, 140.11, 137.13, 136.40, 135.31, 132.05, 131.26, 129.33, 129.16, 128.55, 128.45, 127.53, 127.24, 124.80, 113.01, 14.26. Mass (ESI) [M⁺] = 373.12 amu.

Synthesis characterization of Co (II), Ni (II), and Cu(II) complexes with ligands.

The general procedure for the synthesis of complexes was similar to the previous literature method ^{xvii-xviii}. The (CoCl₂.6H₂O, 2 mmol), nickel (II), (NiCl₂.6H₂O, 2 mmol), and (CuCl₂.2H₂O, 2 mmol) were dissolved in water and slowly added with the solution of ligand PMMH and PMBM (1 mmol) in 20 mL of ethanol. Refluxed this mixer for 2-3 h and obtain precipitated filter and dry in desiccator using CaCl₂. (Scheme 2)

Co (PMMH)₂

Yield 86.9 %; off white solid; FT-IR (cm⁻¹): 1642(C=O), 1594(C=N), 1408, 1136(N-N), 930, 824, 761, 581(M-N), 480(M-O). Λ_M (Ω⁻¹ cm² mol⁻¹):10.2; μ_{eff} (B.M.): 1.9, [M: L] 1:2, Mass (ESI) [M⁺] = 793 amu.

Ni (PMMH)₂

Yield 82.2 %; light greenish blue; FT-IR (cm⁻¹): 1628(C=O), 1587(C=N), 1408, 1373, 1154(N-N) 1007, 822, 761, 586(M-N), 498(M-O). Λ_M (Ω⁻¹ cm² mol⁻¹):11.8; μ_{eff} (B.M.): diamagnetic, [M: L]: 1:2, Mass (ESI) [M²⁺] = 797.9 amu.

Cu (PMMH)₂

Yield 78.9 %; light green; FT-IR (cm⁻¹): 1605(C=O), 1580(C=N), 1400, 1365, 1185(N-N) 1039, 976, 837, 740, 586(M-N), Λ_M (Ω⁻¹ cm² mol⁻¹):14.3; μ_{eff} (B.M.):1.9, [M: L]: 1:2, Mass (ESI) [M²⁺] = 800.3 amu.

Co (PMBH)₂

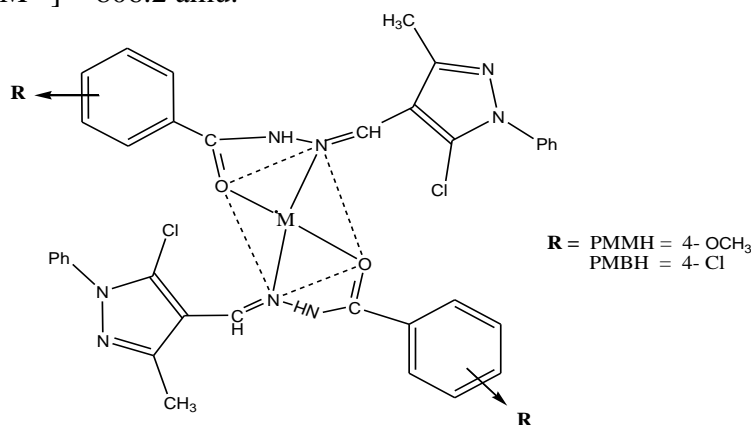
Yield 81.9 %; off white; FT-IR (cm⁻¹): 1621(C=O), 1572(C=N), 1436, 1270, 1121(N-N) 1034, 823, 666, 545(M-N). Λ_M (Ω⁻¹ cm² mol⁻¹):2.1; μ_{eff} (B.M.):2.0, [M: L]: 1:2, Mass (ESI) [M²⁺] = 799.1 amu.

Ni (PMBH)₂

Yield 91.4 %; greenish blue; FT-IR (cm⁻¹): 1604(C=O), 1578(C=N), 1414, 1384, 1122(N-N) 1014, 822, 683, 598(M-N), 470(M-O). Λ_M ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$): 19.7; μ_{eff} (B.M.): diamagnetic, [M: L]: 1:2, Mass (ESI) [M⁺²] = 801.9 amu.

Cu (PMBH)₂

Yield 90.6 %; light blue; FT-IR (cm⁻¹): 1608(C=O), 1560(C=N), 1414, 1384, 1143(N-N) 1011, 815, 690, 601(M-N), 477(M-O). Λ_M ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$): 14.5; μ_{eff} (B.M.): 1.6, [M: L]: 1:2, Mass (ESI) [M⁺²] = 806.2 amu.



Scheme 2. Proposed structure for Co(II), Ni(II) and Cu(II) complexes.

RESULTS AND DISCUSSION

The condensation of 5-chloro-3-methyl-1-phenyl pyrazole-4-carbaldehyde with 4-methoxybenzohydrazide and 4-chlorobenzohydrazide into ethanol to obtain solid the Schiff base ligands PMMH and PMBH. These ligands form complexes with metal ions, Co (II), Ni (II), and Cu (II). These complexes are colored solids, stable at room temperature. The metal contents were analyzed by the gravimetric method^{xix}. These complexes behave as non-electrolytes as indicated by their low molar conductance [Λ_M] values^{xx-xxi}. The metal complexes are soluble in methanol, ethanol, chloroform, DMSO, and DMF.

IR spectral studies

The FT-IR spectrum of the free ligand, PMMH, and PMBH show characteristic bands at 1609-1611 cm⁻¹ assignable to $\nu(\text{C}=\text{O})$. At the time of complexation with metal ions and subsequent coordination of the oxygen, this absorption band is changed means it shows upward or downward shifting of $\nu(\text{C}=\text{O})$ at 1605-1642 cm⁻¹ suggesting the coordination of oxygen to the metal ion^{xxii-xxiii}. The change in position in the absorption band suggested that the metal ions combine with ligand to form complex to get result vibration spectra expected to change their bond position as upward or downward shifting. This resulting data of bond upward or downward shifting during formation and coordination sites between the ligands and the metal ions is mentioned in Table-1.

Table 1. IR spectrum data of ligands and their complexes

Compounds	$\nu(\text{C=O})$	$\nu(\text{C=N})$
PMMH	1609	1572
Co(PMMH) ₂	1642	1594
Ni(PMMH) ₂	1624	1587
Cu(PMMH) ₂	1605	1580
PMBH	1611	1565
Co(PMBH) ₂	1621	1572
Ni(PMBH) ₂	1604	1578
Cu(PMBH) ₂	1608	1560

Also its free ligand, PMMH, and PMBH show characteristic bands at 1565-1572 cm^{-1} corresponding to $\nu(\text{C=N})$ of functional group $>\text{C=N-N}<$. This absorbance band observed at 1560-1594 cm^{-1} is shifted to upward or downward shifting wave numbers in all the FT-IR spectra of the complexes and appeared in the region 1650–1675 cm^{-1} , showing nitrogen to metal ions^{xxiv-xxvi}. For all the Co (II), Ni (II), and Cu (II) metal complexes, the $\nu(\text{C=N})$ band is change the position suggesting the coordination of nitrogen atom from ligand the center metal atom. This change in the band position can be related to molecular individual frequency. In this present study, the coordination of the nitrogen is supported by the appearance of a metal-ligand band at 545-586 cm^{-1} due to $\nu(\text{M-N})$ into all Co (II), Ni (II) and Cu (II) complexes^{xxvii-xxviii}. Also give the additional support for the formation of the metal complexes is provided by the presence of bands at 470-480 cm^{-1} which are attributed to the formation of $\nu(\text{M-O})$ through the oxygen. Hence based on the IR spectrum, the ligands act as monobasic bidentate ligands in the complexes.

UV–Visible absorption studies

Table 2. UV-Visible spectral data of ligands and their complexes

Compounds	Wavelength (λ_{max} , nm) in DMF (10^{-4}M)
PMMH	205 $\pi-\pi^*$, 296 $n-\pi^*$
Co(PMMH) ₂	206 $\pi-\pi^*$, 303 $n-\pi^*$
Ni(PMMH) ₂	208 $\pi-\pi^*$, 310 $n-\pi^*$
Cu(PMMH) ₂	207 $\pi-\pi^*$, 305 $n-\pi^*$
PMBH	230 $\pi-\pi^*$, 300 $n-\pi^*$
Co(PMBH) ₂	236 $\pi-\pi^*$, 296 $n-\pi^*$
Ni(PMBH) ₂	238 $\pi-\pi^*$, 306 $n-\pi^*$
Cu(PMBH) ₂	240 $\pi-\pi^*$, 324 $n-\pi^*$

The UV–Visible spectrum of Schiff base ligands, PMMH and PMBH shows the absorption bands at near 205-230 nm assigned to $\pi-\pi^*$ transitions of the aromatic rings present in their structure. This absorption band changes the position after the coordination with metal ions^{xxix}. Also, the absorption band near at the 296-310 nm may be assigned to $n-\pi^*$ transition of

the -C=N- of functional group $>C=N-N<$ ^{xxx}. Due to the coordination with nitrogen to the metal ions, these bands are seen in the absorption spectra of all complexes at 303-324. The $n-\pi^*$ transition of the -C=N- of functional group $>C=N-N<$ are masked by the strong charge-transfer transition bands which can be accepted in coordination with these metal ions with Schiff base ligands to change the position and height of absorption peak^{xxx1}.

Magnetic moments of complexes

Magnetic moment values provide information about the structure and stereochemistry of metal complexes. The Co (II) complexes having 1:2 (metal: ligand) stoichiometry may be tetrahedral or low spin square planar when the ligand behaves bidentate in coordination^{xxxii}. In the present studies, the magnetic moment value of Co (PMMH)₂ and Co (PMBH)₂ complexes was lies between low 1.9-2.0 B.M. which behave are square planar paramagnetic^{xxxiii}. The Ni (II) complexes show diamagnetic in nature. This diamagnetic nature of Ni (PMMH)₂ and Ni (PMBH)₂ complexes give the evidence for their in square planar geometry around the metal ion,^{xxxiv}. The magnetic moment values of Cu (PMMH)₂ and Cu (PMBH)₂ complexes in range fall 1.9 BM which is indicative of a square planar geometry around the metal ion^{xxxv}. Based on magnetic moment value, the Co (II) and Cu (II) complexes are paramagnetic while Ni (II) complexes show diamagnetic and suggest the mainly square planar geometry in a complex structure.

¹H NMR spectral studies

The ¹H NMR spectra are recorded in DMSO-d₆. The ¹H NMR spectrum of synthesized ligands PMMH and PMBH show signals at 11.66 – 11.83 ppm are attributed to -NH proton, signals observed at 7.49-7.62 ppm for N=C-H proton. The singlets at 7.47-7.62 ppm represent aromatic region Ar-H. Fig.1 shows the ¹H-NMR spectrum of PMMH. These all the position of signals in ¹H- NMR spectra of ligands in full agreement with their proposed structure. The results data of ¹H NMR spectral data of ligands are shown in Table 3.

Table 3. ¹H-NMR (δ , ppm) chemical shifts of ligand PMMH and PMBH

Compound	Singlets (ppm)		
	-NH	N=C-H	Ph, Ar-H, (5H)
PMMH	11.66	8.47	7.49-7.61
PMBH	11.83	8.47	7.56-7.62

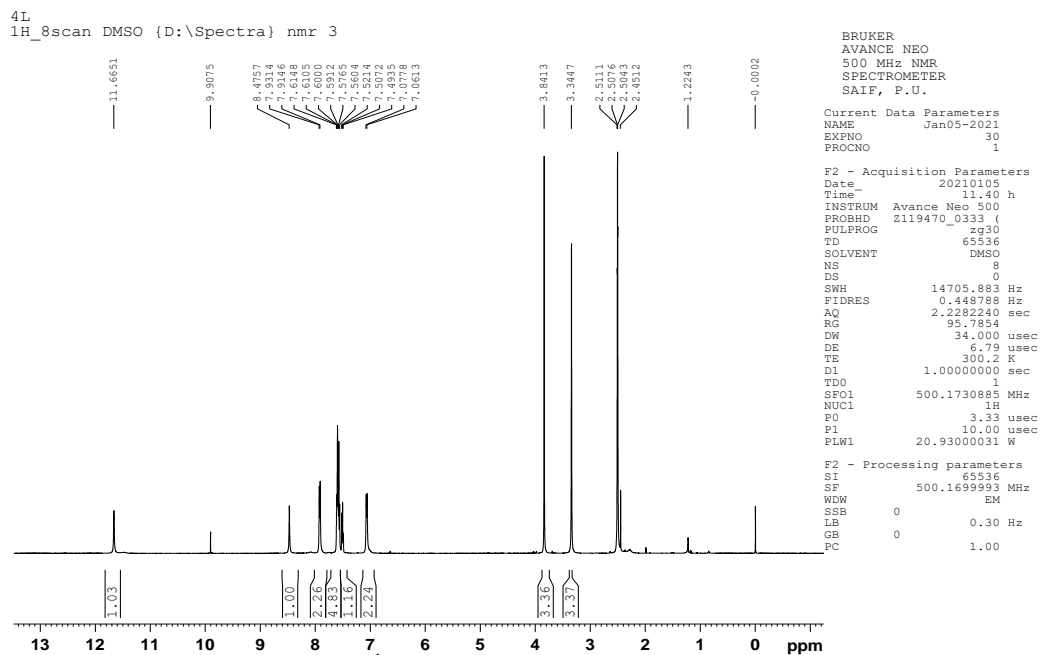


Fig.1. ¹H-NMR spectrum of PMMH

¹³C-NMR spectral studies

The ¹³C-NMR spectra signals are responsible to the total number of carbon atoms present in their structure. The ¹³C-NMR spectral data of PMMH and PMBH shows signal at 161-162 ppm corresponding to N=C-H carbon in synthesized ligand. The synthesis compounds give the signal at 14.25-14.26 ppm corresponding to -CH₃ respectively. Fig.2 is shows ¹³C-NMR spectrum of PMBH. These NMR spectral data support the authenticity of the expected structures.

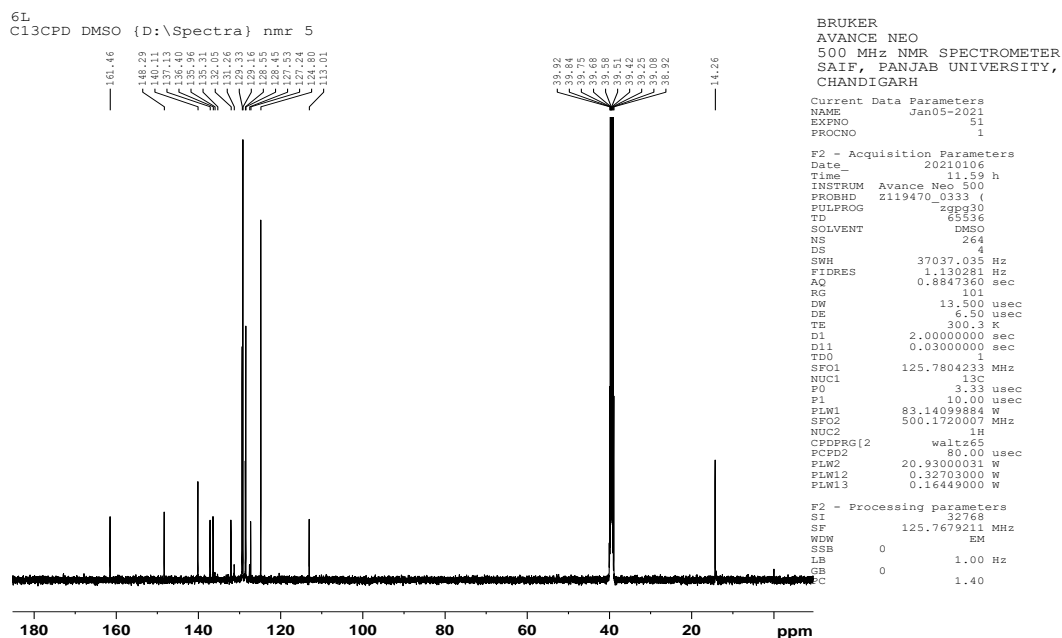


Fig.2. ¹³C-NMR spectrum of PMBH

Mass spectral studies

The ESI mass spectra of the ligands and their divalent metal complexes are recorded at room temperature were used to compare their stoichiometry composition. The Schiff base ligand

PMMH showed a molecular ion peak at 369.2 amu. While their copper complex Cu (PMMH)₂ give shows the molecule ions peak observed at 800.3 amu confirms the stoichiometry of metal chelates as ML₂ type. It is also supported by the mass spectra of other complexes. The experimental molecular weight from mass spectra is near to the expected molecular weight. Fig.3 is shows ESI-MS spectrum of PMBH.

Similarly, the ESI-MS mass spectrum of the ligand PMBH shows molecular ions at m/z = 373.12 amu [M⁺¹] corresponding to their molecular mass [C₁₈H₁₇Cl₂N₄O₂] ion. While after the coordination with metal ions, the ESI-MS of their CO(II), Ni(II) and Cu (II) complexes show molecular ion peaks at m/z = 799.1, 801.9 and 806.2 amu [M⁺] amu respectively which is equivalent to their molecular weight. The intensity of these peaks gives an idea of the stabilities of fragments.

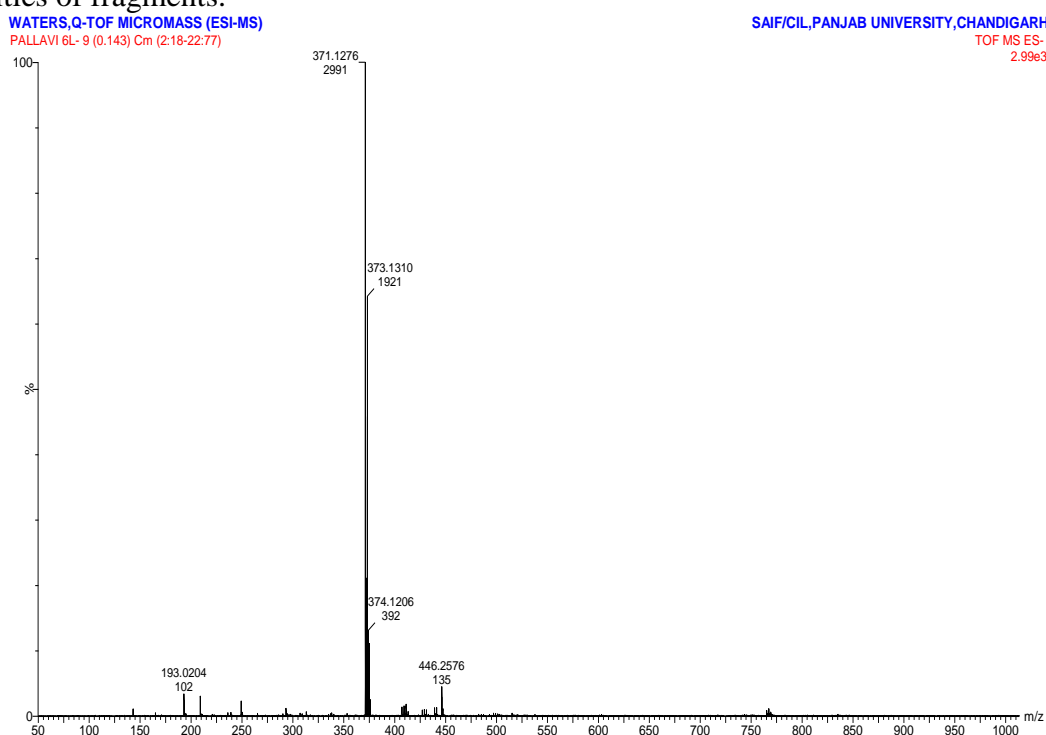


Fig.3. ESI-MS spectrum of PMBH

Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis value is compatible with the suggested geometry and structure of the molecule to get information about whether the coordinated chloride ion and lattice coordinated water molecules are present in the complex structure, ^{xxxvi}. The thermogram of Cu(PMBH)₂ complex shows the decomposition within the temperature range 100-450°C may be attributed to the loss of complex including ligand with a mass loss and leaving metal oxide CuO as residue. The total estimated mass loss is 90.1% (calculated mass loss = 90.9%).

Antimicrobial activity

The metal complexes and their free parent ligand were tested *in vitro* against by disc diffusion method and take a concentration 100 µg/ML, ^{xxxvii-xxxviii}. The aim objective of any antimicrobial compound is to inhibit the causal microbes without any side effects on patients. The ligand and their metal complexes were tested against different bacteria species: *S. aureus* and *E. coli*. Also, they were screened against fungal strain *A. flavus* and *C. albicans*. The biological activities of the ligand and their complexes were compared with those of the standards Ciprofloxacin as an antibacterial agent and Fluconazole as an antifungal agent. The

experimental data are presented in Table 4. These resulting data show that the metal complexes are more potent in inhibiting the growth of microorganisms than the free parent ligand which means that the metal complexes can have better action than the free parent ligand. Specially, the Cu complexes Cu (PMMH)₂ and Cu (PMBH)₂ show excellent antimicrobial activity (**Figure 4**). The variation in the antimicrobial activity of the divalent metal complexes against different species depends on the impermeability of the microorganism cells or on differences in ribosome of microbial cells^{xxxix}.

Table 4. Antimicrobial activity resulting data of ligand and complexes.

Compounds	Zone of inhibition (mm)			
	<i>S. aureus</i>	<i>E. Coli</i>	<i>A. flavus</i>	<i>C. albicans</i>
PMMH	-	-	-	-
Co(PMMH) ₂	-		-	-
Ni(PMMH) ₂	10	8	-	8
Cu(PMMH) ₂	20	23	17	21
PMBH	-	-	7	-
Co(PMBH) ₂	-	9	-	-
Ni(PMBH) ₂	-	-	11	6
Cu(PMBH) ₂	8	7	12	9
Ciprofloxacin	21	23	-	-
Fluconazole	-	-	19	22

- No antimicrobial activity

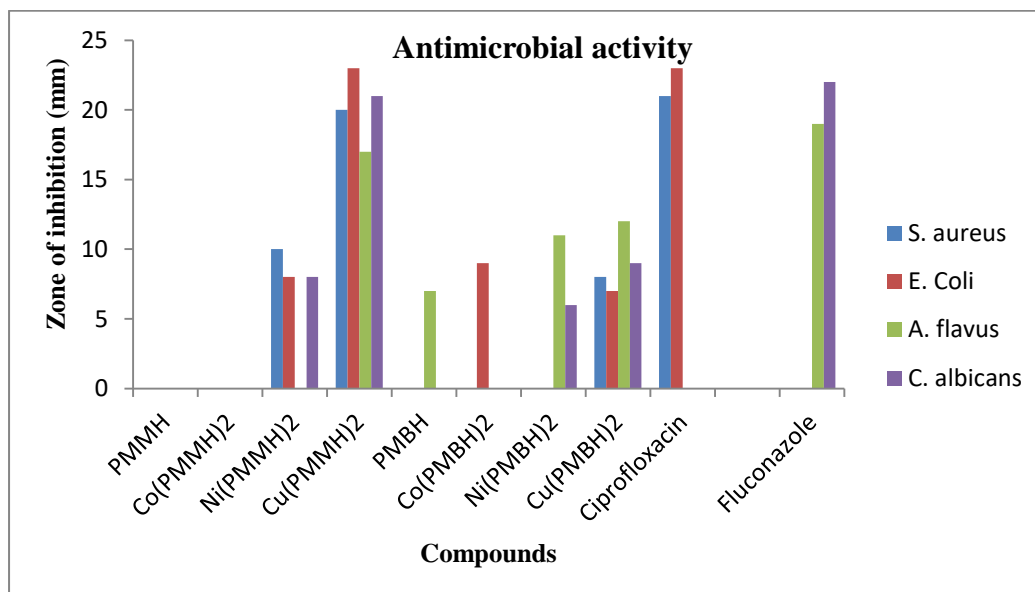


Figure.4. Antimicrobial Activity

Antioxidant activity

The antioxidant activities of these complexes were determined by DPPH and hydrogen peroxide (H₂O₂) scavenging activity^{XI-XII}.

DPPH radical scavenging activity

Percentage activity of methanolic solutions of N'-((5-chloro-3-methyl-1-phenyl-1H-pyrazol-4yl) methylene and their metal complexes were studied and compared mentioned in **Table 5**. On the basis of resulting data free ligand showed minimum DPPH activity, however upon complexation with metal ions (Co, Ni, and Cu) the activity was enhanced significantly. All the metal complexes showed comparable or less activity to that of standard Ascorbic acid. The copper complex Cu (PMMH)₂ and Cu (PMBH)₂ showed significantly higher DPPH activity followed by Nickel and Cobalt complex (**Figure 5**.)

Table 5. Antioxidant activity resulting data of ligand and complexes

Compounds	% Inhibition	
	DPPH	Hydrogen peroxide
PMMH	58.4	48.6
Co(PMMH) ₂	70.6	39.5
Ni(PMMH) ₂	72.4	49.5
Cu(PMMH) ₂	74.1	64.7
PMBH	28.8	14.2
Co(PMBH) ₂	48.5	21.8
Ni(PMBH) ₂	68.5	26.4
Cu(PMBH) ₂	65.6	40.2
Ascorbic acid	88.9	78.4

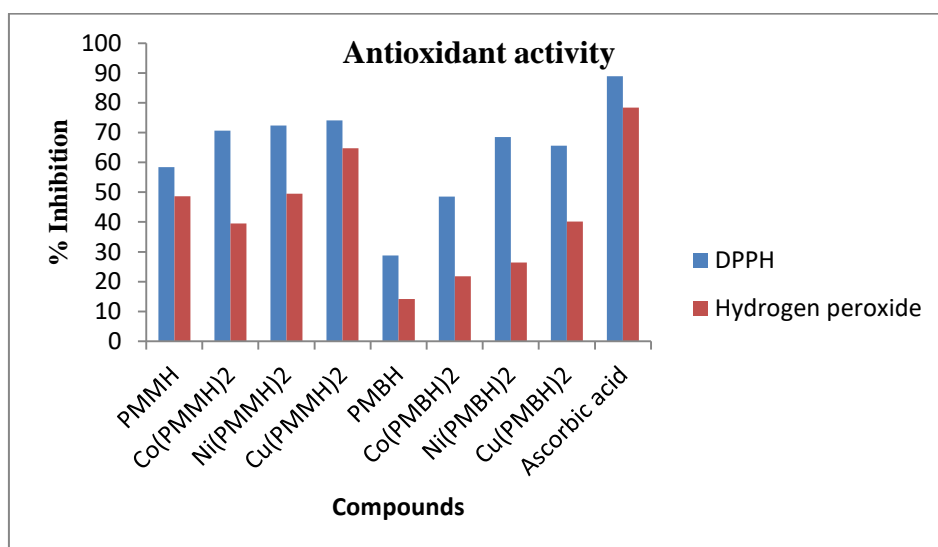


Figure.5. Antioxidant Activity

Hydrogen peroxide scavenging activity

We know that hydrogen peroxide is toxic and induces cell death in vitro. Hydrogen peroxide can attack many cellular energy-producing systems. The ability of N'-((5-chloro-3-methyl-1-phenyl-1H-pyrazol-4yl) methylene and their metal complexes were studied to scavenge hydrogen peroxide is mentioned in table 5. and the results were compared with standard ascorbic acid. The results showed that the free ligand and their metal complexes exhibited a mild to effective hydrogen peroxide scavenging activity. Specially, copper complexes Cu (PMMH)₂ show excellent antioxidant activity but less than standard.

Anti-inflammatory activity

The Anti-inflammatory activity data of Schiff base ligands and their metal complexes is summarized in Table 6. The synthesized Schiff base compounds were screened by using previously reported inhibition of the albumin denaturation method ^{XLi}. The PMMH shows good activity as compared to ligand PMBH. After the coordination of this ligand with metal ions, the anti-inflammatory activity is improved. The copper complexes, Cu (PMMH)₂ and Cu (PMBH)₂ showed significantly moderate activity as compared with free ligand but least as compared with standard aspirin (Figure 6). The free Schiff-based ligands show least or negligible anti-inflammatory activity.

Compounds	% Inhibition of Denaturation
PMMH	20.4
Co(PMMH) ₂	24.5
Ni(PMMH) ₂	38.2
Cu(PMMH) ₂	45.4
PMBH	3.4

Co(PMBH) ₂	12.5
Ni(PMBH) ₂	32.4
Cu(PMBH) ₂	42.1
Aspirin	87.2

Table 6. *In-vitro* anti-inflammatory activity data of ligands and their complexes

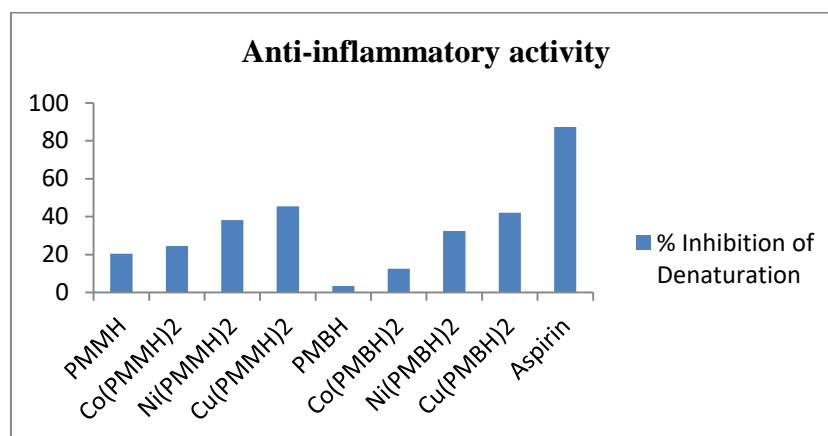


Figure.6. Anti-inflammatory Activity

CONCLUSIONS

The 5-chloro-3-methyl-1-phenyl pyrazole-4-carbaldehyde Schiff's base ligands have been prepared by condensation of 5-chloro-3-methyl-1-phenyl pyrazole-4-carbaldehyde and substituted amine. On the basis of IR spectra, the ligands behaviors is monobasic bidentate in the nature. The complexes show square planer geometry. Thermal analysis reveals thermally stable of metal complexes. The complexes are biologically active as compared to their parent free ligands. The metal complexes have significant antibacterial and antifungal activity comparable with the parent ligand. The Cu (II) complexes have a promising antioxidant activity than their free parent ligand.

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