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Synthesis, Characterization and Biological Evaluation of Schiff base Cu(II), Ni(II) and Co(II) Novel Macrocyclic Complexes Derived from Ethanebis (Thioamide) and 3,4-diphenyl-3H-pyrrole-2,5-Dicarbaldehyde Schiff Base Ligand

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Abstract

M(II) Schiff base macrocyclic complexes of the type [HLMX₂] where M = Cu(II), Ni(II), Co(II) and X = Cl, NO₃, OAc have been synthesized by condensation of ethanebis(thioamide) and 3,4-diphenyl-3H-pyrrole-2,5-dicarbaldehyde (2:2) in the presence of divalent metal salt in methanolic medium. The complexes have been characterized with the help of elemental analysis, conductance measurements, magnetic measurements and their structural configuration have been determined by various spectroscopic (electronic, IR, ¹H NMR, ¹³C NMR, GCMS) techniques. Electronic and magnetic moments of the complexes indicate that the geometries of the metal centers are octahedral. These metal complexes were also screened for their antifungal activities against some fungi viz. *Rizoctonia* sp., *Aspergillus* sp., and *penicillium* sp. to assess their inhibiting potential.

Keywords: Metal Complexes, Antifungal Activity, Spectroscopic Study, Ethanebis (Thioamide) and 3,4-Diphenyl-3H-Pyrrole-2,5-Dicarbaldehyde.

Introduction

Co-ordination chemistry is considered as an additional branch of chemistry for the purpose of study and research. New possibilities have arisen in practice and research due to advancement of structure elucidation techniques like IR, UV, NMR, EPR, X-ray mass spectroscopy, the magnetic susceptibility measurements and the development of ligand field theory and application of the group theory to co-ordination chemistry. A Schiff bases are typically formed by the condensation of a primary amine and an aldehyde/ketone. In which >C=O group is replaced by >C=N-R group. The resultant compound, R₁R₂C=NR₃, is called a Schiff base (named after Hugo Schiff) where R₁ is an aryl group, R₂ is hydrogen atom and R₃ is either an alkyl or aryl group. However usually compounds where R₃ is an alkyl or aryl group and R₂ is an alkyl or aromatic group are also regarded as Schiff bases. Schiff bases that contain aryl substituent are substantially more stable and more readily synthesized, while those which contain alkyl substituent are relatively unstable. Schiff bases of aliphatic aldehydes are relatively unstable and readily polymerizable [1]. While those of aromatic aldehydes having effective conjugation are more stable. [2]. Schiff bases are most widely used as chelating ligand in coordination chemistry. Schiff bases are bidentate (1), tridentate (2), tetradentate (3) or polydentate (4) ligands generally capable of forming very stable complexes with transition metals. They can only act as co-coordinating ligands if they bear a functional group, usually the hydroxyl sufficiently near the site of condensation in such a way that a five or six membered ring can be formed when reacting with a metal ion.

Review of Literature

Schiff bases are used, in many field e.g., inorganic, biological, and analytical chemistry [3-4], optical and electro-chemical sensor, as well as in various chromatographic methods, to enable detection of enhanced

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selectivity and sensitivity [5]. Among the organic reagent actually used Schiff bases, possess excellent characteristics, structural similarities with natural biological substances relatively simple preparation procedures and the synthetic flexibility that enables design of suitable structural properties. Complexes are a special class of compounds in which the central metal atom is surrounded by ions or molecules (called ligand) beyond their normal valency. In the modern terminology these compounds are called co-ordination compounds. Schiff bases and their structural analogues as ligating compounds containing acyclic and cyclic imine C=N bonds are of great importance in modern coordination chemistry [6]. The formation of complexes causes the d-orbitals to split into two energy sublevels, which enables many of the complexes to absorb specific frequencies of light. Thus the complexes form characteristic colored solution and compounds. Complication reactions some time enhance the relatively low solubility of some compound. So we can say that the transition metal has low ionization energies, positive oxidation states, very hard, high melting points, high boiling points, and high electrical conductivity, malleable. 5-d orbital's become more filled, from left to right on periodic table [7]. Heterocyclic compounds are widely distributed in nature and essential to many biochemical processes [8-10]. The compounds containing heterocyclic have important physiological properties ranging from anti-histamine, analgesic, anti-inflammatory, anti-hypertensive and anti-cancer. Such compounds are also used to model important bio-inorganic systems such as metalloproteinase and are finding applications as photosensitizers and catalysts [11, 12]. From the early days, the physiological properties of heterocyclic piperazines have generated interest since they are found to exert, even in small dosages, various physiological effects, including accelerated pulse, breathing and hypersensitivity to external stimuli.

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The relationship between metal ions and biological activity [13] of certain systems is obvious and a subject of great interest. It has been demonstrated through several studies that biologically inactive compounds become active and less biologically active compounds become more active [14-16] upon coordination / chelation with the some transition metal ions. The interaction between metal ions and such biologically active ligands represents an important route in designing new metal-based antibacterial and antifungal therapies against different kinds of bacteria and fungi, viruses that becomes resistant to the use of conventional drugs [17].

Many biologically important Schiff bases have been reported in the literature possessing antimicrobial, antibacterial, antifungal, antiinflammatory, anticonvulsant, antitumor and anti HIV activities [18-20]. Cu (II) complexes with Schiff base ligands are potential antitumor agents. We, therefore, thought it will be worthwhile to synthesize novel metal complexes with ligands like Schiff base and their biological study that could fight more aggressively against fungal strains.

Experimental

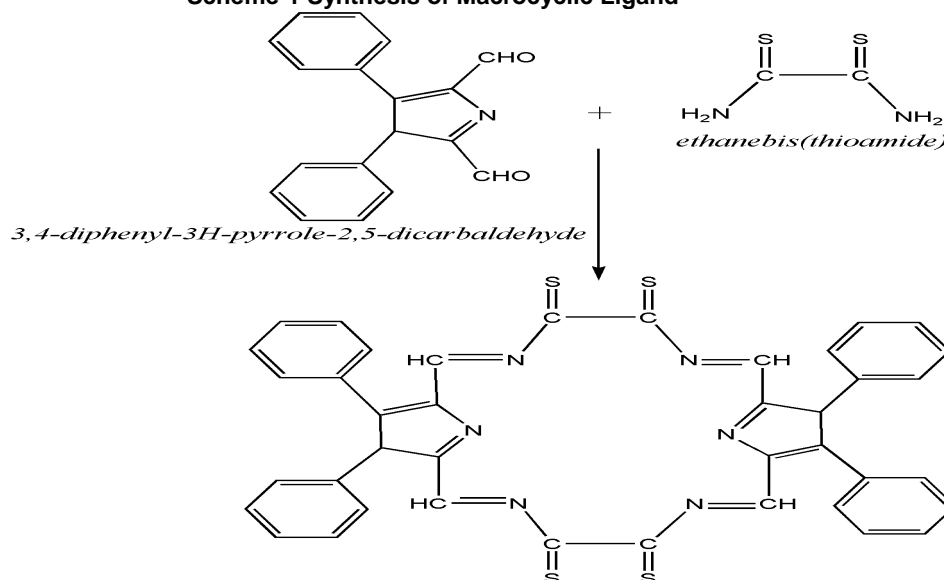
Reagents

The entire chemicals were used of the analytical grade, ethanebis (thioamide) and 3,4-diphenyl-3H-pyrrole-2,5-dicarbaldehyde purchased from S.D.-fine. Metal salts, HCl, CaCl₂, and C₂H₅OH were purchased from Merck.

Synthesis of Schiff base macrocyclic ligand

The macrocyclic Schiff base ligand have been synthesized by refluxing the reaction mixture of ethanebis(thioamide) (2 mmol) in ethanol (30 mL) and 3,4-diphenyl-3H-pyrrole-2,5-dicarbaldehyde (2 mmol) in ethanol (20 mL) for 6-8h with addition of 4-5 drops of concentrate HCl. The reaction mixture was filtered, washed with cold ethanol, dried under vacuum and recrystallized from hot ethanol (yield 55-60%, scheme 1).

Scheme-1 Synthesis of Macrocyclic Ligand



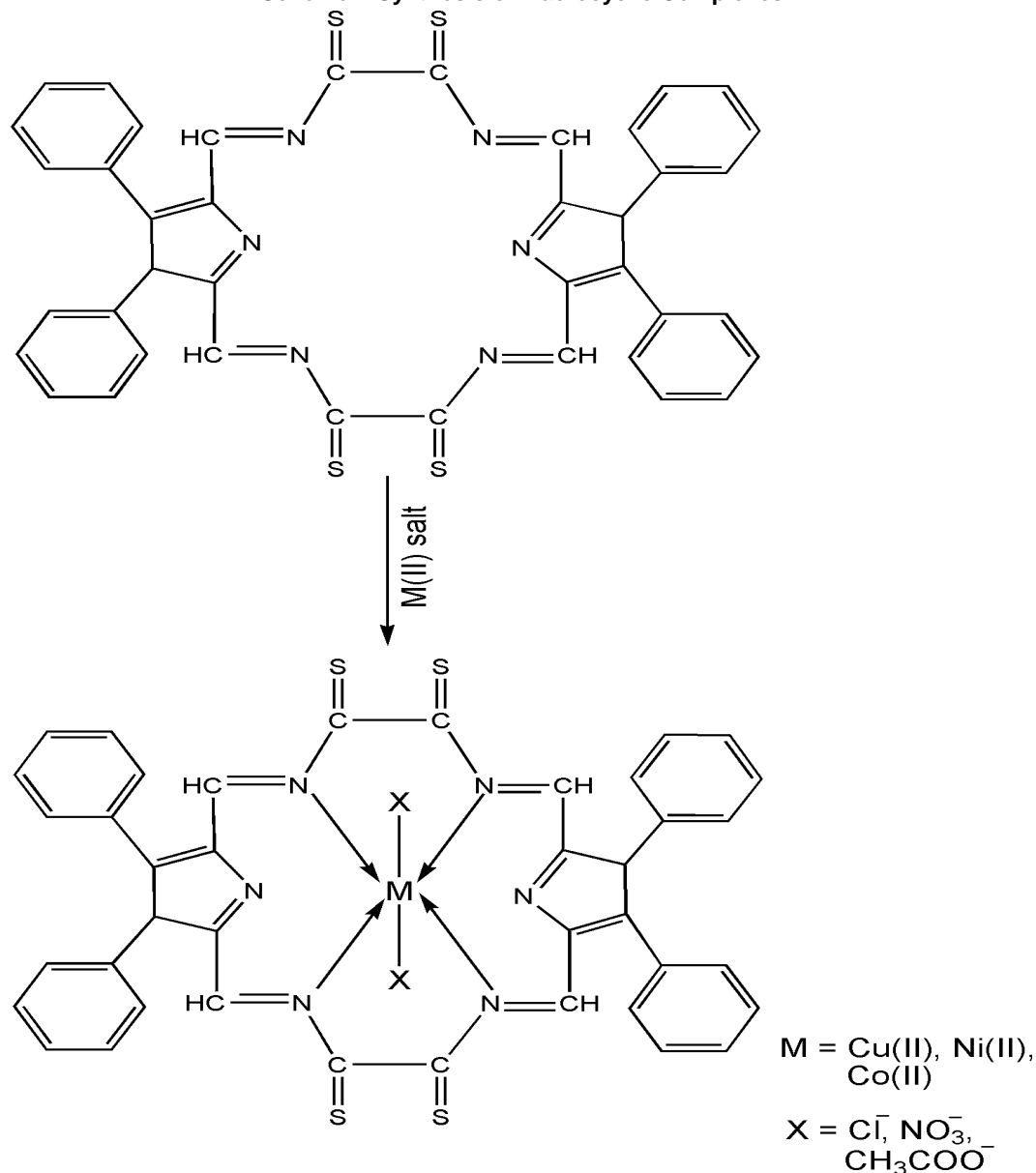
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Synthesis of Cu(II), Ni(II) and Co(II) Macrocyclic Complexes

A solution of divalent metal salt (1 mmol) in methanol (20 mL) was added to a hot solution (75 °C) of macrocyclic ligand in ethanol (40 mL) and the

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reaction mixture was refluxed for 8-10h. The complex were filtered, washed with water and recrystallised from ethanol and dried under vacuum over anhydrous CaCl_2 (yield 40-45%, scheme 2).

Scheme-2 Synthesis of Macrocyclic Complexes**Analytical and Physical Measurements**

The microanalysis of C, H, and N were estimated by elemental analyzer (Perkin Elmer 2400), at SAIF, CDRI, Lucknow, India and the metal contents of Cu (II), Ni (II) and Co (II) was determined using atomic absorption spectrophotometer Perkin Elmer 5000. (See Table I containing also some physical properties of the prepared compounds). The conductivity was measured on digital conductivity meter (HPG system, G-3001) in DMSO at room temperature. The magnetic susceptibility measurements were carried out on Vibrating Sample Magnetometer (Model PAR 155) at room temperature. Electronic spectra (in DMSO) were

recorded on a Hitachi 330 spectrophotometer (5815-32573 cm^{-1}). The IR spectra were performed using a FT-IR spectrophotometer Perkin Elmer 1650 in the range 4000–200 cm^{-1} using Nujol Mull. ^1H NMR and ^{13}C NMR spectra (at room temperature) (in DMSO-d_6) were recorded on a Bruker AVANCE II 300 DRX or average 400 DRX spectrometer with reference to Me_4Si (0.0 ppm). The FAB mass spectra (at room temperature) were recorded on VG-70-S mass spectrometer. The purity of the Schiff base and its M(II) complexes were confirmed also by TLC [microcrystalline cellulose (E. Merck) was used for the preparation of thin layer, complete separation was achieved with the solvent system acetone/conc.

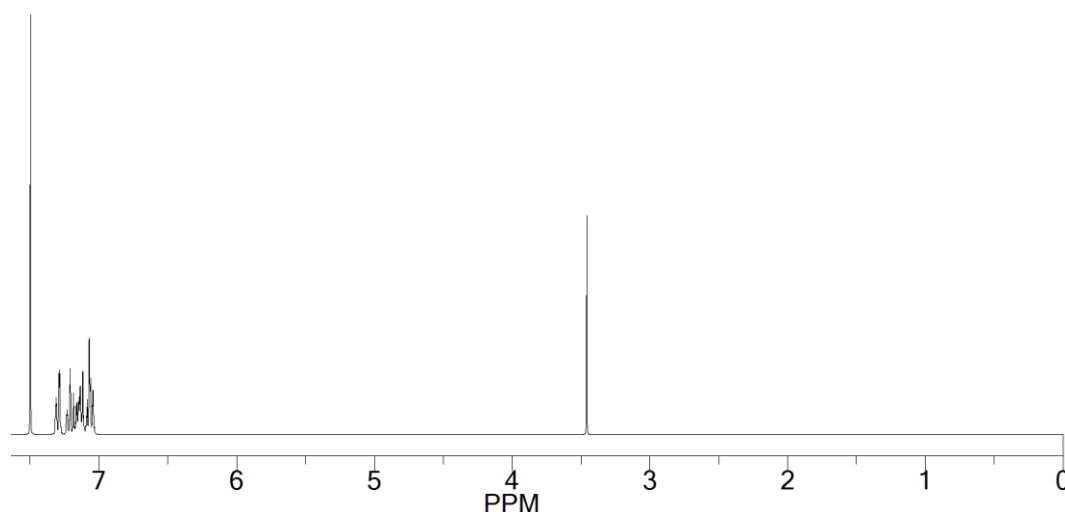


Table-1: FAB Mass Spectral Data of the Divalent Copper, Nickel and Cobalt Complexes

Complexes	Mol. wt.	Molecular ion peak $[M]^+$	Important peak due to complex fragmentation
$C_{40}H_{26}N_6S_4$	718.11	717.11	28.01, 44.97, 66.01, 69.98, 77.03, 88.94, 142.07, 168.06, 213.03, 218.10, 272.11, 360.07, 448.01, 577.15, 631.18
$[Cu(C_{40}H_{26}N_6S_4)Cl_2]$	850.97	849.97	28.01, 44.97, 66.01, 69.98, 77.03, 88.94, 142.07, 168.06, 213.03, 218.10, 272.11, 360.07, 448.01, 577.15, 631.18, 780.03, 815.00.
$[Cu(C_{40}H_{26}N_6S_4)(NO_3)_2]$	905.01	904.01	28.01, 44.97, 66.01, 69.98, 77.03, 88.94, 142.07, 168.06, 213.03, 218.10, 272.11, 360.07, 448.01, 577.15, 631.18, 780.03, 842.02
$[Cu(C_{40}H_{26}N_6S_4)(OAc)_2]$	899.06	898.06	28.01, 44.97, 66.01, 69.98, 77.03, 88.94, 142.07, 168.06, 213.03, 218.10, 272.11, 360.07, 448.01, 577.15, 631.18, 780.03, 839.05
$[Ni(C_{40}H_{26}N_6S_4)Cl_2]$	845.98	844.98	28.01, 44.97, 66.01, 69.98, 77.03, 88.94, 142.07, 168.06, 213.03, 218.10, 272.11, 360.07, 448.01, 577.15, 631.18, 775.04, 810.01
$[Ni(C_{40}H_{26}N_6S_4)(NO_3)_2]$	900.02	899.02	28.01, 44.97, 66.01, 69.98, 77.03, 88.94, 142.07, 168.06, 213.03, 218.10, 272.11, 360.07, 448.01, 577.15, 631.18, 775.04, 837.03
$[Ni(C_{40}H_{26}N_6S_4)(OAc)_2]$	894.05	893.05	28.01, 44.97, 66.01, 69.98, 77.03, 88.94, 142.07, 168.06, 213.03, 218.10, 272.11, 360.07, 448.01, 577.15, 631.18, 775.04, 834.05
$[Co(C_{40}H_{26}N_6S_4)Cl_2]$	846.98	845.98	28.01, 44.97, 66.01, 69.98, 77.03, 88.94, 142.07, 168.06, 213.03, 218.10, 272.11, 360.07, 448.01, 577.15, 631.18, 776.04, 811.02
$[Co(C_{40}H_{26}N_6S_4)(NO_3)_2]$	901.01	900.01	28.01, 44.97, 66.01, 69.98, 77.03, 88.94, 142.07, 168.06, 213.03, 218.10, 272.11, 360.07, 448.01, 577.15, 631.18, 776.04, 838.03
$[Co(C_{40}H_{26}N_6S_4)(OAc)_2]$	895.07	894.07	28.01, 44.97, 66.01, 69.98, 77.03, 88.94, 142.07, 168.06, 213.03, 218.10, 272.11, 360.07, 448.01, 577.15, 631.18, 776.04, 835.05

Antifungal Activity

The free ligand, its metal complexes, fungicide Micronazole and the control DMSO (dimethylsulfoxide) were screened for their antifungal activity against various fungi viz. *Rizoctonia* sp., *Aspergillus* sp., and *penicillium* sp. These species were isolated for the infected organs of the host plants on potato dextrose agar (potato 250g+dextrose 20g+agar 20g) medium. The culture of the fungi was purified by single spore isolation technique. The solution of different concentrations 10 μ g/ml of each compound (free ligand, its metal complexes and fungicides Miconazole) in DMSO was prepared for testing against spore germination [20, 21]. A drop of the solution of each concentration was kept separately on glass slides. The conidia, fungal reproducing spores (approx. 200) lifted with the help of an inoculating needle, which was mixed in every

drop of each compound separately. Each treatment was replicated thrice and a parallel DMSO solvent control set was also run concurrently on separate glass slide. All the slides were incubated in humid chambers at 25°C for 24 h. Each slide was observed under the microscope for spore germination and percent germination was finally calculated. The results were compared with a standard fungicide Micronazole at the same concentrations.

Result and Discussion**Mass Spectra**

The FAB mass spectra of Cu (II), Ni (II) and Co (II) Schiff base complexes have been recorded (table 2). The molecular ion (M^+) peaks obtained from various complexes are as follows: (1) $m/e = 717.11$ (Ligand), (2) $m/e = 849.97$ (complex 1), (3) $m/e = 904.01$ (complex 2), (4) $m/e = 898.06$ (complex 3), (5) $m/e = 844.98$ (complex 4), (6) $m/e = 899.02$ (complex

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5), (7) $m/e = 893.07$ (complex 6), (8) $m/e = 845.98$ (complex 7), (9) $m/e = 900.01$ (complex 8), (10) $m/e = 894.07$ (complex 9). This data is in good agreement with the proposed molecular formula for these complexes. In addition to the peaks due to the

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molecular ion, the spectra exhibit peaks assignable to various fragments arising from the thermal cleavage of the complexes. The peak intensity gives an idea of the stability of the fragments.

Table-2: Analytical Data of the Divalen Copper, Nickel and Cobalt Complexes

Complex	Mol. wt	C	H	N	M	Colour	Yield	Conductance Λ_M
$C_{40}H_{26}N_6S_4$	718.11	66.82 (66.80)	3.65 (3.64)	11.69 (11.68)				
$[Cu(C_{40}H_{26}N_6S_4)Cl_2]$	850.97	56.30 (56.27)	3.07 (3.06)	9.85 (9.83)	7.45 (7.42)	Orange	58%	$77 \Omega^{-1}$
$[Cu(C_{40}H_{26}N_6S_4)(NO_3)_2]$	905.01	53.00 (52.99)	2.89 (2.87)	12.36 (12.37)	7.01 (7.03)	Orange	62%	$79 \Omega^{-1}$
$[Cu(C_{40}H_{26}N_6S_4)(OAc)_2]$	899.06	58.68 (41.26)	3.58 (3.60)	9.33 (9.30)	7.06 (7.04)	Light Yellow	60%	$71 \Omega^{-1}$
$[Ni(C_{40}H_{26}N_6S_4)Cl_2]$	845.98	56.62 (56.60)	3.09 (3.08)	9.90 (9.88)	6.92 (6.90)	Brown	65%	$81 \Omega^{-1}$
$[Ni(C_{40}H_{26}N_6S_4)(NO_3)_2]$	900.02	53.28 (53.27)	2.91 (2.88)	12.43 (12.42)	6.51 (6.50)	Gray	67%	$88 \Omega^{-1}$
$[Ni(C_{40}H_{26}N_6S_4)(OAc)_2]$	894.05	59.00 (59.02)	3.60 (3.59)	9.38 (9.36)	6.55 (6.51)	Light gray	62%	$83 \Omega^{-1}$
$[Co(C_{40}H_{26}N_6S_4)Cl_2]$	846.98	56.60 (56.58)	3.09 (3.07)	9.90 (9.87)	6.94 (6.92)	Light Yellow	60%	$71 \Omega^{-1}$
$[Co(C_{40}H_{26}N_6S_4)(NO_3)_2]$	901.01	53.27 (53.25)	2.91 (2.92)	12.42 (12.40)	6.53 (6.52)	Reddish	64%	$72 \Omega^{-1}$
$[Co(C_{40}H_{26}N_6S_4)(OAc)_2]$	895.07	58.98 (58.96)	3.60 (3.59)	9.38 (9.37)	6.58 (6.56)	Light Yellow	66%	$74 \Omega^{-1}$

Infrared Spectra

The IR spectra provide valuable information regarding the nature of functional group attached to the metal atom. The presence of a single medium band in the region $3250\text{--}3330\text{ cm}^{-1}$ in the complexes may be assigned to N-H stretch [22]. It was noted that a pair of bands corresponding to $\nu(NH_2)$ at 3245 cm^{-1} and 3309 cm^{-1} are present in the spectra of the thiocarbohydrazide. The value of $\nu(C=N)$ stretching vibration is found lower ($1520\text{--}1560\text{ cm}^{-1}$) than the expected value ($1580\text{--}1650\text{ cm}^{-1}$). This lower value of $\nu(C=N)$ stretching may be explained on the basis of a drift of lone pair density of azomethine nitrogen towards the metal atom [23] indicating that coordination takes place through nitrogen of (C=N) groups. The bands present in the range $3020\text{--}3040\text{ cm}^{-1}$ may be assigned due to (C-H) stretching vibrations of benzil and naphthalene ring [24]. The C-N stretch in the range $1000\text{--}1300\text{ cm}^{-1}$. The band near 780 cm^{-1} in thiocarbohydrazide may be assigned as being due to free $\nu(C=S)$. The band at $3292\text{--}3438\text{ cm}^{-1}$ is due to the presence of OH group in the complexes. This band is also present in the spectra of all the complexes, which indicate that sulphur is not coordinating to the metal atom [25]. The far infrared spectra show bands in the region $420\text{--}450\text{ cm}^{-1}$ corresponding to $\nu(M-N)$ vibrations [26]. The presence of bands in all complexes in the region $420\text{--}450\text{ cm}^{-1}$ originates from the (M-N) azomethine vibrational modes and identifies coordination of azomethine nitrogen [27]. The bands present at $290\text{--}310\text{ cm}^{-1}$ may be assigned due to $\nu(M-Cl)$ vibrations [28].

The appearance of two characteristic bands in the ranges $1561\text{--}1559\text{ cm}^{-1}$ and $1370\text{--}1367\text{ cm}^{-1}$

in the case of complexes was attributed to $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$, respectively, indicating the participation of the carboxylate oxygen in the complexes formation. The mode of coordination of carboxylate group has often been deduced from the magnitude of the observed separation between the $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$. The separation value, $\Delta\nu(\text{COO}^-)$, between $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$, in these complexes were more than 190 cm^{-1} ($191\text{--}193\text{ cm}^{-1}$) [29].

¹H NMR

A survey of literature reveals that the NMR spectroscopy has been proved useful in establishing the structure and nature of many Schiff base ligand and their complexes. The ¹H NMR spectra of Schiff base ligand (Fig. 1) was recorded in d_6 -dimethylsulfoxide (DMSO- d_6) solution using Me_4Si (TMS) as internal standard. The ¹H NMR spectra of the ligand shows multiplets in the region $7.12\text{--}7.56\text{ ppm}$ may be assigned to aromatic proton [29, 30].

¹³C NMR of the Schiff base ligand, the signal appeared in the region $113\text{--}158$ are assigned to aromatic carbon. The signal at $198.3\text{--}185.6$ and $182.8\text{--}171.2$, are due to C=S and C=N respectively.

Magnetic Measurements and Electronic Spectral Studies

The electronic spectrum of the Cu(II) shows single broad d-d band centered at 500 nm , as expected for square planar geometry as encountered for related copper(II) complexes [31]. The ESR spectrum of this complex is of axial shape with $g_{\parallel} > g_{\perp}$ characteristic of complexes with $^2B_{1(dx^2-y^2)}$ ground state. The average g values were calculated according to the equation $g_{\text{av}} = 1/3[g_{\parallel} + 2g_{\perp}]$. Complexes exhibits $g_{\parallel} < 2.3$, suggesting covalent

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characters of the copper–ligand bonding in this complex. The parameter $G = g_{\parallel} - 2.0023/g_{\perp} - 2.0023$ shows the possibility of exchange interaction in the Cu(II) complex. The G values for the complex ($G > 4$) indicate that there is no direct copper–copper interaction in the solid state [32]. The $g_{\parallel}/A_{\parallel}$ is taken as an indication for the stereochemistry of the Cu(II) complexes. Addison [32] has suggested that this ratio may be an empirical indication of the tetrahedral distortion of the square planar geometry. The values lower than 135 cm are observed for square planar structures and those higher than 150 cm for tetrahedral distorted complexes. The value of $g_{\parallel}/A_{\parallel}$ quotient for the complex under investigation lies below 135 cm, indicating square planar geometry around copper in this complex. The magnetic moment value for this complex was found to be 1.76 B.M. per Cu ion which was in the usual range for square planar copper complexes and indicating no direct interaction between the two copper centers in the solid state at room temperature [32].

The absorption spectral bands of Ni(II) complexes 3,4 showed three spin allowed transitions: $^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$, $^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$ appearing in the ranges 1145–1054, 706–695 and 461–443 nm, respectively consistent with a typical Ni(II) in an octahedral environment. The magnetic moment values for these complexes were found in the range 3.10–3.14 B.M. [33] expected for octahedral nickel complexes.

The electronic spectra of the Co (II) complexes (5) and (6) gave three bands at 1200–1051, 700–622 and 489–433 nm, which could be assigned to the transitions $^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$ (ν_1) $^4T_{1g}(F) \rightarrow ^4A_{2g}(F)$ (ν_2) and $^4T_{1g}(F) \rightarrow ^4T_{2g}(P)$ (ν_3),

Table-3: Fungicidal Screening Data of the Ligand and Their Corresponding Metal Complexes

Compound	% Inhibition of spore germination								
	Aspergillus sp. (mg/ml)			Penicillium sp. (mg/ml)			Rizoctonia sp. (mg/ml)		
	1.0	1.5	2.0	1.0	1.5	2.0	1.0	1.5	2.0
C ₂₂ H ₂₆ N ₁₀ O ₈ S ₄	28	36	41	09	17	22	30	35	39
[Cu ₂ (C ₄₄ H ₅₂ N ₂₀ O ₂ S ₈)Cl ₄]	60	70	76	53	60	68	46	51	63
[Cu ₂ (C ₄₄ H ₅₂ N ₂₀ O ₂ S ₈)(NO ₃) ₄]	43	53	70	46	51	63	41	42	50
[Cu ₂ (C ₄₄ H ₅₂ N ₂₀ O ₂ S ₈)(OAc) ₄]	71	75	79	58	61	71	51	53	66
[Ni ₂ (C ₄₄ H ₅₂ N ₂₀ O ₂ S ₈)Cl ₄]	66	77	78	56	60	72	50	57	56
[Ni ₂ (C ₄₄ H ₅₂ N ₂₀ O ₂ S ₈)(NO ₃) ₄]	53	60	71	45	51	63	43	45	53
[Ni ₂ (C ₄₄ H ₅₂ N ₂₀ O ₂ S ₈)(OAc) ₄]	72	78	82	64	68	77	61	62	71
[Co ₂ (C ₄₄ H ₅₂ N ₂₀ O ₂ S ₈)Cl ₄]	63	69	71	56	59	61	50	55	58
[Co ₂ (C ₄₄ H ₅₂ N ₂₀ O ₂ S ₈)(NO ₃) ₄]	54	57	62	46	50	58	47	50	51
[Co ₂ (C ₄₄ H ₅₂ N ₂₀ O ₂ S ₈)(OAc) ₄]	70	72	81	56	61	64	49	39	55
Miconazole (standard)	59	71	100	65	78	83	76	82	94

Conclusion

The analytical data show the presence of one metal ion per ligand molecule and suggest a mononuclear structure for the complexes. The electronic spectral data is in the favor of octahedral geometry of the complexes. The ligand and its Cu(II), Ni(II) and Co(II) complexes were tested for antifungal activity against some fungi. Antifungal study reveals that, metal complexes have more biological activity than free ligand. Complex (6) [Ni₂(C₄₄H₅₂N₂₀O₂S₈)(OAc)₄] show best biological action.

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respectively, suggesting an octahedral geometry around Co(II) ion [34]. The complexes 5 and 6 show magnetic moment values in the range 3.2–3.5 B.M., which is smaller than the calculated value for two Co (II) ions in octahedral geometries and this may be due to antiferromagnetism between the two ion-centers.

Antifungal Activity

For the experimental data Table 3, it has been observed that the ligand as well as its complexes shows a significant degree of antifungal activity against *Aspergillus sp.*, *Rizoctonia sp.* and *Penicillium sp.* DMSO control has showed a negligible activity as compare to the metal complexes and ligand. However, the metal complexes are show better activity than the ligand [35,36]. The complexes are highly effective against *Aspergillus sp.* HLNi(OAc)₂ is the only complex to show 78% activity against *Aspergillus sp.* the antifungal activity of the complexes varies in the following order of fungal species: *Aspergillus sp.* > *penicillium sp.* > *Rizoctonia sp.*

The antifungal experimental results of the compounds were compared with the standard antifungal drugs Miconazole at the same concentration. All the metal complexes exhibited greater antifungal activity against *Aspergillus sp.* as compare to the standard drug Miconazole. However, they show slightly lesser activity against *Rizoctonia sp.* than standard drug Miconazole. The Ni(II) and Co(II) complexes are more effective against *Penicillium sp.* than the standard drug. From the data it has been also observed that the activity depends upon the type of metal ion and varies in the following order of the metal ion: Ni > Co > Cu.

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