

Crystal Structure, Spectral Characterization and Biologically Studies of Mononuclear Transition Metal Complexes Derived from New N_2O_2 Type Ligand

Samina K Tadavi¹, Jamatsing D Rajput¹, Suresh D Bagul¹, Jaiprakash N Sangshetti³, Amar A Hosamani² and Ratnamala S Bendre^{1*}

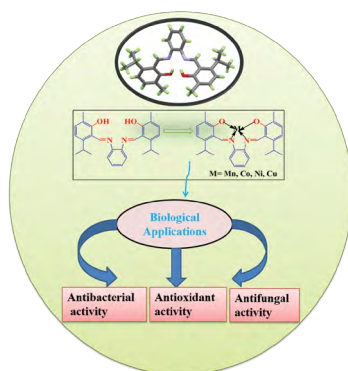
¹School of Chemical Sciences, North Maharashtra Jalsaon, Maharashtra, India

²Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore, Karnataka, India

³YB Chavan College of Pharmacy, Dr. Rafiq Zakaria Campus, Aurangabad, Maharashtra, India

Abstract

The new mononuclear metal complexes viz Mn(III), Co(II), Ni(II) and Cu(II) have been synthesized by using tetradentate N_2O_2 donor symmetric schiff base 6,6'-((1E,1'E)-(1,2-phenylenebis(azanylylidene))bis(methanylylidene)) bis(5-isopropyl-2-methylphenol) HL and employing with corresponding metal chloride or acetate salts. After successful synthesis of compounds were thoroughly characterized by Elemental analysis, FT-IR, Uv-visible, NMR spectroscopy, LC-MS spectrometry, SEM analysis, Magnetic susceptibility measurement, Molar conductance, ESR spectroscopy. X-ray single crystal structure of HL schiff base has been determined. The synthesized compounds have been screened for their antimicrobial and antioxidant activities, which show significant results.



Keywords: Schiff base; Mononuclear transition metal complexes; ESR; Antimicrobial activity; Antioxidant activity

Introduction

Schiff bases (RHC=NR) are a class of organic compounds typically formed by condensation of a primary amine and an aldehyde and they are considered as privilege ligand [1,2]. Schiff base ligands with N_2O_2 donor atoms are well known to coordinate with a variety of metal ions. They have attracted much interest in recent years, due to ease of synthesis, their stability under a variety of oxidative and reductive conditions and their structural versatility associated with various applications. These compounds have various applications in industries as dyes, drug synthesis [3] bioinorganic chemistry [4] electrochemistry [5] dioxygen uptake and catalysis [6-10]. Tetra-dentate N_2O_2 donors schiff bases derived from o-phenylenediamine and salicylaldehyde have been widely studied in solid state. They have been studied for a variety of applications including biological, clinical and analytical. The previous work has shown that some drugs showed increased activity when administered as metal chelates rather than as organic compounds [11-13]. A search through literature reveals that no work has been done on the transition metal complexes of the symmetrical schiff base derived from o-phenylenediamine and 2-hydroxy-6-isopropyl-3-methyl benzaldehyde. In this paper, we report synthesis of a new type of tetradentate Schiff base ligand formed by the simple condensation of o-phenylenediamine with 2-hydroxy-6-isopropyl-3-methyl benzaldehyde and its Mn(III), Co(II), Ni(II) and Cu(II) mononuclear complexes. The prepared ligand and complexes were characterized using Elemental analysis, FT-IR, UV-visible, NMR, LC-

MS, ESR and crystal structure and further screened for antimicrobial and antioxidant activity.

Experimental

All the solvents and chemicals were of commercial reagent grade and used as received without further purification. FT-IR spectra were recorded as KBr pellets on a SHIMADZU FT-IR- 8400 spectrometer from range 4000 to 400 cm^{-1} . The electronic spectra were recorded in DMF solutions on the UV 2400 series spectrophotometer. ¹H and ¹³C-NMR spectra were precise with a BRUKER AVANCE III (400 MHz) spectrometer and proton chemical shifts are recorded in ppm relative to tetramethylsilane as an internal standard using $CDCl_3$ as solvent and the LC-MS spectra have been carried out with Waters Micromass Q-ToF Micro instrument. The elemental analyses were carried out with a Thermo Finnigan elemental analyzer. The X-band ESR spectra of

*Corresponding author: Bendre RS, School of Chemical Sciences, North Maharashtra University, Maharashtra, India, Tel: 9422211435; E-mail: bendrers@gmail.com

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copper complex are recorded on a JES-FA200 EPR spectrometer with DPPH as standard. Magnetic susceptibilities are measured at room temperature on a guoy balance using Hg[Co(NCS)₄] as reference. SEM-EDS analyses were performed on SEM JEOL JSM 6360 and JEOL JSM 5400, Japan. Molar conductance of metal complexes was calculated in DMF at room temperature on Systronic Conductivity Bridge.

Synthesis of Schiff base (L)

The ligand was prepared by dropwise addition of a warm ethanolic solution of o-phenylenediamine (1 mmol) to constantly stirring warm solution of 2-hydroxy-6-isopropyl-3-methyl benzaldehyde (2 mmol) in ethanol. The resulting solution was refluxed for 3 h, formation of orange precipitate. The obtained product was filtered, washed with cold ethanol and recrystallized from ethanol and dried at room temperature. Yield: 77 % Colour: Orange. Anal. calcd for C₂₈H₃₂N₂O₂ (%): C 78.47, H 7.53, N 6.54; Found: C 78.31, H 8.16 N 6.61. FT-IR (KBr pellet, cm⁻¹) ν_{max}: 3412 (OH), 1601 (C=N), 1460 (C=C), 1253 (C-O). UV-vis (DMF) λ_{max} (nm): 268, 341. ¹H- NMR (CDCl₃, 400 MHz) (δ, ppm): 14.16(s, 2H, -OH), 7.39-7.37 (m, 2H, Ar), 7.32-7.30 (m, 2H, Ar), 7.20 (d, 2H, J=8Hz), 6.74 (d, 2H, Ar), 3.48-3.45 (m, 2H, -(CH₃)), 2.17 (s, 6H, 2(CH₃)), 1.19-1.24 (m, 12H, 4(CH₃)). ¹³C- NMR (CDCl₃, 400 MHz) (δ, ppm): 162.31, 160.88, 147.99, 142.74, 134.72, 127.34, 124.05, 121.16, 114.95, 28.09, 24.07, 15.60. MS (m/z): calcd 428.57; obsv 429.4.

General procedure for the synthesis of mononuclear metal complexes

The complexes were prepared by dropwise addition of (1 mmol) warm ethanolic solution of ligand to the corresponding suitable ethanolic metal acetate or chloride salts (2 mmol) in basic condition under inert atmosphere nitrogen gas. The reaction mixture was refluxed till completion of reaction, the precipitate was obtained and collected product was washed with cold ethanol and then diethyl ether.

Mononuclear Mn(III) complex [1]: Yield: 71%. Colour: reddish brown. Anal. calcd for C₃₀H₃₃MnN₂O₄ (%): C 66.66, H 6.15, N, 5.18; Found: C 64.93, H 5.91, N 5.97. FT-IR (KBr, pellet cm⁻¹) ν_{max}: 1591 (C=N), 1276 (C-O), 1382 (C=C), 530 (M-O), 480 (M-N). UV-Vis (DMF) λ_{max} (nm): 268, 342, 471. LC-MS (m/z): calcd 540.53; obsv 481.3. μ_{eff}: 4.82 B.M. Conductance (Λ_M, Ω⁻¹ cm² mol⁻¹) in DMF: 9.60.

Mononuclear Co(II) complex [2]: Yield: 65%. Colour: brown. Anal. calcd for C₂₈H₃₀CoN₂O₂ (%): C 69.27 H 6.23, N 5.77; Found: C 68.29, H 5.14, N 5.58. FT-IR (KBr pellet, cm⁻¹) ν_{max}: 1541 (C=N), 1205 (C-O), 1382 (C=C), 530 (M-O), 480 (M-N). UV-Vis (DMF) λ_{max} (nm): 264, 506, 620. LC-MS (m/z): calcd 485.48; obsv 485.3 μ_{eff}: 3.80 B.M. Conductance (Λ_M, Ω⁻¹ cm² mol⁻¹) in DMF: 14.35.

Mononuclear Ni(II) complex [3]: Yield: 80%. Colour: reddish orange. Anal. calcd for C₂₈H₃₀N₂NiO₂ (%): C 69.31, H 6.23, N 5.77; Found: C 70.34, H 6.03, N 6.35. FT-IR (KBr pellet, cm⁻¹) ν_{max}: 1560 (C=N), 1234 (C-O), 1452 (C=C), 474 (M-O), 432 (M-N). UV-Vis (DMF) λ_{max} (nm): 267, 307, 386, 490, 547. LC-MS (m/z): calcd 485.23; obsv 485.41. Conductance (Λ_M, Ω⁻¹ cm² mol⁻¹) in DMF: 15.64.

Mononuclear Cu(II) complex [4]: Yield: 78%. Colour: Shining dark green. Anal. calcd for C₂₈H₃₀CuN₂O₂ (%): C 68.62, H 6.17, N 5.72, Found: C 66.79, H 5.18, N 5.67. FT-IR (KBr, cm-1) ν_{max}: 1600 (C=N), 1240 (C-O), 1404 (C=C), 550 (M-O), 455 (M-N). UV-Vis: (DMF) λ_{max} (nm): 264, 444, 632. LC-MS (m/z): calcd 490.10; obsv 490.40. μ_{eff}: 1.75 B.M. Conductance (Λ_M, Ω⁻¹ cm² mol⁻¹): 12.67. g₁=2.2317, g₂=2.0472.

Bioassay

Protocol for antibacterial activity: The antibacterial activity of

the compounds was performed by enumerating the viable number of cells upon in the nutrient broth containing various concentrations of compounds. The viable number is represented by colony count method. The test organisms used on which the antibacterial activity was performed were *Escherichia Coli*, *Bacillus subtilis* (NCIM-2063), *Pseudomonas aeruginosa* (NCIM-2036) and *Staphylococcus aureus* (NCIM-2901). The minimum inhibitory concentration (MIC μg/mL) values were determined. The lowest MIC values show the potent activity. Ciprofloxacin and Ampicillin were used as standard drugs. All the experiment were carried out in triplicate and the averaged results are considered [14].

Protocol for antifungal activity: The antifungal activity was evaluated against different fungal strains, such as *Candida albicans* (NCIM 3471), *Fusarium oxysporum* (NCIM1332), *Aspergillus flavus* (NCIM 539), *Aspergillus niger* (NCIM 1196), and *Cryptococcus neoformans* (NCIM 576). Minimum inhibitory concentration (MIC, μg/mL) values of all the compounds were determined using the standard agar dilution method as per CLSI guidelines. By using miconazole and fluconazole as standard antifungal drugs. All the experiments are performed in triplicate and average results are considered [15].

Protocol for antioxidant activity: DPPH (2,2-diphenyl-1-picrylhydrazyl) radical scavenging activity was evaluated according to the reported method [16,17]. Ascorbic acid was used as standard. Each sample and positive control (ascorbic acid) were performed in triplicate. Scavenging activity versus concentration in ppm were plotted to estimate a 50% reduction of its initial value (EC₅₀). Lower absorbance of the reaction mixture indicates higher free radical scavenging activity. The capability to scavenge the DPPH radical was calculated using the following equation:

$$\text{DPPH radical scavenging activity (\%)} = \frac{\text{Absorbance}_{(\text{control})} - \text{Absorbance}_{(\text{standard})}}{\text{Absorbance}_{(\text{control})}} \times 100$$

Where, Absorbance_(control): Absorbance of DPPH radical+methanol
Absorbance_(standard): Absorbance of DPPH radical+extract/standard.

Results and Discussion

The symmetrical Schiff base was prepared by simply condensation of 2-hydroxy-3-methyl-benzaldehyde [18] with o-phenylenediamine in 2:1 molar ratio in ethanolic solution (Figure 1). The Mn(III),

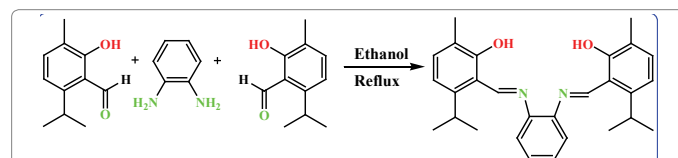


Figure 1: Synthesis of Ligand HL 6,6'-((1E,1'E)-(1,2-phenylenebis(azanylylidene))bis(methanylylidene))bis(5-isopropyl-2-methylphenol).

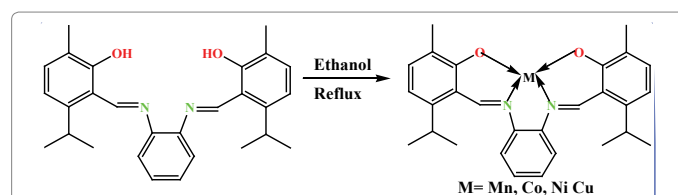


Figure 2: Synthesis of mononuclear metal (II) complexes with 6,6'-((1E,1'E)-(1,2-phenylenebis(azanylylidene))bis(methanylylidene))bis(5-isopropyl-2-methylphenol).

Compounds Name	<i>E. coli</i> (MIC µg/mL)	<i>P. aeruginosa</i> (MIC µg/mL)	<i>B. subtilis</i> (MIC µg/mL)	<i>S. aureus</i> (MIC g/mL)
Carvacrol	72	97	56	129
Carvacrol aldehyde	95	120	75	193
Ligand	102	49	63	77
Mn(II)	111	101	81	115
Co(II)	168	170	230	99
Ni(II)	63	93	74	56
Cu(II)	74	85	102	74
Ciprofloxacin	25	25	50	50
Ampicillin	100	100	250	250

Table 1: The antibacterial activity representation.

Compounds Name	<i>C. albicans</i> (MIC µg/ mL)	<i>A. flavus</i> (MIC µg/ mL)	<i>A. niger</i> (MIC µg/ mL)	<i>C. neoformans</i> (MIC µg/ mL)
Carvacrol	125	125	125	100
Carvacrol aldehyde	*	125	*	225
Ligand	100	150	150	*
Mn(II)	125	225	125	*
Co(II)	100	100	*	150
Ni(II)	150	*	100	125
Cu(II)	150	*	*	*
Miconazole	25	12.5	25	25
Fluconazole	12.5	6.25	12.5	6.25

Table 2: The antifungal activity representation.

Co(II), Ni(II) and Cu(II) mononuclear complexes were synthesized by the direct reaction of ligand with an equimolar amount of metal(II) acetate/ chloride salts in ethanol in 1:1 molar ratio (Figure 2). All the compounds are soluble in polar solvents. The spectral analyses agree well with the proposed structure of the complexes. All the compounds were subjected to *in vitro* antibacterial, antifungal and antioxidant activities.

Biological activity

As per the literature survey carvacrol possess good antibacterial, antifungal and antioxidant activities [19]. Our antibacterial data illustrated in Table 1, that the antibacterial activity decreases upon formylation of carvacrol to carvacrol aldehyde as compared to the carvacrol. While schiff base ligand possesses the superior activity as compared to the carvacrol against *Pseudomonas aeruginosa*, *Bacillus subtilis* and *Staphylococcus aureus*. All the metal complexes presented better antibacterial activity against the *Staphylococcus aureus* as compared to carvacrol (Table 2). The Ni(II) and Co(II) complexes exhibited better antibacterial activity than the ligand against all the microbes and standard ampicillin. The antifungal activity results indicated that carvacrol aldehyde possesses good antifungal activity against the *Aspergillus flavus* and *Cryptococcus neoformans*. The schiff base ligand shows the better activity in contrast to carvacrol for the fungal strain *Candida albicans* and moderate to *Aspergillus flavus* and *Aspergillus niger*. All the complexes show good activity against the *Candida albicans*. The Co(II) and Ni(II) complexes showed better activity against *Candida albicans*, *Aspergillus flavus* and *Aspergillus niger*, *Cryptococcus neoformans* respectively. The better antibacterial and antifungal activities of these complexes as compared to the ligand may be explained on the basis of chelation theory [20]. The process of scavenging DPPH-free radicals has been used to assess the antioxidant activity of specific compounds [21]. DPPH is a stable free radical that can accept an electron or hydrogen radical and get converted to a stable, diamagnetic molecule. DPPH has an odd electron and has strong absorption band at 517 nm. When this electron becomes paired

off, the absorption decreases stoichiometrically with respect to the number of electrons or hydrogen atoms taken up. Such a change in the absorbance by this reaction has been extensively adopted to test the capacity of several molecules to act as free radical scavengers (Table 3). Hence, more rapidly the absorbance decreases, the more potent is the antioxidant activity of the compound [22]. Our result indicate that carvacrol aldehyde possesses the strong activity as compared to the carvacrol while the Schiff base ligand possess lesser activity as compared to both. However upon complexation with metal ions *viz* Mn(III) and Cu(II) the activity was improved significantly. All the compounds showed comparable or better activity to that of standard ascorbic acid. The Mn(III) and Cu(II) complex showed significantly higher antioxidant activity followed by Ni(II) and Co(II) complexes at different concentrations.

X-ray crystallographic analysis

Yellow colored crystal of suitable size 0.23 × 0.22 × 0.21 mm³ and mounted on 'Bruker APEX-II CCD' diffractometer equipped with graphite monochromated Mo K α radiation in the wavelength of 0.71073 Å at room temperature. The summary of crystallographic parameters, data collection and refinement is given in Table 4 and the additional details concerning the data collections, structure solution and refinement are included in the supporting data. The CCDC No. for Ligand is 1443334. The single crystal of the Schiff base demonstrated the monoclinic system having P2₁ space group with the two molecules in the unit cell. The ORTEP diagram with numbering and packing diagram are shown in the Figure 3. The selected bond lengths and bond angles are depicted in Table 6 While, the hydrogen bonding parameters are given in Table 5. The crystal structure of the symmetric Schiff base ligand represented, the N1-C15 and C₈-N₂ distances as 1.286(8) and 1.277(8) Å respectively for C=N double bonding. The two C₄-O₁ and C₂₁-O₂ having bond distances 1.339(8) and 1.349(8)Å respectively illustrated the C-O phenolic single bond. The intramolecular hydrogen bonding formed by the H₁-O₁-N₂ and H₂-O₂-N₁, with distances of 2.617 and 2.579 Å has resulted in the formation of a five membered

chelating ring. There is no solvent molecule appear in the structure. From this crystal structure study, it is confirmed that the symmetric Schiff base having two imine nitrogen atoms and two phenolic oxygen atoms (N₁, N₂, O₁, O₂) has been successfully synthesized and suggests that this ligand can easily act as tetradentate donor [23,24].

Spectral characterization

FT-IR: The IR spectroscopy is used to determine the characteristic peaks (OH, C=N, C-O) in ligand before and after complexation. The IR spectra of the ligand and complexes are compared, the band at 1601 cm⁻¹ is characteristic of the azomethine nitrogen atom present in the schiff base ligand is found to shift to lower frequency region 1546-1556 cm⁻¹ in all the complexes and illustrated the involvement of the azomethine nitrogen atom in coordination. The peak at 3412 cm⁻¹ appear for the phenolic -OH group. The absence of the broad band at 3500-3100 cm⁻¹, indicated the absence of coordinated water molecule to complexes. The C-O peak appearing in the ligand at 1298 cm⁻¹ is shifted to 1340-1388 cm⁻¹ in all complexes. The involvement of oxygen and nitrogen atoms in coordination with metal is further defined by the appearance of weak and low frequency bands in the range 400-600 cm⁻¹ corresponding to the M-O and M-N respectively [25].

Electronic spectra: The absorption value of high energy 265-280 nm and 340-490 nm are assigned to the intraligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively. The electronic spectra of copper consist of weak d-d transition in the visible region as a broad band at 632 nm attributed to square planar complexes of similar tetradentate schiff base ligands with o-phenylenediamine. The nickel complex shows the absorption at 547 nm indicating that the complex is diamagnetic nature and possesses square planar geometry. The absorption at 506 nm and 620 nm shows cobalt complex possess the square planar geometry [26].

Mass: In the mass spectra of the ligands and complexes the molecular ion peak is significantly more abundant than other fragment ions. The proposed fragmentations are equivalent with the empirical

formula of proposed structure of the ligands and complexes.

NMR: In the ¹H NMR spectrum of the ligand in DMSO shows the following signals: 4.16 δ singlet are assigned to the phenolic -OH group and the values 7.39-7.37, 7.32-7.30, 7.20, 6.74 δ are assigned to the aromatic region, the peak at multiplet 3.48-3.45 δ and 1.19-1.24 δ are attributed to the 2-CH and of four methyl group of isopropyl group respectively and singlet peak at 2.17 δ assigned for methyl group.

SEM: Scanning electron micrograph (SEM) have been currently used to determine the morphology and the grain size of the metal complexes. The SEM photograph of the complexes are illustrated in the Figure 4 for all the metal complexes the SEM photograph were taken in the different scale range from 1 μ m to 50 μ m. From the SEM photograph it was noted there is a uniform matrix in all the metal complexes. The photograph of Mn(II) complex shows the flakes like morphology while Co(II) complex exhibit the rod like morphology. The Ni(II) and Cu(II) displays the fibre like morphology.

Conductivity measurement: The molar conductivity values of the complexes were in the range 15-25 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. This value indicated that the complexes having non-electrolytic in nature [27].

Magnetic susceptibility: The Mn(III) complex shows the distorted square planer geometry having magnetic moment 4.85 B.M. The magnetic moment of the Co(II) complexes exhibit at 2.81 BM [28] consistent with Square planar geometry Ni(II) complexes are square planar and diamagnetic in nature [29] while the magnetic moment of Cu(II) complex exhibited in the range 1.75 representing that copper has square planar geometry showing one unpaired electron [30,31].

ESR spectra: The ESR spectra of the CuL complex in DMF solution at 77 K at liquid nitrogen temperature exhibits in the perpendicular region, three of four hyperfine features are well resolved while the fourth one is overlapped by g features [32]. The values of ESR parameters G_{avg} , G , α^2 , f for Cu(II) complex calculated are 2.22, 2.040, 2.1, 5.75, 186×10^{-4} , 0.79, 118, respectively. From the calculated values it illustrated that

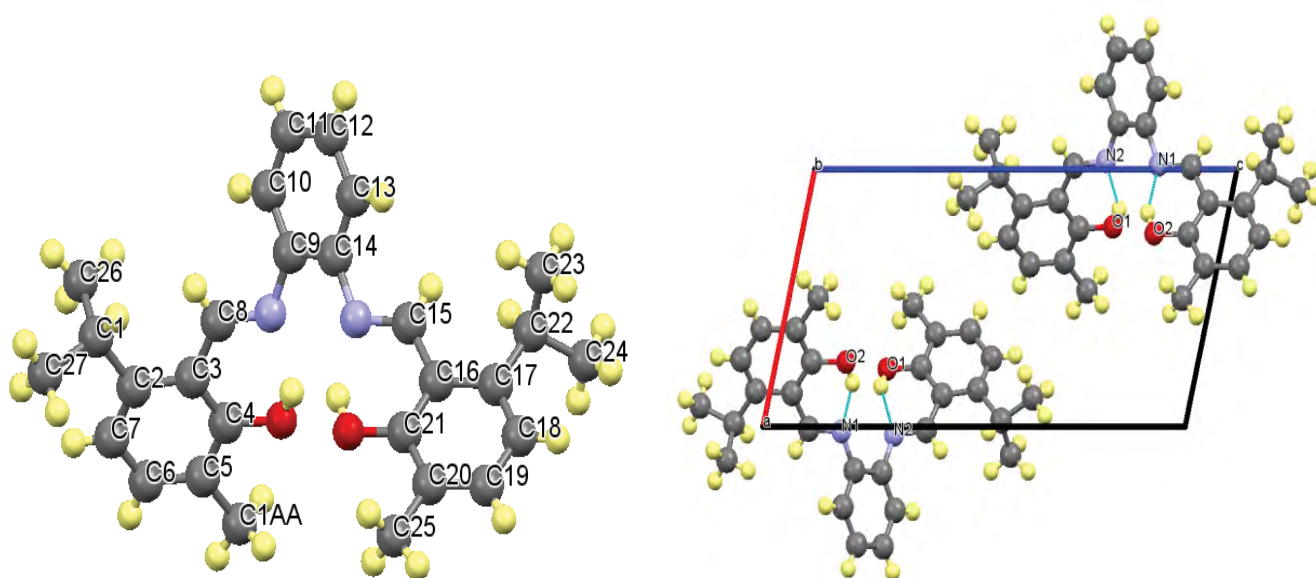
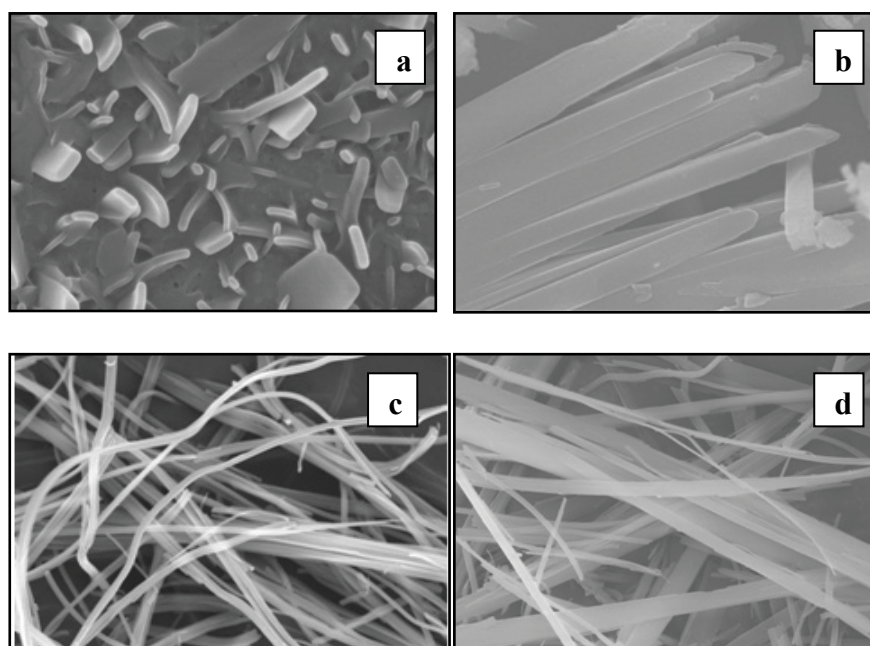


Figure 3: ORTEP diagram with atomic labeling and crystal packing diagram viewed along b with O—H—N intramolecular hydrogen bond is shown as a light blue dashed line.



a=Mn(III), b=Co(II), c=Ni(II), d=Cu(II)

Figure 4: SEM photograph of all the mononuclear complexes.

Compound Name	EC ₅₀
Carvacrol	0.1137
Carvacrol aldehyde	0.1107
Ligand	0.1142
Mn(II)	0.1124
Co(II)	0.1172
Ni(II)	0.1158
Cu(II)	0.1135
Ascorbic acid	0.1203

Table 3: The antioxidant activity representation.

Empirical formula	C ₂₈ H ₃₂ N ₂ O ₂
Formula weight	428.55
Temperature/K	296.15
Crystal system	monoclinic
Space group	P2 ₁
a/Å	8.561(2)
b/Å	8.705(2)
c/Å	16.556(4)
α/°	90
β/°	103.736(11)
γ/°	90
Volume/Å ³	1198.6(5)
Z	2
ρ _{calc} g/cm ³	1.187
μ/mm ⁻¹	0.074
F(000)	460.0
Crystal size/mm ³	0.23 × 0.22 × 0.21
Radiation	MoKα (λ=0.71073)
2θ range for data collection/°	2.532 to 50
Index ranges	-10 ≤ h ≤ 10, -10 ≤ k ≤ 10, -19 ≤ l ≤ 19
Reflections collected	16503
Independent reflections	4178 [R _{int} =0.0816, R _{sigma} =0.0720]

Data/restraints/parameters	4178/1/297
Goodness-of-fit on F ²	1.127
Final R indexes [$I > 2\sigma(I)$]	R ₁ =0.1051, wR ₂ =0.2745
Final R indexes [all data]	R ₁ =0.1275, wR ₂ =0.2945
Largest diff. peak/hole / e Å ⁻³	0.92/-0.29
Flack parameter	-1.2(10)

Table 4: Crystallographic parameters, data collection and refinement is given as follows.

Bond Lengths		Bond Angles	
C ₈ -N ₂	1.277(8)	O ₁ -C ₄ -C ₃	123.1(6)
N ₁ -C ₁₅	1.286(8)	O ₂ -C ₂₁ -C ₁₆	121.5(6)
N ₂ -C ₉	1.422(8)	N ₂ -C ₈ -C ₃	124.1(6)
N ₁ -C ₁₄	1.422(9)	N ₁ -C ₁₅ -C ₁₆	122.0(6)
O ₁ -C ₄	1.339(8)	C ₈ -N ₂ -C ₉	118.6(6)
C ₂₁ -O ₂	1.349(8)	C ₁₅ -N ₁ -C ₁₄	115.5(6)

Table 5: Selected bond lengths/Å° and angles/° for Ligand HL.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(D-H...A)
O ₂ -H ₂ ...N ₁	0.820	1.847	2.580	148.10
C ₂₇ -H ₂₇ ...O ₁	0.960	2.895	3.819	161.80
C ₂₄ -H ₂₄ ...O ₂	0.960	2.916	3.841	161.93
C ₁₂ -H ₁₂ ...O ₂	0.930	2.867	3.717	152.52

Table 6: The intramolecular hydrogen bonds and angles.

the copper complex follows the trend and also provides information about the unpaired electron that it is localized in d_{x²-y²} orbital having ²B_{1g} as ground state which is consistent with the square planar geometry [33]. The extent of geometrical distortion is measured by the $f=g/A$ ratio [34]. It has been reported that complex falls between 105–135 cm⁻¹ and also ratio for tetragonally distorted complex falls in the range 135-250 cm⁻¹ [35]. The current complex has $f=118$ cm⁻¹ indicating that copper complex has square planar geometry. The value of the exchange coupling interaction between two Cu(II) ions in terms of G has been explained by the Hathway expression (0023)/(0023). From the expression, if G>4.0, the exchange interaction is negligible while when the value of G<4.0 significant exchange coupling is present in the solid complex [36]. This result indicates that the exchange coupling effects are not effective in the present complex. The value of in plane sigma bonding parameter α^2 was expected from following expression,

$$\alpha^2 = -(A_1/0.036) + (g_1 - 2.0023) + 3/7(g_2 - 2.0023) + 0.04$$

The value of $\alpha^2=0.5$, indicates complete covalent bonding, while the value of $\alpha^2=1.0$ suggests complete ionic bonding. The observed value of α^2 is less than 1, which indicated that the complex has some covalent character in the ligand environment [37].

Conclusion

In this investigation we are reporting the synthesis and characterization of symmetrical salen based ligand and their Mn(III), Co(II), Ni(II) and Cu(II) complexes. The single crystal structure of Schiff base ligand have been solved by single x-ray crystallography which having two imine nitrogen atoms and two phenolic oxygen atoms act as tetradentate donor. The Schiff base ligand and metal complexes were screened for their biological activities such as, *in vitro* antibacterial, antifungal and antioxidant activities. The results indicated Ni(II) and Cu(II) complexes exhibit better antibacterial activity against *Escherichia coli*, *Pseudomonas aeruginosa*, *Bacillus subtilis* and *Staphylococcus aureus* as compared to carvacrol and standard drug (ciprofloxacin). The Co(II) complex show the good antifungal activity against *Candida albicans*, *Aspergillus flavus*, *Cryptococcus neoformans* as compared to parent molecule (carvacrol). The Mn(III) and Cu(II)

complex shows the good antioxidant activity as comparable to standard drug (ascorbic acid).

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