*Nat.Volatiles&Essent.Oils,2021;8(5):8991-9003*

# Preparation and Characterization of sulfathiazole Schiff Base Complexes of Co(II), Ni(II), Cu(II), and Mn(II)

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**Abstract**

Chemical and electrochemical techniques were used to synthesize complexes of Co(II), Ni(II), Cu(II), and Mn(II) containing Schiff base NOS donor ligands. Elements analysis, conductance, magnetic susceptibility measurements, IR, electronic spectral studies, and thermal techniques have all been used to determine the structure of the complexes (TGA and DTA). The antimicrobial activity of the title Schiff base and its complexes has been tested against various microorganisms.

**Keywords**. Schiff base; sulfathiazole; Complexes ; NOS donor.

## Introduction

*Sulfonamides were studied extensively as the first effective antibacterial agents. Sulfonamides act as structural analogues for 4-aminobenzoic acid and thus inhibit the dihydropteroate synthase[1].*

They were less commonly used than other antibiotics, but their synergic activity, such as when combined with trimethoprim, drew attention later[2]. Due to the sequential inhibition of the bacterial synthesis of tetrahydrofolic acid and thus disrupting nucleic bases and acids synthesis, the antibacterial activity of the combination of sulfamethoxazole (SMX) and trimethoprim is more efficient[3]; it is a broad-spectrum antibiotic widely used for the treatment of many infections. Unfortunately, some clinically significant pathogens are either naturally or acquiredly resistant[4].
Resistance among important pathogens is increasing, according to reports from around the world[5].
The chances of synthesizing a chelating agent with absolute specificity are slim, but significant research has been done and is being done in this direction. Among such promising agents is the group which is known as Schiff bases also referred to as anils, imines or azomethines[6]. Schiff bases, first synthesized by Schiff, have the general formula -RC=NR', where R and R' are alkyl, cycloalkyl, aryl or heterocyclic radicals which may be variously substituted[8].
The most common method for preparing Schiff bases is the reaction of aldehydes and ketones with amines[9]. The reaction is generally carried out by refluxing the carbonyl compound and amine, with an azeotroping agent, if necessary, and separating the water as formed[10]. Schiff bases also include hydrazones, substituted hydrazones, semicarbazones, thiosemicarbazones, etc. formed respectively by the condensation of hydrazine, substituted hydrazine, semicarbazide, thiosemicarbazide, etc. with an active carbonyl group[11].
Schiff bases are relatively easy to prepare and because of their synthetic flexibility, they can be obtained with widely varied substitution by selection of appropriate reactants[12]. By changing the nature and the position of donor atoms or groups, it is possible to control the size of chelate rings formed and to exploit the effect of substitution[13]. These factors make Schiff bases, with appropriate structure, chelating agents of great potential and analytical reagents of general interest[14]. The preparation, properties and chemical reactions of Schiff bases have been reviewed[15].

A Schiff base, to be effective as a chelating agent, must possess, besides azomethine nitrogen >C=N-, an additional, appropriately located ligating group such as -OH, -SH, -N02, -NH2, etc[16]. so that, at least, one five- or six-membered chelate ring be formed upon complexation with a metal ion[17].

Schiff bases are considered a very important class of organic ligands possessing diverse applications[18]. Copious transition metal complexes with polydentate Schiffbases containing nitrogen, oxygen, or sulphur donor atoms contribute immensely in biological systems[19]. These complexes exhibit applications in clinical[10], analytical[11], and industrial processes[12]. Studies on transitional metal compounds of Schiff base ligands have been of great significance due to their spectral properties and wide applications[13] . These complexes are used as model molecules for biological oxygen carrier systems[14]. Tetradentate Schiff base complexes have been shown to form stable complexes, with coordination taking place through the dinitrogen-dioxygen donor atoms[15]. we present the synthesis, characterization, and biological studies of Co(II), Ni(II), Cu(II), and Zn(II) complexes containing unsymmetrical tetradentate Schiff base ligand derived from 4-Diethylamino-2-hydroxybenzaldehyde.

## 2. Materials and Methods

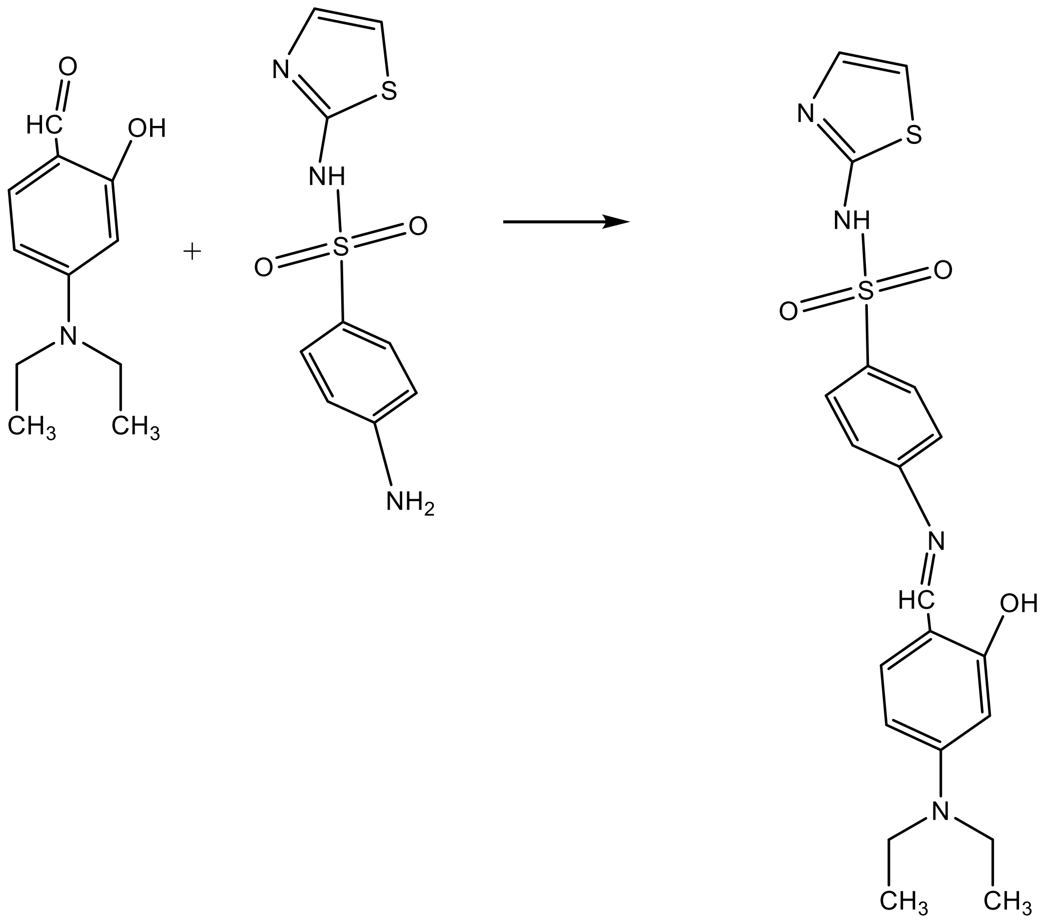
*2.1. Materials.* All of the chemicals and solvents used were of the highest quality: Fluka provided 4-Diethylamino-2-hydroxybenzaldehyde; Merck provided ascorbic acid, and Zn(II)/Co(II)/Cu(II)/Ni(II) acetate; and Aldrich provided sulfathiazole Sigma Chemical Co. supplied (DPPH), (ABTS), and (BHT).

### *2.2. Physical Measurements.*

Each sample was elementally analyzed using a PerkinElmer elemental analyzer. IR spectra were recorded in KBr using a PerkinElmer Paragon 2000 FT-IR spectrophotometer in the 4000–400 $cm^{-1}$ range. The molar conductance of the complex in DMF was measured at room temperature using a Crison EC-Meter Basic 30+ conductivity cell. The electronic absorption spectra of the ligand and metal complexes were measured on a PerkinElmer Lambda-25UV-Vis spectrometer in the 200–800 nm range with DMF as the solvent. Powder X-ray diffraction (XRD) patterns were captured using a Bruker AXS D8 Advance powder X-ray diffractometer (X-ray source: Cu, wavelength 1.5406 A).

### *2.3. Synthesis of the Ligand*

*A mixture of an ethanol solution of sulfathiazole (1mmol in 30cm3) and an ethanol solution of 4-Diethylamino-2-hydroxybenzaldehyde (1mmol in 20cm3) was refluxed for 3 hours to make the Schiff base. The formed product was filtered off, recrystallized from ethanol, washed with diethyl ether, and dried in a vacuum desiccator over silica gel after the reaction mixture was cooled (see Scheme 1).*



***Preparation of Complexes***

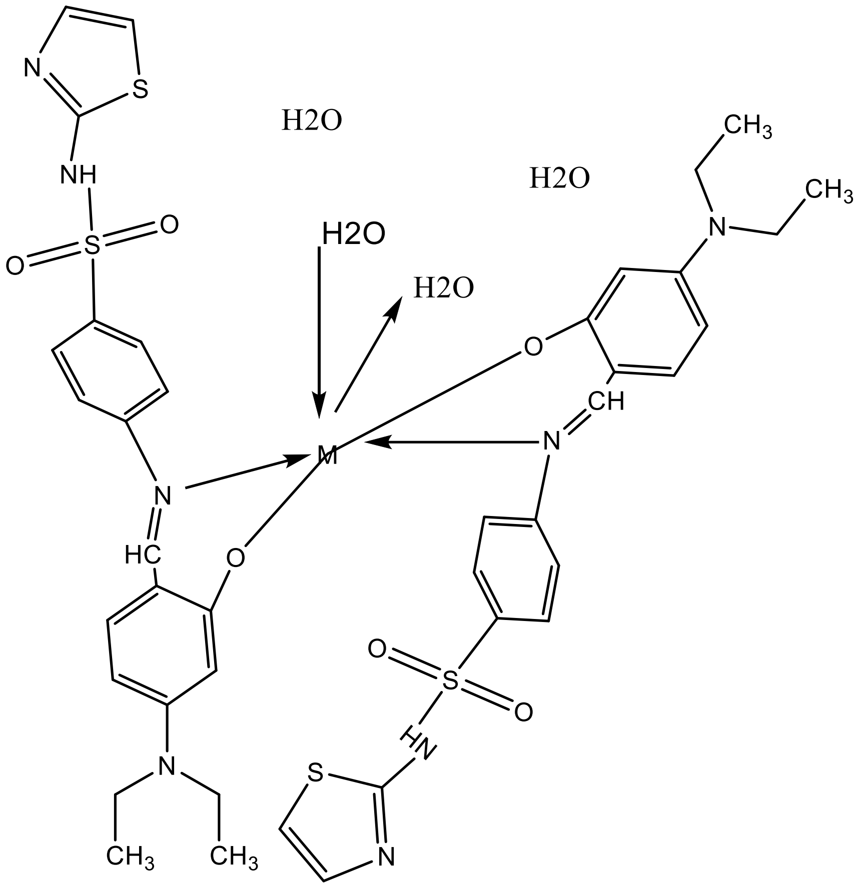
*Chemical techniques were used to make metal complexes of the sulfadiazine Schiff base with Cu(II), Ni(II), Co(II) , and Mn(II) ions. The metal complexes were made chemically by refluxing ethanolic solutions of the ligand (1mmol in 30cm3) and each of the metal acetates (2mmol in 20cm3) for 3 hours with sodium acetate solution (0.5 g in 5 cm3) as a buffering agent. The separated solids were filtered off after cooling the reaction mixture, washed with ethanol and diethyl ether, and dried over silica gel.Table 1 lists the analytical data and physical measurements.*

*General Procedure for the Preparation of the Complexes.*

The complexes were made by dissolving 1.5mmol of $Cu(CH3COO)_2 2H2O$, $Zn(CH3COO)_2.2H2O$, $Co(CH3COO)_2 4H2O$ , $Ni(CH3COO)_2 4H2O$, or in about 30mL of 40% ethanol (v/v) solution in a hot ethanolic solution (30 mL) (1.5mmol, 0.4145 g) of H2L in a(1 : 1). In a matter of minutes, the color of the complexes changed. The mixture that resulted was refluxed for 2 hours. The precipitated solids were filtered from the reaction mixture, thoroughly washed with ethanol and then with diethyl ether, and dried over anhydrous calcium chloride.

Table 1. Analytical and physical data of Schiff base complexes

| .No | Compounds | formula | Molecular Weight | Colour | Yield% | M.P. | %Elemental Analysis Found % (Calculated) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | C | H | N | M |
| A1 | HL | $C_{20}H_{22}N_4O_3S_2$ | 430.54 | Dark yellow | 75 | 206 | 55.12<br>(55.79) | 4.76<br>(5.15) | 12.87<br>(13.01) | - |
| B1 | $[Co(L)_2(H_2O)_2]$ $2H_2O$ | $C_{40}H_{50}CoN_8O_{10}S_4$ | 957.90 | Brown | 68 | 287 | 48.11<br>(48.53) | 4.67<br>(5.09) | 10.74<br>(11.32) | 5.95<br>(5.95) |
| B2 | $[Co_2L(AcO)_2(H_2O)_4]$ $H_2O$ | $C_{24}H_{39}Co_2N_4O_{13}S_2$ | 755.56 | Brown | 60 | 272 | 38.04<br>(38.15) | 4.46<br>(4.94) | 6.81<br>(7. 4) | 14.83<br>(15.60) |
| C1 | $[Ni(L)_2(H_2O)_2]2H_2O$ | $C_{40}H_{50}NiN_8O_{10}S_4$ | 989.82 | Green | 73 | 265 | 48.11<br>(48.54) | 4.89<br>(5.09) | 11.07<br>(11.53) | 5.67<br>(6.04) |
| C2 | $[Ni_2L(AcO)_2(H_2O)_4]$ $H_2O$ | $C_{24}H_{37}Ni_2N_4O_{12}S_2$ | 696.39 | Brown | 78 | 281 | 41.23<br>(41.39) | 5.17<br>(5.36) | 7.89<br>(8.05) | 8.12<br>(8.43) |
| D1 | $[CuL_2]3H_2O$ | $C_{40}H_{42}CuN_8O_5S_4$ | 922.61 | Redith Brown | 60 | 256 | 49.12<br>(52.94) | 4.54<br>(4.98) | 11.12<br>(11.53) | 6.21<br>(6.04) |
| D2 | $[Cu_2L(AcO)_2(H_2O)_2]$ $H_2O$ | $C_{20}H_{21}CuN_4O_3S_2$ | 493.08 | Brown | 68 | 270 | 43.57<br>(44.08) | 5.21<br>(5.47) | 8.10<br>(8.22) | 9.41<br>(9.33) |
| E1 | $[MnL_2(H_2O)_2]2H_2O$ | $C_{40}H_{42}MnN_8O_6S_4$ | 91.400 | Dark Brown | 73 | 263 | 52.11<br>(52.07) | .382<br>(4.59) | 12.24<br>(12.15) | 5.68<br>(6.89) |
| E2 | $[Mn_2L(AcO)_2(H_2O)_4]$ $H_2O$ | $C_{20}H_{21}MnN_4O_3S_2$ | 484.47 | Brown | 71 | 285 | 49.29<br>(49.58) | 4.14<br>(4.37) | 11.14<br>(11.56) | 10.78<br>(11.34) |



## Results and Discussion

Table 1 shows the analytical and physical data for the metal complexes. The complexes are air stable for a long time, soluble in DMF but insoluble in other organic solvents. For chemical and electrochemical methods of preparation, the analytical data of the metal complexes indicate that the complexes have 1:2 and 2:1 and metal-ligand stoichiometry, respectively. The molar conductance (10 3 M solutions in DMF) ranges from 10.1 to 19.31 cm2 mol$^{-1}$, indicating that these complexes are non-electrolytic. This demonstrates the acetate ion's participation in the coordination sphere of the metal ions in binuclear complexes B2, C2, D2, and E2. Anions are not present in the mononuclear complexes B1, C1, D1, and E1.

## Thermal Analysis

Table 2 presents the thermogravimetric results of mononuclear and binuclear Co(II) and Ni(II) complexes B1, B2, E1, and E2. The weight losses in the temperature ranges 35–100 and 25–110˚C are attributed to the removal of two lattice water molecules associated with endothermic peaks at 70 and 90 ˚C in the DTA thermogram for mononuclear Co(II) and Ni(II) complexes B1 and E1, respectively. The elimination of the two coordinated $H_2O$ molecules with endothermic peaks at 130 and 170 C for both complexes is attributed to the weight losses in the temperature ranges of 100–260and *110–225*˚C. The removal of 2-iminopyrimidine in the temperature ranges 260–385˚C and *225–415* ˚C with exothermic peaks at 348 and 367 ˚C in the DTA thermogram, followed by the loss of two $SO_2$ molecules and two benzene rings occurs in the temperature ranges 385–580 and *415*–560˚C, respectively, with exothermic peaks at 550 and 525˚C in the DTA thermogram, The decomposition steps within the temperature ranges 585–750˚C and *560–780* ˚C with broad exothermic peaks at 612 and 636˚C are due to decomposition of the remainder ligand molecule leading to CoO and NiO as final products. The binuclear Co(II) and Ni(II) complexes $B_2$ and $E_2$ were thermally decomposed in several steps supported by DTA data. The thermograms of complexes $B_2$ and $E_2$ show that the one or three lattice water molecules for complex $B_2$ and $E_2$ are eliminated at the temperature ranges 35–135 and *25–125* ˚C with endothermic peaks at 70 and 90˚C. The four coordinated water molecules are eliminated for both complexes 2 and 8 within the temperature ranges 135–245 and 125–260˚C with endothermic peaks at 175 and 190˚C for complexes $B_2$ and $E_2$. The losses in weight within the temperature ranges 245–435 and 260–450˚C are due to removal of two acetate groups with strong exothermic peaks at 398 and 408˚C for complexes $B_2$ and $E_2$. The decrease in weight in the temperature ranges 435–585 and 450–600 ˚C are due to the elimination of a benzene ring. This step is confirmed by strong exothermic peaks at 582 and 557˚C for complexes $B_2$ and $E_2$, respectively. The last step of decomposition lies within the temperature ranges 585–760 and 600–750˚C associated with broad exothermic peaks at 622 and 634˚C, corresponding to the decomposition of the ligand leading to $Co_2O_3$ and NiO for complexes

Table 2. Results of thermogravimetric analysis of mononuclear and binuclear Co(II) and Ni(II) complexes

| Comp. no | Complex (mol. wt) | Process Temp. | range˚ C | Mass loss=% | |
|---|---|---|---|---|---|
| | | | | Found | Calc. |
| A1 | $[Co(L)_2(H_2O)_2]2H_2O$ (957.90) | Loss of lattice water molecule | 35–100 | 3.65 | 3.76 |
| | $[CoL_2(H_2O)_2]$ (918.00) | Loss of coordinated water | 100–260 | 4.04 | 3.90 |
| | $[CoL_2]$ (764.93) | Loss of 2-imino-pyrimidine part | 260–385 | 21.14 | 20.85 |
| | $[CoL_2]$ (639.72) | Loss of $2SO_2$+ 2 benzene rings | 385–580 | 33.56 | 33.21 |
| | CoO is formed as a final product after the whole molecule degrades (585–750°C). | | | | |
| B1 | $[Ni(L)_2(H_2O)_2]2H_2O$ (989.82) | Loss of lattice water molecule | 25–110 | 3.96 | 3.77 |
| | $[NiL_2(H_2O)_2]$ *(953.79)* | *Loss of coordinated water molecule* | *110–225* | *4.12* | *3.92* |
| | $[NiL_2]$ *(917.76)* | *Loss of 2-imino- pyrimidine* | *225–415* | *23.34* | *22.25* |
| | $[NiL_2]$ *(715.54)* | Loss of $2SO_2$+ 2 benzene rings | *415–560* | 34.12 | *33.87* |

| | | | | | |
|---|---|---|---|---|---|
| | *Degradation of whole molecule and formation of NiO as a final product (560–780˚C)* | | | | |
| A2 | *$[Co_2L(AcO)_2(H_2O)_4]$ $H_2O$ (755.56)* | Loss of lattice water molecule | *35–135* | *2.45* | *2.38* |
| | $[Co_2L(AcO)_2(H_2O)_4]$ (737.55) | Loss of coordinated water | 135–245 | 10.54 | 9.87 |
| | $[Co_2L(AcO)_2]$ (665.49) | Loss of 2 acetic acid | 245–435 | 17.07 | 17.74 |
| | [CoL] (547.40) | Loss of benzene ring | 435–585 | 16.12 | 16.53 |
| | The entire molecule is degraded, and $Co_2O_3$ is formed as a by product (585–760˚C) | | | | |
| B2 | *$[Ni_2L(AcO)_2(H_2O)_4]$ $3H_2O$ (789.08)* | Loss of lattice water molecule | *25–125* | *2.64* | *2.30* |
| | $[Ni_2L(AcO)_2(H_2O)_4]$ (737.07) | Loss of coordinated water | 125–260 | 10.42 | 9.85 |
| | $[Ni_2L(AcO)_2]$ (665.49) | Loss of 2 acetic acid | 260–450 | 17.76 | 17.52 |
| | [NiL] (547.40) | Loss of benzene ring | 450–600 | 11.61 | 11.4 |
| | The entire molecule is degraded, and NiO is formed as a by product (600–750˚C) | | | | |

**IR Spectra**

A careful comparison of the spectrum of the ligand and its metal complexes revealed the most important IR assignments in the spectrum of the free Schiff base as well as the bonding sites (Table 6). Broad bands can be seen in the IR spectrum of Schiff base at 3474 $cm^{-1}$ (υ OH) and 3176 $cm^{-1}$ (υ NH). The υ C=N vibration of the azomethine and pyrimidine rings is responsible for the strong bands at 1627 and 1575 $cm^{-1}$. The intramolecular H-bonding vibration (O–H–N) is assigned to a medium intensity band at 2593 $cm^{-1}$ in the Schiff base. This is a common occurrence for aromatic azomethine compounds with an OH group in the ortho position of a C=N group. This band vanished entirely from the metal complexes. The SO2 group's vasy and vsym are assigned to the two bands at 1343 and 1166 cm

1. The Schiff base behaves as a dibasic tetradentate ligand in the IR spectra of the binuclear metal complexes B2, C2, D2, and E2, whereas the Schiff base is monobasic bidentate in the mononuclear complexes B1, C1, D1, and E1. The mode of chelation is elucidated from the following evidences: 1) . The deprotonation of the enolic and phenolic OH groups is revealed by the disappearance of vOH bands in the complexes, indicating that the proton of the OH group is displaced by the metal ions during complex formation.

2) The IR spectra of complexes A2, B2, C2, and D2 showed a 11–22 cm $^{-1}$ shift to lower wavenumbers in vC=N of both the pyrimidine and azomethine moieties. These findings indicate that the azomethine and one O-atom of the pyrimidine ring are both involved in metal ion coordination. The vC=N band of the pyrimidine ring in the range 1584–1546 cm$^{-1}$ is unaffected by complexation for mononuclear complexes B1, C1, D1, and E1, indicating that the N-atoms of the pyrimidine ring are not involved in complex formation.

3) For Co(II) complex B2, the bands due to vasy and vsym of the acetate group can be found at 1432 and 1367 cm$^{-1}$, and for the acetate complexes at 1453 and Table 3. IR and electronic spectra of complexes 1375 cm$^{-1}$ for Ni(II) complex C2. The Δv values in cm $^{-1}$ for complexes B2 and C2 are 90 and 70 cm$^{-1}$, respectively, indicating the presence of bidentate acetate groups. Cu(II) complex D2 and Mn(II) complex E2 exhibit two bands at 1625 and 1394 cm$^{-1}$ and 1620 and 1412 cm $^{-1}$, respectively, due to vasy and vsym of the acetate group. For complexes 6 and 8, the Δv values between vasy and vsym are 213 and 205 cm $^{-1}$, respectively. These values exceed 210 cm$^{-1}$, indicating the presence of monodentate acetate groups.

4) For both lattice and coordinated water molecules, the presence of water molecules in the complexes results in broad bands at 3474-3423

cm $^{-1}$ (v$H_2O$) and 1610–1595 cm$^{-1}$ (δ$H_2O$). Bands at 954 –932 cm$^{-1}$ (ρ$H_2O$) and 882–851 cm$^{-1}$ (ω$H_2O$) are also produced by coordinated $H_2O$ molecules. The latter bands (ρ$H_2O$+ ω$H_2O$) are missing from the spectrum of complex D1, which contains only lattice water. The IR bands of the lattice water molecules are absent in the spectrum of complex D1 heated at 150 ˚C for 2 hours, whereas the intensity of the v$H_2O$ and δ$H_2O$ bands was noticeably reduced in the spectrum of complex E1. Bands caused by various types of vibrations of the coordinated water molecules vanished after complex E1was heated to 250 C for 2 hours. However, in the latter case, the IR spectrum was found to be altered, presumably due to some decomposition in the anhydrous complex.

5) In the IR spectra of the complexes, 936–931 cm$^{-1}$, the v S-N band shifts with respect to the ligand, 913 cm$^{-1}$. This could be attributed to deprotonation of the sulfonamido group and, as a result, a shortening of the S–N bond length.

6) The appearance of new bands in the 580-595 cm $^{-1}$ and *362- 378* cm $^{-1}$ regions, respectively, attributed to vM- O and vM- N, reflects the metal ions' bonding to oxygen and nitrogen atoms.

7) The spectra of complexes B2, C2, D2, and E2 lack characteristic sulfonamide (–SO2NH–) group frequencies [v$_{SO2}$ asy and v$_{SO2}$ sym] and NH vibrations. This corresponds to the fact that in these complexes, the O of the $SO_2$ group coordinates in the enolic form via deprotonation. The appearance of new δ$_{NSO}$ bands in the 1451–1418 and 1357–1348 cm$^{-1}$ ranges confirms the Schiff base's enolisation.

Table 3. IR spectra of complexes

| No. | Compound | υ(OH) | υ (C=N) $_{imine}$ | υ (C=N) | υ(M-N $_{phenolic}$ | υ (M-N | υ (M-O) |
|---|---|---|---|---|---|---|---|

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| A1 | HL | 3474 | 1626 | 1575 | | | |
| B1 | $[Co(L)_2(H_2O)_2]2H_2O$ | 3437 | 1578 | 1590 | 449 | 367 | 595 |
| B2 | $[CoL(AcO)_2(H_2O)_4]2H_2O$ | 3435 | 1576 | 1586 | 451 | 369 | 593 |
| C1 | $[Ni(L)_2(H_2O)_2]2H_2O$ | 3431 | 1581 | 1589 | 453 | 372 | 591 |
| C2 | $[Ni_2L(AcO)_2(H_2O)_4]H_2O$ | 3425 | 1583 | 1593 | 455 | 374 | 589 |
| D1 | $[CuL_2]3H_2O$ | 3423 | 1572 | 1595 | 457 | 378 | 587 |
| D2 | $[Cu_2L(AcO)_2(H_2O)_2]\ H_2O$ | 3429 | 1572 | 1597 | 455 | 376 | 586 |
| E1 | $[MnL_2(H_2O)_2]2H_2O$ | 3433 | 1586 | 1591 | 461 | 365 | 582 |
| E2 | $[Mn_2L(AcO)_2(H_2O)_4]\ H_2O$ | 3427 | 1583 | 1596 | 463 | 362 | 580 |

**Electronic Spectra and Magnetic Moments**

The magnetic moments at room temperature (Table 4) for Co(II) complexes B1 and B2 are 5.23 and 4.96 BM, respectively, confirming the octahedral structure of these complexes. Two bands can be seen in the electronic spectra of Co(II) complexes B1 and B2 recorded as Nujol mull: 15621, 18765 $cm^{-1}$ and 17567, 20854 $cm^{-1}$. These bands are assigned to $^4T_1g \rightarrow {}^4T_2g$ (v2) and $^4T_1g \rightarrow {}^4T_2g(p)$ (v3). Additionally, the ligand field parameters support the octahedral structure. The magnetic moment values of Ni(II) complexes C1 and C2 are *3.54*and *3.09* BM, respectively, as expected for spin free octahedral Ni(II) complexes. Two bands can be assigned to the $^3A_2g \rightarrow {}^3T_1g(F)$ (v2) and $^3A_2g \rightarrow {}^3T_1g(p)$ (v3) transitions in the Nujol mull electronic spectra of Ni(II) complexes C1 and C2, respectively, at 14685, 23794 $cm^{-1}$ and 16103, 25543 $cm^{-1}$. The calculated Dq, B, and values are within the range previously reported for an octahedral environment surrounding a Ni(II) ion. The obtained values are less than one, indicating that the metal ligand bonds have a significant amount of covalent character. Furthermore, the values for the complexes are lower than the value for the free ion, indicating orbital overlap and d-orbital delocalization. Cu(II) complexes $D_1$ and $D_2$ have magnetic moment values of 1.86 and 1.77BM, respectively. These data reveal that there is no significant spin coupling between unpaired electrons from various copper atoms. Cu(II) complexes $D_1$ and $D_2$ had electronic spectral bands at 14321, 18878 and 15396, 20356 $cm^{-1}$, respectively. These bands can be assigned to the transitions $^2B_1g \rightarrow {}^2A_1g$ as well as $^2B_1g \rightarrow {}^2Eg$ with a square planar geometry. The magnetic moment values for Mn(II) complexes E1 and E2 are 5.32 and 4.89 BM, respectively, indicating that these complexes have an octahedral structure. Complex E2 has a lower value due to antiferromagnetic interaction between adjacent Mn(II) ions. The electronic absorption spectra of Mn(II) complexesE1 and E2 show two bands that correspond to the octahedral configuration at 15475, 21312 and 18797, 23210 $cm^{-1}$, respectively. $^6A_1g \rightarrow {}^4T_1g(4G)$ and $^6A_1g \rightarrow {}^4Eg(G)$ transitions are assigned to these bands.

Table 4 Electronic spectra and magnetic moments for complexes

| NO. | Compound | $\mu_{eff}$ | **$\Lambda_m$. S cm$^2$ mol$^{-1}$** | **λ nm** | **ʋ cm$^{-1}$** | **Transition** | |
|---|---|---|---|---|---|---|---|
| A1 | HL | - | - | 274<br>300 | 3,571<br>3,333 | $\pi \rightarrow \pi*$<br>n $\rightarrow \pi *$ | - |
| B1 | $[Co(L)_2(H_2O)_2]2H_2O$ | 5.23 | 11.2 | 640<br>569 | 15621<br>17567 | $^4T_1g \rightarrow {}^4T_2g(p)$ (v3) $^4T_1g \rightarrow {}^4T_2g$ (v2) | Octahedral |
| B2 | $[CoL(AcO)_2(H_2O)_4]$ $2H_2O$ | 4.96 | 14.4 | 479<br>532 | 20854<br>18765 | $^4T_1g \rightarrow {}^4T_2g(p)$ (v3)<br>$^4T_1g \rightarrow {}^4T_2g$ (v2) | Octahedral |
| C1 | $[Ni(L)_2(H_2O)_2]2H_2O$ | 3.54 | 17.6 | 420<br>680 | 23794<br>14685 | $^3A_2g \rightarrow {}^3\ T_1g(p)$ (v3)<br>$^3A_2g \rightarrow {}^3\ T_1g(F)$ (v2) | Octahedral |
| C2 | $[Ni_2L(AcO)_2(H_2O)_4]$ $H_2O$ | 3.09 | 10.9 | 391<br>621 | 25543<br>16103 | $^3A_2g \rightarrow {}^3T_1g(p)$ (v3)<br>$^3A_2g \rightarrow {}^3\ T_1g(F)$ (v2) | Octahedral |
| D1 | $[CuL_2]3H_2O$ | 1.86 | 18.4 | 529<br>698 | 18878<br>14321 | $^2B_1g \rightarrow {}^2A_1g$<br>$^2B_1g \rightarrow {}^2Eg$ | square planar |
| D2 | $[Cu_2L(AcO)_2(H_2O)_2]$ $H_2O$ | 1.77 | 15.1 | 649<br>649 | 20356<br>15396 | $^2B_1g \rightarrow {}^2A_1g$<br>$^2B_1g \rightarrow {}^2Eg$ | square planar |
| E1 | $[MnL_2(H_2O)_2]2H_2O$ | 5.32 | 15.7 | 469<br>646 | 21312<br>15475 | $^6A_1g \rightarrow {}^4\ T_1g(4G)$ $^6A_1g \rightarrow {}^4Eg(G)$ | Octahedral |
| E2 | $[Mn_2L(AcO)_2(H_2O)_4]$ $H_2O$ | 4.89 | 12.4 | 430<br>531 | 23210<br>18797 | $^6A_1g \rightarrow {}^4\ T_1g(4G)$ $^6A_1g \rightarrow {}^4Eg(G)$ | Octahedral |

## Biological Effects

Table 8 shows the results of a primary study of the Minimum Inhibitor Concentrations (MIC) of Schiff base and its complexes on Gram positive bacteria (Staphylococcus aureus and Bacillus subtilis) and Gram negative bacteria (Escherichia coli and Pseudomonas aeruginosa). Table 8 shows that the inhibition is much greater for most metal complexes than the Schiff base on Gram positive and Gram negative bacteria. In comparison to the other metal complexes, Cu(II) complexes D1 and D2 have the best inhibitory effect on Gram negative and Gram positive bacteria. Binuclear Ni(II) complex C2 inhibits both Gram positive and Gram negative bacteria, but it is less effective on Staphylococcus aureus than complex D1. Binuclear Cu(II) complex D2 has a stronger antibiotic effect on Gram negative and Gram positive bacteria than complex D1. According to the data in Table 8, the order of inhibition of all complexes in the activity of the bacteria studied is as follows. For Escherichia coli, D1>C1, C2>D2>B2> ligand, Pseudomonos aeruginosa, C2>D2>D1>D2, C1>ligand, Bacillus subtilis, B2, D2>C1, C2, D1, ligand, and Staphylococcus aureus, 5>C1, C2, D2>B2> ligand. The increased activity of metal chelates can be explained using chelation theory. Because of the overlap with the ligand orbital, the polarity of the metal ion is greatly reduced during chelation. Furthermore, it improves the lipophilicity of the complexes by increasing the delocalisation of π -electrons across the entire chelate ring. The bonding of the metal ions to the ligand can be represented as shown in Scheme 3 based on the information obtained in this study.

Table 8. The lowest inhibitor concentration of Schiff base and complexes against Gram negative and Gram positive bacteria

| Compound | *E. coli* | *S. aureus* | *P. aeruginosa* | *B.subtilis* |
|---|---|---|---|---|
| HL | 300 | 200 | 150 | 300 |
| $[Co(L)_2(H_2O)_2]2H_2O$ | 300 | 200 | 150 | 300 |
| $[CoL(AcO)_2(H_2O)_4]2H_2O$ | 150 | 150 | 5 | 150 |
| $[Ni(L)_2(H_2O)_2]2H_2O$ | 150 | 150 | 5 | 150 |
| $[Ni_2L(AcO)_2(H_2O)_4]H_2O$ | 70 | 150 | 150 | 70 |
| $[CuL_2]3H_2O$ | 80 | 7 | 150 | 80 |
| $[Cu_2L(AcO)_2(H_2O)_2]\ H_2O$ | 8 | 70 | 150 | 8 |
| $[MnL_2(H_2O)_2]2H_2O$ | 80 | 9 | 8 | 80 |
| $[Mn_2L(AcO)_2(H_2O)_4]\ H_2O$ | 70 | 70 | 7 | 8 |

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