

Synthesis, structural characterization and biological aspects of divalent transition metal complexes derived from 2, 5 diacetyl furan and 2-thia-6-aza-bicyclo [4.2.0]oct-4-en-7-one based Schiff base

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Biologically active dinuclear complexes $[M_2(C_{44}H_{52}N_{20}O_2S_8)X_4]$ of Cu(II), Ni(II) and Co(II) with Schiff base ligand ($C_{22}H_{26}N_{10}OS_4$) got through the buildup of 2,5-diethylidene furan bis (thiocarbohydrazide) with 2-thia-6-aza-bicyclo[4.2.0]oct-4-en-7-one. The recently prepared Schiff base and its metal derivatives have been basically portrayed with the assistance of elemental analysis, condensation measurement, magnetic measurement and their structure configuration explain with the help of different spectroscopic (electronic, IR, 1H NMR, ^{13}C NMR, GCMS) systems. The electronic spectra of the metal complexes (metal ligand derivatives) demonstrate an octahedral geometry of the middle metal ion. The ligand and its metal derivatives have been screened for their antioxidant and antimicrobial hindering potential and compared with standard medications butylated hydroxyanisol (free radical searching active), Imipenem (antibacterial) and Miconazole (antifungal). $[Ni_2(C_{44}H_{52}N_{20}O_2S_8)(OAc)_4]$ demonstrates best antimicrobial action against the contemplated microorganism, and $[Cu_2(C_{44}H_{52}N_{20}O_2S_8)(OAc)_4]$ demonstrates the best free radical searching action.

Keyword: Schiff base, 2, 5-diacetyl furan, Thiocarbohydrazide, M(II) complexes, Antimicrobial activity, Antioxidant assay, Spectroscopic study

Schiff base is a premium class of compound in modern organic chemistry with a variety of uses such as they have been equipped for forming extremely stable complexes (derivatives) with transition metal¹. Hugo Schiff depicted the condensation between dynamic $-C=O$ and $-NH_2$ to form Schiff base ($-C=NH-$)². Moreover the field of Schiff bases is rapidly evolving in coordination chemistry in light of extensive variety of potential utilization of their biological, analytical and catalytical action³⁻⁶. There have been distinctive prominent cases on action of Schiff base complexes in heterogenous and additionally homogenous catalysis such as, carboxylation, oxidation, epoxidation and hydrolysis⁷⁻¹¹. Metal complexes are additionally utilized as common oxygen transporters, antifertility, enzymatic operators and in addition planning of chemical reactions^{12,13}. Various examinations on Schiff base hydrazone of pyridoxal phosphate and its comparable derivatives to have been accounted for to help in understanding the action of mechanism for vitamin B6-containing free ligand¹⁴. Amid the most recent couple of years the point of 3d metal complexes of Schiff base ligands to get ready dinuclear complexes¹². The development of

macrocyclic complexes depends on the extent of the macrocycles (ligand), nature of donor atom and complexometry behavior of ions involved in coordination¹³⁻¹⁶. Dinuclear metal complexes of Schiff base ligand have been utilized beforehand to study several aspects related to various industrial processes such as catalytic oxidation, formation of oxygenates and hydrolysis of capped mono ribonucleotides, these process are not done by the analogous mononuclear complexes¹⁷⁻¹⁹.

In present a broad literature study reveals that no work has been done for the synthesis of Schiff base metal derivative with the condensation of 2,5-diacetyl furan, thiocarbohydrazide and 2-thio-6-aza-bicyclo[4,2,0]octo-4-ene-7-one, hence it engrossed our attention regarding synthesis, structure elucidation and biological action of the compounds.

Experiment

Synthesis of 2,5 diethylidene furan bis (thiocarbohydrazide)

2, 5-diacetyl furan (2.46 g, 16.01 mmol) was dissolved in ethanol and to this solution was added thiocarbohydrazide (3.67 g, 0.034 mol) in a 1:2 molar ratio containing a few drop of concentrated HCl.

The solution was refluxed for 300 min. The yield was separated, recrystallized by ethanol and dried under reduced pressure.

Synthesis of ligand 2,5 diethylidene furan bis [1-(2-thia-6-aza-bicyclo[4.2.0]oct-4-en-7-ylidene)thiocarbonohydrazide]

2-thia-6-aza-bicyclo[4.2.0]oct-4-en-7-one (2.02 g, 14.32 mmol) in ethanol (20 mL) was added in a solution of 2,5 diethylidene furan bis (thiocarbohydrazide) (8.22 g, 14.32 mmol) in 45 mL ethanol containing a couple of drops of concentrated HCl. The response blend was refluxed for 360 min. The blend was cooled at room temperature and the solvent recovered under reduced pressure by rotavapor until a solid product was formed, washed with chilled ethanol and dried under vacuum. Yield 65%; Melting point 131 °C (scheme 1). IR (KBr ν , cm^{-1}): (N^2H) 3233, (C=S) 2140, (C=N) 1612, (N-N) 1112, (C-C) 766, (C=C, aromatic) 1544, (C-H, aromatic) 3044, (NH, hydrazide) 3154. UV/vis (Nujol mul , nm): $\lambda = 366, 422, 478$. UV/vis (1×10^{-4} mol, DMSO, nm):

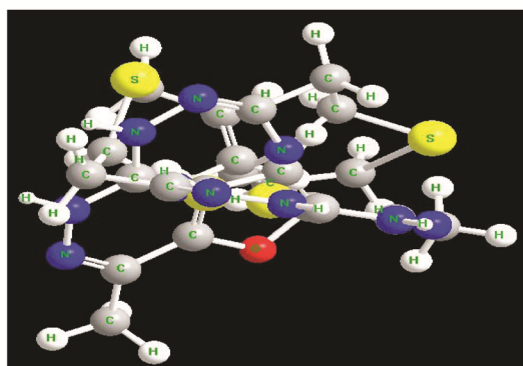
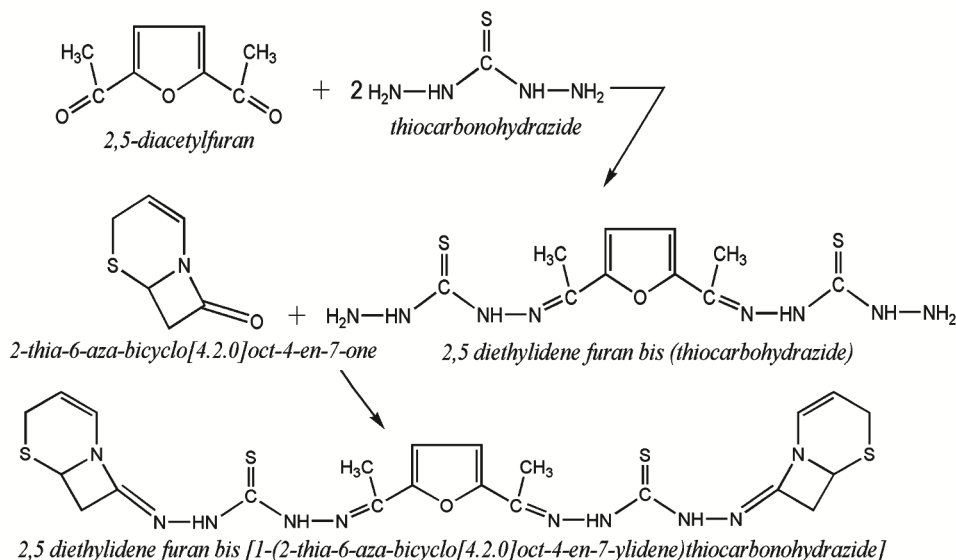
$\lambda = 366, 388, 454$. ^1H NMR (300 MHz, DMSO- d_6) $\delta = 6.35\text{--}7.55$ (m, 4H, β -lactam ring), 8.13 (s, furan), 10.15 (s, 4x1H, NH of Hydrazide). ^{13}C NMR (300 MHz, DMSO- d_6 , ppm) $\delta = 172.8$ (C=N), 198.3 (C=S), 155.6, 139.9, 104.7, 137.6, 59.6, 35.3 (Ar-C), 12.3 (CH_3).

Synthesis of the Cu(II), Ni(II) and Co(II) edifices

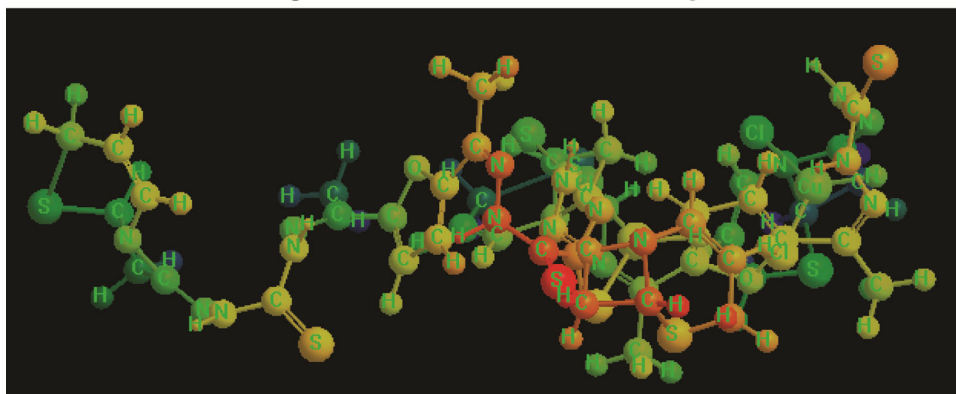
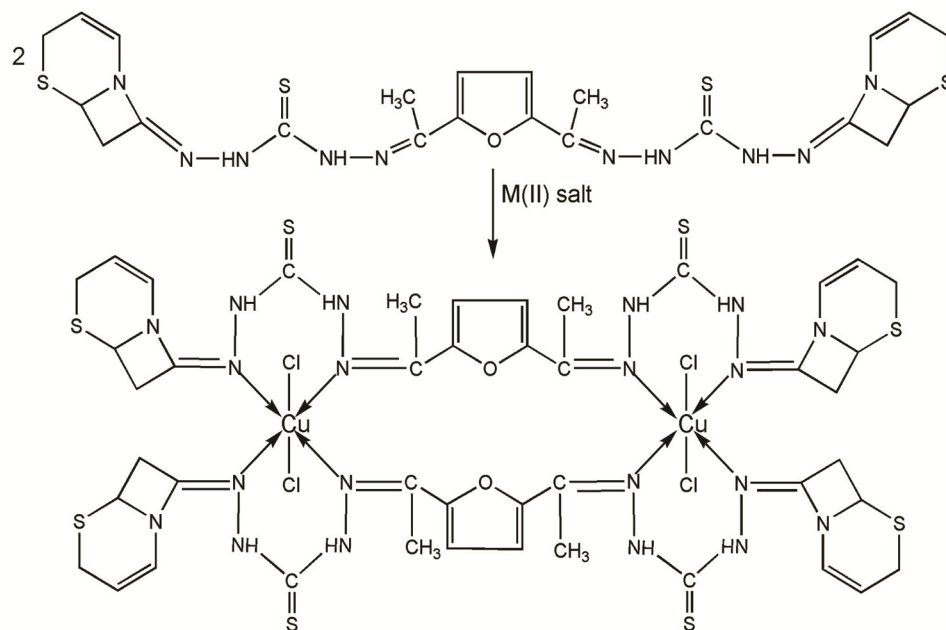
The solution of divalent metal salt Cu (II), Ni (II) and Co (II) (2.0 mmol) in methanol was added to a hot ethanolic solution (75 °C) of ligand (2.0 mmol), the blend was refluxed for 8 h and concentrated. The precipitate was separated washed with methanol and dried under vacuum over anhydrous CaCl_2 (60–71% yield) (Scheme 2).

Synthesis of the metal complex (1)

Synthesis of $[\text{Cu}_2(\text{C}_{44}\text{H}_{52}\text{N}_{20}\text{O}_2\text{S}_8)\text{Cl}_4]$ complex (1). A solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.525 g, 3.112 mmol) in methanol (15 mL) was added to a hot ethanolic solution (75 °C) of HL (1.617 g, 2.817 mmol, 30 mL),



Synthesis of Schiff base ligand
Scheme 1



Synthesis of Schiff base metal complexes

Scheme 2

and the response blend was refluxed for 480 min. The solution was concentrated, the precipitate was separated, washed with methanol and dried under vacuum over anhydrous CaCl_2 (Yield 1.39 g, 65%). Conductance Λ_m : $57\Omega^{-1}\text{cm}^2\text{mol}^{-1}$. IR (KBr ν , cm^{-1}): (N^2H) 3241, ($\text{C}=\text{N}$) 1639, ($\text{C}=\text{O}$) 1723, ($\text{N}-\text{N}$) 1120, ($\text{C}-\text{C}$) 759, ($\text{C}=\text{C}$, aromatic) 1544, ($\text{C}-\text{H}$, aromatic) 31401, (NH , hydrazide) 3041, ($\text{M}-\text{N}$) 422, ($\text{M}-\text{Cl}$) 311. UV/vis (Nujol mul (nm)): $\lambda=278, 325, 371, 420, 511, 717$ and 1151 .

Synthesis of the metal complex (2)

Solution of $[\text{Cu}_2(\text{C}_{44}\text{H}_{52}\text{N}_{20}\text{O}_2\text{S}_8)(\text{NO}_3)_4]$ complex (2). The solution of $\text{Cu}(\text{NO}_3)_2\cdot\text{H}_2\text{O}$ (0.691 g, 3.374 mmol) in methanol (18 mL) was added to a hot solution (75°C) of HL (1.670 g, 2.910 mmol) in ethanol (35 mL), response blend was refluxed for 480 min and concentrated. The precipitate was

separated with methanol and dried under vacuum over anhydrous CaCl_2 (Yield 1.59 g, 68%). Conductance Λ_m : $69\Omega^{-1}\text{cm}^2\text{mol}^{-1}$. IR (KBr ν , cm^{-1}): (H_2O) 3421, (N^2H) 3269, ($\text{C}=\text{O}$) 1723, ($\text{C}=\text{N}$) 1648, ($\text{C}-\text{C}$) 773, ($\text{C}=\text{C}$, aromatic) 1541, ($\text{C}-\text{H}$, aromatic) 3111, (NH , hydrazide) 3133, ($\text{N}-\text{N}$) 1119, ($\text{M}-\text{N}$) 429, ($\text{M}-\text{O}$) 481. UV/vis (Nujol mul, nm): $\lambda=261, 272, 352, 413, 522, 729$ and 1149 .

Synthesis of the metal complex (3)

Synthesis of $[\text{Cu}_2(\text{C}_{44}\text{H}_{52}\text{N}_{20}\text{O}_2\text{S}_8)(\text{OAc})_4]$ complex (3). The solution of $\text{Cu}(\text{OAc})_2\cdot 2\text{H}_2\text{O}$ (0.782 g, 3.512 mmol) in methanol (17 mL) was added to a hot solution (75°C) of HL (1.654 g, 2.881 mmol) in ethanol (35 mL), the response blend was refluxed for 480 min and concentrated. The precipitate was separated washed with methanol and dried under vacuum over anhydrous CaCl_2 (Yield 1.72 g, 71%).

Conductance Λ_m : $61 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. IR (KBr ν , cm^{-1}): (H₂O) 3341, (N²H) 3249, (C=O) 1699, (C=N) 1700, (N-N) 1122, (C-C) 761, (C=C, aromatic) 1544, (C-H, aromatic) 3029, (NH, hydrazide) 3149, (M-N) 421, (M-O) 511 $\nu_{\text{sym}}(\text{OC}(\text{O})\text{CH}_3)$ 1555 (m), $\nu_{\text{asym}}(\text{OC}(\text{O})\text{CH}_3)$ 1366, ($\Delta=193\text{cm}^{-1}$). UV/vis (Nujol mul, nm): $\lambda=266, 269, 341, 522, 729$ and 1155.

Synthesis of the metal complex (4)

Synthesis of [Ni₂(C₄₄H₅₂N₂₀O₂S₈)Cl₄] complex (4). The solution of NiCl₂.6H₂O (0.736 g, 3.121 mmol) in methanol (20 mL) was added to a hot solution (75 °C) of HL (1.650 g, 2.875 mmol) in ethanol (40 mL), the response blend was refluxed for 480 min and concentrated. The precipitate was separated, washed with methanol and dried under vacuum over anhydrous CaCl₂ (Yield 1.45 g, 61 %). Conductance Λ_m : $45 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. IR (KBr ν , cm^{-1}): (H₂O) 3299, (N²H) 3266, (C=O) 1739, (C=N) 1679, (N-N) 1166, (M-N) 448, (C-C) 751, (C=C, aromatic) 1544, (C-H, aromatic) 3039, (NH, hydrazide) 3139, (M-Cl) 333. UV/vis (Nujol mul, nm): $\lambda=262, 291, 367, 483, 711, 1156$.

Synthesis of the metal complex (5)

Synthesis of [Ni₂(C₄₄H₅₂N₂₀O₂S₈)(NO₃)₄] complex (5). The solution of Ni(NO₃)₂.6H₂O (0.931 g, 3.214 mmol) in methanol (15 mL) was added to a hot ethanolic solution (35 mL) at 75 °C of HL (1.785 g, 3.110 mmol), the response blend was refluxed for 480 min and concentrated. The precipitate was separated, washed with methanol and dried under vacuum over anhydrous CaCl₂ (Yield 1.73 g, 64%). Conductance Λ_m : $57 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. IR (KBr ν , cm^{-1}): (H₂O) 3431, (N²H) 3269, (C=O) 1729, (C=N) 1654, (N-N) 1112, (C-C) 755, (C=C, aromatic) 1551, (C-H, aromatic) 3042, (NH, hydrazide) 3139, (M-N) 421, (M-O) 499. UV/vis (Nujol mul, nm): $\lambda=251, 277, 411, 521, 768$ and 1161.

Synthesis of the metal complex (6)

Synthesis of [Ni₂(C₄₄H₅₂N₂₀O₂S₈)(OAc)₄] complex (6). The solution of Ni(OAc)₂.4H₂O (0.790 g, 3.186 mmol) in methanol (16 mL) was added to a hot solution (75 °C) of HL (1.699 g, 2.961 mmol) in ethanol (30 mL), the response blend was refluxed for 480 min and concentrated. The precipitate was separated washed with methanol and dried under vacuum over anhydrous CaCl₂ (Yield 1.59 g, 64%). Conductance Λ_m : $48 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. IR (KBr ν , cm^{-1}): (H₂O) 3319, (N²H) 3271, (C=O) 1729, (C=N) 1649, (N-N) 1122, (C-C) 751, (C=C, aromatic) 1542,

(C-H, aromatic) 3033, (NH, hydrazide) 3141, (M-N) 477, (M-O) 515, $\nu_{\text{sym}}(\text{OC}(\text{O})\text{CH}_3)$ 1555, $\nu_{\text{asym}}(\text{OC}(\text{O})\text{CH}_3)$ 1363, ($\Delta=193\text{cm}^{-1}$). UV/vis (Nujol mul, nm): $\lambda=257, 288, 329, 455, 681$ and 1144.

Synthesis of the metal complex (7)

Synthesis of [Co₂(C₄₄H₅₂N₂₀O₂S₈)Cl₄] complex (7). The solution of CoCl₂.6H₂O (0.773 g, 3.265 mmol) in methanol (15 mL) was added to a hot solution (75 °C) of HL (1.601 g, 2.789 mmol) in ethanol (38 mL), the response blend was refluxed for 480 min and concentrated. The precipitate was separated, washed with methanol and dried under vacuum over anhydrous CaCl₂ (Yield 1.42 g, 60 %). Conductance Λ_m : $126 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. IR (KBr ν , cm^{-1}): (H₂O) 3416, (N²H) 3277, (C=O) 1799, (C=N) 1633, (N-N) 1144, (C-C) 777, (C=C, aromatic) 1499, (C-H, aromatic) 3044, (NH, hydrazide) 3212, (M-N) 441, (M-Cl) 329. UV/vis (Nujol mul, nm): $\lambda=259, 333, 464, 651$ and 1066.

Synthesis of the metal complex (8)

Synthesis of [Co₂(C₄₄H₅₂N₂₀O₂S₈)(NO₃)₄] complex (8). The solution of Co(NO₃)₂.4H₂O (0.844 g, 3.314 mmol) in methanol (15 mL) was added to a hot solution (75 °C) of HL (1.717 g, 3.314 mmol) in ethanol (30 mL), the response blend was refluxed for 480 min and concentrated. The precipitate was separated, washed with methanol and dried under vacuum over anhydrous CaCl₂ (Yield 1.69 g, 66%). Conductance Λ_m : $132 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. IR (KBr ν , cm^{-1}): (H₂O) 3388 (br), (N²H) 3274, (C=O) 1689, (C=N) 1635, (N-N) 1133, (C-C) 758, (C=C, aromatic) 1530, (C-H, aromatic) 3048, (NH, hydrazide) 3135, (M-N) 421, (M-O) 491. UV/vis (Nujol mul, nm): $\lambda=248, 271, 326, 531, 718$ and 1153.

Synthesis of the metal complex (9)

Synthesis of [Co₂(C₄₄H₅₂N₂₀O₂S₈)(OAc)₄] complex (9). The solution of Co(OAc)₂.4H₂O (0.866 g, 3.481 mmol) in methanol (18 mL) was added to a hot solution (75 °C) of HL (1.728 mg, 3.010 mmol) in ethanol (35 mL), the response blend was refluxed for 480 min and concentrated. The precipitate was separated, washed with methanol and dried under reduce pressure over anhydrous CaCl₂ (Yield 1.58 g, 61%). Conductance Λ_m : $114 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. IR (KBr ν , cm^{-1}): (H₂O) 3338, (N²H) 3287, (C=O) 1712, (C=N) 1618, (N-N) 1122, (C-C) 761, (C=C, aromatic) 1544, (C-H, aromatic) 3042, (NH, hydrazide) 3155, (M-N) 466, (M-O) 532 cm^{-1} $\nu_{\text{sym}}(\text{OC}(\text{O})\text{CH}_3)$ 1571 (m), $\nu_{\text{asym}}(\text{OC}(\text{O})\text{CH}_3)$

1360 (m) ($\Delta=191\text{cm}^{-1}$). UV/vis (Nujol mul, nm): $\lambda = 272, 286, 343, 492, 641, 1121$.

Pharmacology

Antifungal action

The parasitic species viz. *Rizoctonia sp.*, *Aspergillus sp.*, and *Penicillium sp.* were collected from the tainted host plants on potato dextrose agar (potato (250 g) + dextrose (20 g) + agar (20 g)) medium and culture of the disengaged parasites was purified by single spore confinement technique²⁰. All the recently orchestrated mixes free ligands, its Cu(II), Ni(II), Co(II) metal complexes, standard medication miconazole and control DMSO (dimethylsulfoxide) were screened for their antifungal efficiency against all the selected microorganisms. The solution of each compound at various concentration 1, 1.5 and 2 mg/mL (free ligand, its metal complexes and standard medication miconazole) in DMSO were set up for testing against spore germination. A drop of the arranged solution of each compound (each concentration) was kept independently on glass slides, and reproducing spores of parasitic were lifted with the assistance of an immunizing needle and blended in each drop of each compound independently. All the treatment of every compound, standard medication miconazole and DMSO (control) were recreated thrice on isolated glass slide. Each slide were brooded in humid chambers at 25 °C for 24 h. Each slide was watched for spore germination under the magnifying lens and percentage of inhibition was finally calculated. Every one of the outcomes was compared with standard fungicide miconazole at similar factors.

Antibacterial action

The bacterial strain *Staphylococcus aureus*, *Bacillus subtilis* (gram positive), *Pseudomonas aeruginosa*, *Escherichia coli* and *Salmonella typhi* (gram negative) were acquired from Microbial Type Collection and Gene Bank, Institute of Microbial Technology (IMTECH) Chandigarh, India. All the recently prepared compounds, free ligand, its Cu(II), Ni(II), Co(II) metal derivatives, standard medication Imipenem were screened for their antibacterial action against all the given bacterial strains. Antibacterial exercises were assessed utilizing agar well dispersion technique²¹. The arrangements of each compound (free ligand, its metal derivatives and standard medication Imipenem 2 mg/mL) were set up in DMSO for testing against every one of the pathogen.

Centrifuged pellets of pathogen from a 24 h old culture containing around 104-106 CFU (colony forming unit) / mL were spread on the surface of agar media (agar (20 g) + beef extricate (3 g) + peptones (5 g) out of 1000 mL of distilled water (pH 7.0)) in petri plates. Wells were made in supplements medium with the assistance of a metallic borer and solution of testing compounds was filled in the wells. The tried medium of supplements was autoclaved at 25 °C for 24 h. The antimicrobial inhibition potential of the compounds was calculated by measuring the diameter of hindrance zone (in mm).

Antioxidant test (free radical scavenging action)

Because of the delocalization of the extra electron on the whole molecule DPPH (2,2-diphenyl-1-picrylhydrazyl) is a steady free radical for testing the free radical rummaging action of the metal ligand derivatives. The free radical rummaging action of the recently integrated Schiff base ligand, its metal derivatives were screened at various fixation (25 μg , 50 μg , 75 μg and 100 μg) and compared with standard compound butylated hydroxyanisole. Compounds were taken in various test tubes and volume was made up to 1000 μL by DMF^{22,23}. The relative absorption of DPPH was computed to the deliberate retention of control. The free radical rummaging was ascertained by utilizing the accompanying formula.

$$\% \text{ Radical scavenging activity} = \frac{[A_0 - A_c]}{A_0} \times 100 \quad \dots(1)$$

where

A_0 = Absorption of the control

A_c = Absorption of the sample

Results and Discussion

FAB Mass spectra

The FAB mass spectra (at room temperature) were recorded on JEOL JMS-AX-500 mass spectrometer, GC-MS investigation was performed on a Shimadzu GCMS-QP5050A instrument, Indian Institute of Petroleum Dehradun, India. The FAB mass spectra of recently integrated compound Schiff base ligand and its Cu(II), Ni(II) and Co(II) metal complexes have been recorded (Table 1). The molecular ion (M^+) crests obtained from different compounds are as per the following: (1) $m/z = 573.11$ $C_{22}H_{26}N_{10}OS_4$ (Ligand), (2) $m/z = 1412.96$ $[Cu_2(C_{44}H_{52}N_{20}O_2S_8)Cl_4]$ (complex 1), (3) $m/z = 1521.04$ $[Cu_2(C_{44}H_{52}N_{20}O_2S_8)(NO_3)_4]$ (complex 2), (4) $m/z = 1509.14$ $[Cu_2(C_{44}H_{52}N_{20}O_2S_8)(OAc)_4]$ (complex 3),

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 ₂₂ H ₂₆ N ₁₀ OS ₄	574.11	573.11	42.02, 67.02, 75.00, 139.04, 149.07, 198.02, 213.03, 254.06, 320.07, 361.09, 376.10, 435.09, 545.08,
[Cu ₂ (C ₄₄ H ₅₂ N ₂₀ O ₂ S ₈)Cl ₄]	1413.96	1412.96	42.02, 67.02, 75.00, 139.04, 149.07, 198.02, 213.03, 254.06, 320.07, 361.09, 376.10, 435.09, 545.08, 572.05, 638.06, 704.07, 891.10, 957.11, 1210.16, 1273.09, 1343.03.
[Cu ₂ (C ₄₄ H ₅₂ N ₂₀ O ₂ S ₈)(NO ₃) ₄]	1522.04	1521.04	42.02, 67.02, 75.00, 139.04, 149.07, 198.02, 213.03, 254.06, 320.07, 361.09, 376.10, 435.09, 545.08, 572.05, 638.06, 704.07, 891.10, 957.11, 1210.16, 1273.09, 1397.06.
[Cu ₂ (C ₄₄ H ₅₂ N ₂₀ O ₂ S ₈)(OAc) ₄]	1510.14	1509.14	42.02, 67.02, 75.00, 139.04, 149.07, 198.02, 213.03, 254.06, 320.07, 361.09, 376.10, 435.09, 545.08, 572.05, 638.06, 704.07, 891.10, 957.11, 1210.16, 1273.09, 1391.12.
[Ni ₂ (C ₄₄ H ₅₂ N ₂₀ O ₂ S ₈)Cl ₄]	1403.98	1402.98	42.02, 67.02, 75.00, 139.04, 149.07, 198.02, 213.03, 254.06, 320.07, 361.09, 376.10, 435.09, 545.08, 567.05, 633.06, 699.07, 886.11, 952.12, 1205.17, 1263.10, 1333.04.
[Ni ₂ (C ₄₄ H ₅₂ N ₂₀ O ₂ S ₈)(NO ₃) ₄]	1512.05	1511.05	42.02, 67.02, 75.00, 139.04, 149.07, 198.02, 213.03, 254.06, 320.07, 361.09, 376.10, 435.09, 545.08, 567.05, 633.06, 699.07, 886.11, 952.12, 1205.17, 1263.10, 1387.08.
[Ni ₂ (C ₄₄ H ₅₂ N ₂₀ O ₂ S ₈)(OAc) ₄]	1500.15	1499.15	42.02, 67.02, 75.00, 139.04, 149.07, 198.02, 213.03, 254.06, 320.07, 361.09, 376.10, 435.09, 545.08, 567.05, 633.06, 699.07, 886.11, 952.12, 1205.17, 1263.10, 1381.13.
[Co ₂ (C ₄₄ H ₅₂ N ₂₀ O ₂ S ₈)Cl ₄]	1405.97	1404.97	42.02, 67.02, 75.00, 139.04, 149.07, 198.02, 213.03, 254.06, 320.07, 361.09, 376.10, 435.09, 545.08, 568.05, 634.06, 700.07, 887.11, 953.12, 1206.16, 1265.10, 1335.03
[Co ₂ (C ₄₄ H ₅₂ N ₂₀ O ₂ S ₈)(NO ₃) ₄]	1514.05	1513.05	42.02, 67.02, 75.00, 139.04, 149.07, 198.02, 213.03, 254.06, 320.07, 361.09, 376.10, 435.09, 545.08, 568.05, 634.06, 700.07, 887.11, 953.12, 1206.16, 1265.10, 1389.07.
[Co ₂ (C ₄₄ H ₅₂ N ₂₀ O ₂ S ₈)(OAc) ₄]	1502.15	1501.15	42.02, 67.02, 75.00, 139.04, 149.07, 198.02, 213.03, 254.06, 320.07, 361.09, 376.10, 435.09, 545.08, 568.05, 634.06, 700.07, 887.11, 953.12, 1206.16, 1265.10, 1383.12

(5) $m/z = 1402.98$ [Ni₂(C₄₄H₅₂N₂₀O₂S₈)Cl₄] (complex **4**), (6) $m/z = 1511.05$ [Ni₂(C₄₄H₅₂N₂₀O₂S₈)(NO₃)₄] (complex **5**), (7) $m/z = 1499.15$ [Ni₂(C₄₄H₅₂N₂₀O₂S₈)(OAc)₄] (complex **6**), (8) $m/z = 1404.97$ [Co₂(C₄₄H₅₂N₂₀O₂S₈)Cl₄] (complex **7**), (9) $m/z = 1513.05$ [Co₂(C₄₄H₅₂N₂₀O₂S₈)(NO₃)₄] (complex **8**), (10) $m/z = 1501.15$ [Co₂(C₄₄H₅₂N₂₀O₂S₈)(OAc)₄] (complex **9**). This information is in complete concurrence with the recently synthesized compounds. The spectra display peaks because of the molecular ions assignable to various fragments emerging from the thermal cleavage of the compounds (Fig. 1).

IR spectra

IR spectra was recorded on a FT-IR spectrophotometer (Perkin Elmer) in the range 4000–200 cm⁻¹ utilizing Nujol Mull. In IR range the vanishing of groups 1700 cm⁻¹ ν (C=O), 3380 cm⁻¹ ν_{sym} (NH₂) and 3250 cm⁻¹ ν_{asym} (NH₂) confirmed by the elimination of H₂O molecule²⁴. A band comparing to ν (C=N) shows up at 1641–1658 cm⁻¹ in the spectra,

the position of this band is moved to bring down recurrence in the complex which might be clarified based on drifting of lone pair electron formed by the heteroatom towards the centre metal ion sign that coordination occurs through the nitrogen²⁵ of C=N. A sharp signal shows up at 1170 cm⁻¹ indicating that oxygen of furan is not associated with coordination, the range 3150–3200 cm⁻¹ demonstrates the presence of (N-H) group of thiocarbohydrazide²⁶. A medium range band around 2140 cm⁻¹ demonstrates non-inclusion of S of C=S in coordination. The groups shows in the range ~3020–3060 cm⁻¹ and ~1455–1570 cm⁻¹ might be assigned because of ν (C–H) stretching and ν (C=C) fragrant stretching vibrations of aromatic ring, respectively^{27,28}. The appearance of absorption band at 1400–1445, 1280–1315 and 1020–1045 cm⁻¹ in the IR spectra of the nitrate compound proposes that the nitrates are facilitated to the central metal ion in a unidentate mold²⁹. In IR spectra of the acetic acid derivation gathering can be composed to the metal particle in either bidentate or monodentate design. The two bands groups

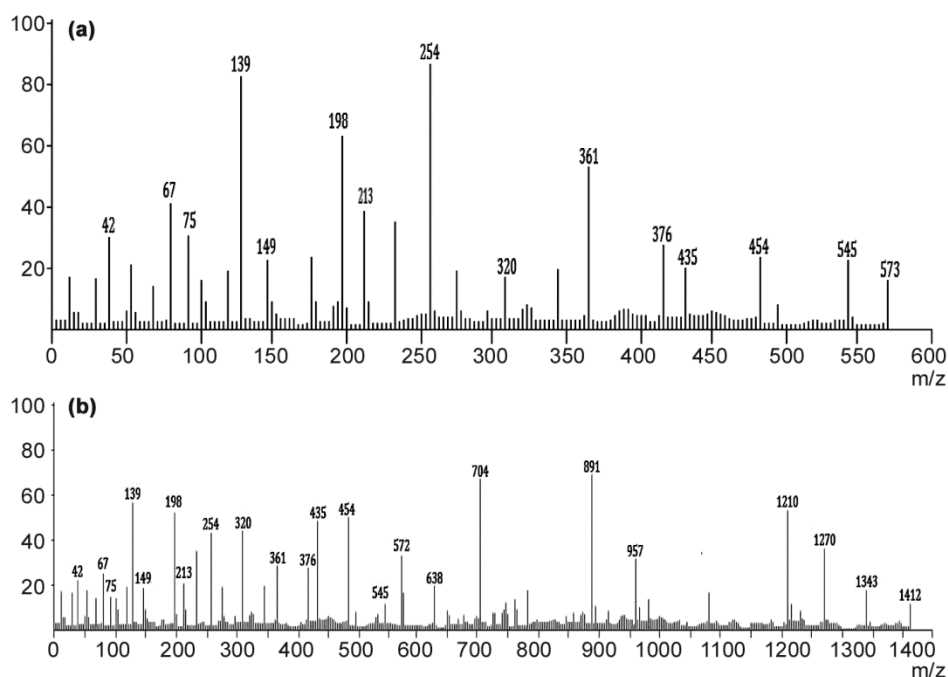


Fig. 1 — FAB mass spectra of (a) Ligand and (b) $[\text{Cu}_2(\text{C}_{44}\text{H}_{52}\text{N}_{20}\text{O}_2\text{S}_8)\text{Cl}_4]$ metal complex.

in the extents $1585\text{--}1590\text{ cm}^{-1}$ and $1370\text{--}1385\text{ cm}^{-1}$ on account of coordination was attributed to $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$, respectively, demonstrating the participation of the carboxylate oxygen in the complex arrangement. The partition esteem $\Delta\nu(\text{COO}^-)$ amongst $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$ in these complexes were in excess of 190 cm^{-1} proposing the coordination of carboxylate group in a monodentate form³⁰. The IR spectra of nitrate complex compound shows groups at $1290\text{--}1310\text{ cm}^{-1}$, $1050\text{--}1065\text{ cm}^{-1}$ and $1435\text{--}1450\text{ cm}^{-1}$ which can be associated to NO_2 symmetric stretching (ν_1); N–O stretching (ν_2); NO_2 awry stretching (ν_5); and out of plane rocking respectively. These frequencies are good with monodentately arranged coordinated nitro groups³¹. The far infrared spectra distinguish coordination of azomethine nitrogen and show band in the range $420\text{--}450\text{ cm}^{-1}$ originate from (M–N) vibration, and band introduce in the range $310\text{--}330\text{ cm}^{-1}$ might be doled out because of $\nu(\text{M}\text{--}\text{Cl})$ vibration^{32–35}. The IR. band shows in the region $235\text{--}260\text{ cm}^{-1}$ in all the nitrate complexes and are assignable to $\nu(\text{M}\text{--}\text{O})$ stretching vibration^{33,34}.

¹H NMR

¹H NMR and ¹³C NMR spectra (at room temperature) (in DMSO-*d*₆) were recorded on a Bruker AVANCE II 300 DRX or AVANCE 400 DRX spectrometer with reference to Me₄Si (0.0 ppm). Schiff bases have been characterized by ¹H and ¹³C

NMR spectra to ensure the structure of ligand *d*₆-dimethylsulfoxide (DMSO-*d*₆) using Me₄Si (TMS) as reference compound. The ¹H NMR spectra of the ligand demonstrates a multiplet at 5.21 ppm, corresponding to the two protons of the furan 2,5-diacetyl moiety. Because of the deshielding environment of –NH, in thiocarbohydrazide, a broad signal appears at the position 9.4–12.1 ppm³⁶. The bunch of signal given by N=C–CH and N–CH on the β-lactam ring showed up at 4.90 and 5.45 ppm, individually. The group of resonance signal attributed to S–CH₂ on the dihydrothiazine ring was seen at position 3.18–3.49 ppm with coupling constant $J=16.9\text{ Hz}$, signal position appears at 2.1–2.8 ppm due to the –CH₂– (cyclic ring)^{37,38}. The multiplets in the region 6.54–8.76 ppm might be assigned to aromatic proton^{39,40}.

¹³C NMR of the Schiff base ligand, the peak position at region 113–158 ppm are associated to aromatic carbon. The peak position 172.8–165.6, 198.3–185.6, and 148.1–12.3 ppm are due to the appearance of C=N, C=S and CH₃ respectively.

Electron turn reverberation

The ESR spectra of Cu(II) complexes were estimated in powder form at room temperature under the applied magnetic field 3000 G. Anisotropic signs with *g* esteem $g_{\parallel} = 2.21$ and $g_{\perp} = 2.18$ fulfilled the condition $g_{\parallel} > g_{\perp} > 2.0023$ demonstrates that

unpaired electron present in dx^2-dy^2 orbital. This shows prolonged bending in Cu(II) complexes from octahedral to D_4h symmetry. At the point when the estimated $G < 4.0$ shows considerable exchange interaction of the complex ($G = 1.523$)⁴¹. Kivelsan and Neiman demonstrated that for an ionic environment g_{\parallel} is regularly 2.3 or more however for covalent condition g_{\parallel} is under 2.3.

Electronic spectral studies, magnetic measurements and molar conductance

Magnetic susceptibility measurement was done at SAIF, on vibrating sample magnetometer (Model PAR 155). Electronic spectra in DMSO were recorded on a Hitachi 330 spectrophotometer (1300–200 nm) at room temperature. The electronic spectra of the Cu(II) complexes shows three signals at the region 10169–10218 cm^{-1} , 14688–14754 cm^{-1} , and 22175–23155 cm^{-1} assigned to the transition ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow T_{1g}(P)$, respectively, band position and magnetic moment value 1.85 B.M. shown that the Cu(II) complex have an octahedral geometry. The band at 19455 cm^{-1} , 26882 cm^{-1} and 29940 cm^{-1} might be credited to $Cl \rightarrow Cu(II)$, $O \rightarrow Cu(II)$ and $N \rightarrow Cu(II)$ charge exchange transition⁴².

The nickel complex shows magnetic moment 2.92 B.M. at room temperature. The absorption band of nickel(II) derivative (complex) demonstrated three

spin permitted transitions: ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ showing up in the range 13330–14411 cm^{-1} , 18580–18641 cm^{-1} and 26375–27841 cm^{-1} individually. The spectral values indicate an octahedral domain of Ni (II) complexes⁴³.

The electronic spectra of the Co (II) complexes gave three groups at 12370–12510 cm^{-1} , 16048–17154 cm^{-1} and 22112–22238 cm^{-1} corresponding to the transition ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1), ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2) and ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$ (ν_3), respectively. Co(II) complex demonstrate magnetic moment at 4.2–4.5 B.M., proposing an octahedral geometry around Co(II) ion^{44,45}. The microanalysis of C, H and N were estimated by elemental analyzer (Perkin-Elmer 2400). Every single metal substance of Cu (II), Ni (II) and Co (II) was determined by atomic absorption spectrophotometer (Perkin-Elmer 5000). The conductivity was measured on computerized digital conductivity meter (HPG framework, G-3001). All complexes give acceptable basic information and conductivity results as shown in Table 2.

Thermal analysis

TG and DTG investigations of the complexes were completed at ambient temperature 900 °C to confirm their molecular structure. Thermal decay of the ligand and its metal derivative (complex) was recorded at temperature increasing rate 10 °C min^{-1} under

Table 2 — Analytical data of the divalent copper, nickel and cobalt complexes

Complex	Mol. wt	C	H	N	M	Colour	Yield	Conductance Λ_M
$C_{22}H_{26}N_{10}OS_4$	574.11	45.97 (45.95)	4.56 (4.54)	24.37 (24.38)				
$[Cu_2(C_{44}H_{52}N_{20}O_2S_8)Cl_4]$	1413.96	37.26 (37.25)	3.70 (3.66)	19.75 (19.72)	8.34 (8.32)	Orange	71%	147 Ω^{-1}
$[Cu_2(C_{44}H_{52}N_{20}O_2S_8)(NO_3)_4]$	1522.04	34.66 (34.65)	3.44 (3.42)	22.05 (22.02)	8.24 (8.26)	Orange	78%	169 Ω^{-1}
$[Cu_2(C_{44}H_{52}N_{20}O_2S_8)(OAc)_4]$	1510.14	41.28 (41.26)	4.26 (4.22)	18.52 (18.55)	8.40 (8.42)	Light Yellow	75%	161 Ω^{-1}
$[Ni_2(C_{44}H_{52}N_{20}O_2S_8)Cl_4]$	1403.98	37.51 (37.50)	3.72 (3.71)	19.89 (19.88)	8.33 (8.30)	Brown	73%	141 Ω^{-1}
$[Ni_2(C_{44}H_{52}N_{20}O_2S_8)(NO_3)_4]$	1512.05	34.88 (34.89)	3.46 (3.44)	22.19 (22.17)	7.75 (7.76)	Gray	72%	158 Ω^{-1}
$[Ni_2(C_{44}H_{52}N_{20}O_2S_8)(OAc)_4]$	1500.15	41.55 (41.54)	4.29 (4.30)	18.64 (18.66)	7.81 (7.82)	Light gray	77%	143 Ω^{-1}
$[Co_2(C_{44}H_{52}N_{20}O_2S_8)Cl_4]$	1405.97	37.50 (37.52)	3.72 (3.71)	19.88 (19.87)	8.36 (8.35)	Light Yellow	75%	131 Ω^{-1}
$[Co_2(C_{44}H_{52}N_{20}O_2S_8)(NO_3)_4]$	1514.05	34.87 (34.86)	3.46 (3.45)	22.18 (22.16)	7.78 (7.77)	Reddish	74%	152 Ω^{-1}
$[Co_2(C_{44}H_{52}N_{20}O_2S_8)(OAc)_4]$	1502.15	41.52 (11.50)	4.29 (4.30)	18.64 (18.62)	7.84 (7.85)	Light Yellow	76%	154 Ω^{-1}

nitrogen environment within a temperature range of 25–900 °C. The DTG bands of the ligand and its metal derivatives were studied by utilizing the rate equation⁴⁶.

$$d\alpha/dt = Ae^{-E^*/(RT)} (1-\alpha)^n \quad \dots(2)$$

where α = decomposed fraction

n = reaction order

E^* = activation Energy

A = frequency factor

R = gas constant

T = temperature in Kelvin

The thermogravimetric examination of the ligand happen in two stage temperature range between 65–192 °C is comparing to 4.12% TG weight reduction and 197–598 °C relating to 92.82 % TG weight reduction due to decay of ligand⁴⁷. The TG band of Cu(II) complex **1** indicates three stage deterioration in temperature range 25–634 °C. The primary weight reduction is seen in temperature range 25–266 °C corresponding to the loss of ethanol and water from the complex. The DTG band related with weak signal at T_{max} 42, 169, 222 °C. The second and third weight reduction occurs in temperature range 266–442 °C and 442–634 °C with strong DTG band T_{max} 332, 485 and 605 °C this weight reduction relates to dehalogenation because of pyrolysis of ligand and metal derivative complex⁴⁸ **1**. The TG band of Ni (II) complex **5** demonstrates weight reduction temperature range 25–388 °C comparing to the expulsion of ethanol and water, related with DTG band at T_{max} 62 °C and 205 °C. After this the thermal decay of complex **5** occur in two stages, the strong DTG band T_{max} 475 °C and 578 °C this weight reduction was due to decarboxylation and deterioration of

complex⁴⁹ **5**. The thermogravimetric after effect of Co(II) complex **7** show weight reduction in temperature range 25–399 °C and 399–612 °C. The temperature range 25–399 °C portrayed by three DTG signals at T_{max} 51, 221 and 202 °C relating to the expulsion of ethanol and water, after this TG band displays signal between the temperature range 399–612 °C because of the dehalogenation, lastly at 588 °C, strong DTG signal was portrayed deterioration of complex⁵⁰ **7** (Fig. 2).

Powder X-ray diffraction analysis

The powder XRD of the metal complexes was utilized for the confirmation of structure and cross section measurement of unit cell (Table 3). The appearance of signal in control X ray diffraction pattern indicates the marginally crystalline nature of the complex. The X ray pattern of metal complexes were recorded at the wavelength $\lambda = 1.5416 \text{ \AA}$ and 2θ esteem between 5–65 °C. The diffractogram delight the crystalline idea of the complexes⁵¹.

Biological Evaluation

Antifungal activity

The results of antifungal action of all the recently integrated compound were compared with standard antifungal medications Miconazole against the *Aspergillus sp.*, *Rizoctonia sp.* also, *Penicillium sp.* at reported concentration 1, 1.5 and 2 mg/mL. From the results (Table 4) it has been additionally seen that the action relies on the lipophilic nature of metal. The compounds are exceptionally powerful against *Aspergillus sp.* at 2 mg/mL compound concentration. The activity is incredibly improved at the higher fixation. DMSO (control) is approximately biologically

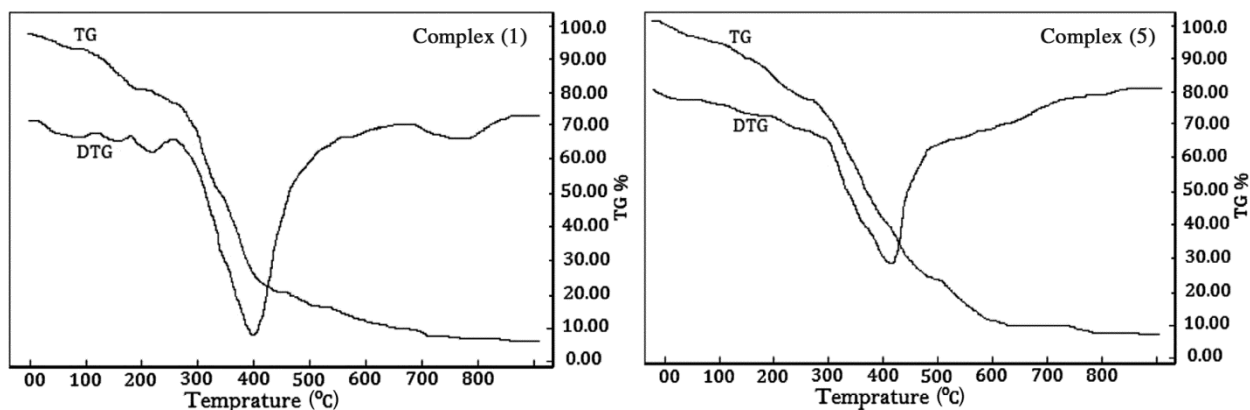


Fig. 2 — T G/DTG curves for the curve-1 (complex-1) and curve-2 (complex-5).

Table 3 — Crystallographic data of Schiff base complexes $[\text{Cu}_2(\text{C}_{44}\text{H}_{52}\text{N}_{20}\text{O}_2\text{S}_8)\text{Cl}_4]$, $[\text{Ni}_2(\text{C}_{44}\text{H}_{52}\text{N}_{20}\text{O}_2\text{S}_8)\text{Cl}_4]$ and $[\text{Co}_2(\text{C}_{44}\text{H}_{52}\text{N}_{20}\text{O}_2\text{S}_8)\text{Cl}_4]$

Data	Copper Complex	Nickel Complex	Cobalt Complex
Empirical formula	$[\text{Cu}_2(\text{C}_{44}\text{H}_{52}\text{N}_{20}\text{O}_2\text{S}_8)\text{Cl}_4]$	$[\text{Ni}_2(\text{C}_{44}\text{H}_{52}\text{N}_{20}\text{O}_2\text{S}_8)\text{Cl}_4]$	$[\text{Co}_2(\text{C}_{44}\text{H}_{52}\text{N}_{20}\text{O}_2\text{S}_8)\text{Cl}_4]$
Formula weight (g/mol)	1413.96	1403.98	1405.97
Wavelength (Å)	1.5416	1.5408	1.5418
Crystal system	Tetragonal	Orthorhombic	Triclinic
2θ range	14.26–54.85	14.54–55.87	17.15–66.64
Rf	0.000028	0.000082	0.000024
Unit cell dimensions (Å)			
a (Å)	7.1864	7.1864	11.1153
b (Å)	11.3032	11.3032	15.3122
c (Å)	15.2432	15.2432	21.4433
α (°)	90 °C	90 °C	90 °C
β (°)	90 °C	90 °C	90 °C
γ (°)	90 °C	90 °C	90 °C
Volume (Å ³)	4238.66	4153.42	5884.97
Crystal size (mm ²)	0.42×0.31×0.19 mm ²	0.44×0.33×0.21 mm ²	0.46×0.35×0.25 mm ²
Limiting indices	–25≤h≤24 –13≤k≤13 –8≤l≤18	–17≤h≤24 –13≤k≤13 –11≤l≤19	–25≤h≤20 –9≤k≤9 –23≤l≤25
Z	4	4	4
D _{calc} (gm/cm ^{–3})	1.9222	1.8744	1.4948
Final R indices [I>2σ(I)]	R ₁ = 0.0392 wR ₂ = 0.1055	R ₁ = 0.0497 wR ₂ = 0.9132	R ₁ = 0.0589 wR ₂ = 0.1239
R indices (all data)	R ₁ = 0.0487 wR ₂ = 0.1097	R ₁ = 0.0513 wR ₂ = 0.9754	R ₁ = 0.0598 wR ₂ = 0.1334
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max and min transmission	0.9754 and 0.8012	0.9132 and 0.5832	0.7654 and 0.6243
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data/restraints/parameters	3498/0/248	5287/0/5134	5151/0/5011
Goodness-of-fit (GOF) on F ²	1.225	1.109	0.999

Table 4 — 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 ₄ S ₄	38	46	51	19	27	32	40	45	49
$[\text{Cu}_2(\text{C}_{44}\text{H}_{52}\text{N}_{20}\text{O}_2\text{S}_8)\text{Cl}_4]$	70	80	86	63	70	78	56	61	73
$[\text{Cu}_2(\text{C}_{44}\text{H}_{52}\text{N}_{20}\text{O}_2\text{S}_8)(\text{NO}_3)_4]$	53	63	80	56	61	73	50	53	62
$[\text{Cu}_2(\text{C}_{44}\text{H}_{52}\text{N}_{20}\text{O}_2\text{S}_8)(\text{OAc})_4]$	82	87	91	68	71	81	61	64	77
$[\text{Ni}_2(\text{C}_{44}\text{H}_{52}\text{N}_{20}\text{O}_2\text{S}_8)\text{Cl}_4]$	77	87	89	67	72	84	61	66	68
$[\text{Ni}_2(\text{C}_{44}\text{H}_{52}\text{N}_{20}\text{O}_2\text{S}_8)(\text{NO}_3)_4]$	65	71	82	58	63	75	54	57	64
$[\text{Ni}_2(\text{C}_{44}\text{H}_{52}\text{N}_{20}\text{O}_2\text{S}_8)(\text{OAc})_4]$	84	89	95	76	80	89	72	73	83
$[\text{Co}_2(\text{C}_{44}\text{H}_{52}\text{N}_{20}\text{O}_2\text{S}_8)\text{Cl}_4]$	75	80	84	68	70	76	61	65	68
$[\text{Co}_2(\text{C}_{44}\text{H}_{52}\text{N}_{20}\text{O}_2\text{S}_8)(\text{NO}_3)_4]$	64	68	73	57	61	69	58	60	62
$[\text{Co}_2(\text{C}_{44}\text{H}_{52}\text{N}_{20}\text{O}_2\text{S}_8)(\text{OAc})_4]$	81	83	91	68	72	76	60	50	67
Miconazole (standard)	59	71	100	65	78	83	76	82	94

inactive as compared to the recently synthesized compounds. Be that as it may, the metal complexes demonstrate preferable action over the ligand^{52,53}. The concentration of the compound is vulnerable for hindrance. $[\text{Ni}_2(\text{C}_{44}\text{H}_{52}\text{N}_{20}\text{O}_2\text{S}_8)(\text{OAc})_4]$ is the complex to indicate 90% action against *Aspergillus sp.*

Minimum inhibitory concentration (MIC) of synthesized compounds

Macrodilution tube was utilized to screen minimum inhibitory concentration of the compounds. MIC is the base concentration of bactericides that will hinder the noticeable development of microorganisms after

overnight incubation⁵⁴. The MIC against *B. subtilis*, *S. aureus*, *E. coli*, *S. typhi* and *P. aeruginosa* were 123, 122, 54, 54 and 51 $\mu\text{g/mL}$ for $\text{C}_{22}\text{H}_{26}\text{N}_{10}\text{O}_4$ (ligand) 29, 28, 25, 22 and 24 $\mu\text{g/mL}$ for the $[\text{Cu}_2(\text{C}_{44}\text{H}_{52}\text{N}_{20}\text{O}_2\text{S}_8)\text{Cl}_4]$, 27, 26, 25, 22 and 23 $\mu\text{g/mL}$ for $[\text{Cu}_2(\text{C}_{44}\text{H}_{52}\text{N}_{20}\text{O}_2\text{S}_8)(\text{NO}_3)_4]$, 25, 24, 24, 20 and 22 $\mu\text{g/mL}$ for $[\text{Cu}_2(\text{C}_{44}\text{H}_{52}\text{N}_{20}\text{O}_2\text{S}_8)(\text{OAc})_4]$, 18, 18, 17, 16 and 17 $\mu\text{g/mL}$ for $[\text{Ni}_2(\text{C}_{44}\text{H}_{52}\text{N}_{20}\text{O}_2\text{S}_8)\text{Cl}_4]$, 14, 14, 12, 12 and 11 $\mu\text{g/mL}$ for $[\text{Ni}_2(\text{C}_{44}\text{H}_{52}\text{N}_{20}\text{O}_2\text{S}_8)(\text{NO}_3)_4]$, 12, 12, 11, 11 and 11 $\mu\text{g/mL}$ for $[\text{Ni}_2(\text{C}_{44}\text{H}_{52}\text{N}_{20}\text{O}_2\text{S}_8)(\text{OAc})_4]$, 38, 35, 37, 35 and 35 $\mu\text{g/mL}$ $[\text{Co}_2(\text{C}_{44}\text{H}_{52}\text{N}_{20}\text{O}_2\text{S}_8)\text{Cl}_4]$, 35, 34, 35, 35 and 33 $\mu\text{g/mL}$ $[\text{Co}_2(\text{C}_{44}\text{H}_{52}\text{N}_{20}\text{O}_2\text{S}_8)(\text{NO}_3)_4]$, 30, 28, 28, 26 and 30 $\mu\text{g/mL}$ $[\text{Co}_2(\text{C}_{44}\text{H}_{52}\text{N}_{20}\text{O}_2\text{S}_8)(\text{OAc})_4]$, 10, 10, 09, 09 and 09 $\mu\text{g/mL}$ for standard medication Imipenem. MIC esteem demonstrated that the Ni derivatives were discovered more intense against all pathogens when contrasted with the other considered complex.

Antibacterial action

The recently synthesized compounds, standard medication Imipenem ($\text{C}_{12}\text{H}_{17}\text{N}_3\text{O}_4\text{S}$) and DMSO (control) were screened for their antibacterial hindrance potential against the bacterial strain *Staphylococcus aureus* and *Bacillus subtilis* (as gram positive strain) and *Pseudomonas aeruginosa*, *Escherichia coli* and *Salmonella typhi* (as gram negative strain) every one of the outcomes against all the strain were compared in Fig. 3. It is observed that the walls of gram negative strains are more complex than gram positive strains because of this all bactericides were less biologically active towards

gram negative strains. $-\text{NH}$ group change transformation action in the biological system, due to this it plays an important role to improve the penetration power/ lipophilicity of the compound. Chelation decreased polarity of the metal ion by neutralizing fractional charge and delocalization of π electrons; chelation expands the lipophilic nature of metal ion, which supports its porousness through the lipid layer of the cell membrane and hindering the metal restricting destinations of enzyme secreted by strain^{55,56}. HPLC instrument comprised of a model waters 600 pump with waters 600 controller, waters 2,996 photodiode array detector, a non polar C_{18} column, 15 cm \times 4.6 mm I.D. with 5 μm particles size (all from waters, Milford Mama, USA) was utilized to examine the lipophilicity of the compound²⁷. HPLC ultra violet detection method at 254 nm, stream rate of 1 mL/min, a column temperature of 25 $^\circ\text{C}$, an infusion volume of 5 μL and a 25 min isocratic mobile phase method methanol, 25 mmol KH_2PO_4 , pH_3 (20:80) was utilized to determine the lipophilicity of the compound⁵⁷.

Antioxidant measure (free radical searching action)

All the results of free radical scavenging action of recently synthesized compounds systematized in Table-5 where free ligand is the main compound which shows excellent (91%), Cu(II) complexes are good, Ni(II) are complexes significant and Co(II) complexes are negligible free radical scavenging activity. These test results were compared with standard medication butylated hydroxyanisol at a same parameter.

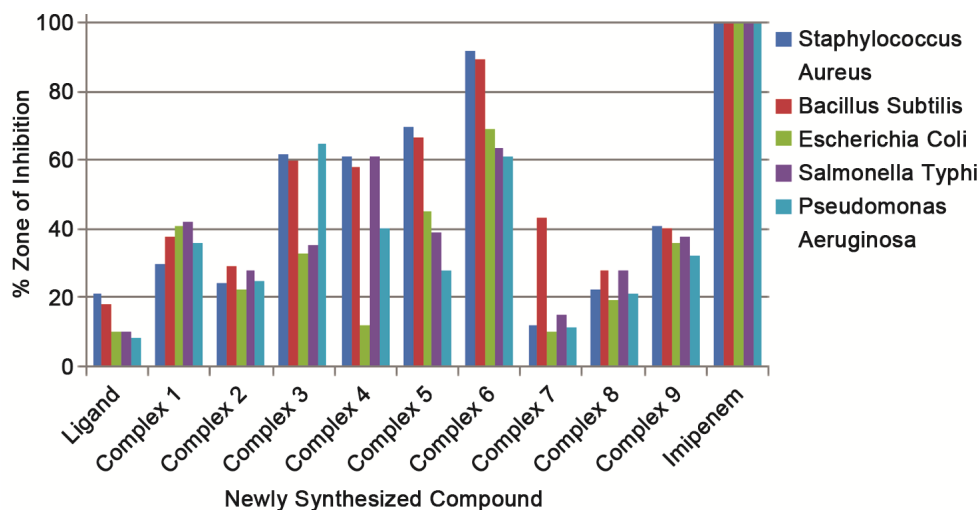


Fig. 3 — Bactericidal screening data of the ligand and their corresponding metal complexes (inhibition zone in mm).

Table 5 — Free radical scavenging activity data of the ligand and their corresponding metal complexes

Concentration	% Radical scavenging activity										
	Ligand ^a	Complexes ^b									BHA (Standard)
	1	2	3	4	5	6	7	8	9		
25 µg	45	22	23	35	18	19	20	11	13	15	60
50 µg	68	41	40	51	32	32	35	18	18	19	77
75 µg	75	60	61	69	48	49	55	28	31	32	85
100 µg	91	72	75	78	61	63	64	32	36	40	100
125 µg	91	72	75	78	61	63	64	32	35	40	100

^aFree radical scavenging activity excellent (90–100%), Good activity (70–80%), Significant activity (40–60%), negligible activity (10–40%),

^bComplex 1 = [Cu₂(HL)Cl₄], 2 = [Cu₂(HL)(NO₃)₄], 3 = [Cu₂(HL)(OAc)₄], 4 = [Ni₂(HL)Cl₄], 5 = [Ni₂(HL)(NO₃)₄], 6 = [Ni₂(HL)(OAc)₄], 7 = [Co₂(HL)Cl₄],

8 = [Co₂(HL)(NO₃)₄], 9 = [Co₂(HL)(OAc)₄], Butylated hydroxyanisol (BHA) = Standard drug.

Conclusions

The spectral data of recently orchestrated compound is in the support of an octahedral geometry of the compounds. These metal complexes, ligand and standard medication were screened biological evaluation against some pathogenic strains. Biological studies reveal that metal complexes are more biologically active than free ligand. Complex [Ni₂(C₄₄H₅₂N₂₀O₂S₈)(OAc)₄] and [Cu₂(C₄₄H₅₂N₂₀O₂S₈)(OAc)₄] indicates best antimicrobial and free radical scavenging results, respectively.

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