



Synthesis, characterization and biological studies of cobalt(II), nickel(II), copper(II) and zinc(II) complexes of vanillin-4-methyl-4-phenyl-3-thiosemicarbazone

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Abstract. Complexes of vanillin-4-methyl-4-phenyl-3-thiosemicarbazone with cobalt(II), nickel(II), copper(II) and zinc(II) metal ions were synthesized and characterized by elemental analysis, molar conductance, magnetic moment, infrared spectra, electronic spectra, ^1H and ^{13}C NMR, mass spectrum and thermal analysis. The low molar conductance values indicate that all the complexes are non-electrolytes. Spectral studies indicate that the ligand act in a tridentate manner coordinating with the metal ion through sulphur, oxygen and nitrogen atoms. Based on magnetic moment measurements, spectral studies and thermal analysis, suitable geometry was proposed for the metal complexes. Thermal stability of the complexes was ascertained on the basis of thermo gravimetric analysis and the lattice parameters, space group and grain size of the ligand and complexes were determined by using powder XRD measurements. Surface morphology of ligand and complexes were studied using SEM analysis. Antimicrobial studies were carried out against gram-positive, gram-negative bacteria and two fungal pathogens.

Keywords. Thiosemicarbazone; transition metal complexes; antimicrobial study.

1. Introduction

Thiosemicarbazones find various applications depending on the donor atoms of ligands, their flexibility and their ability to coordinate either in neutral or deprotonated form.¹⁻³ Thiosemicarbazones are chelating ligands and their complexes are tools useful for a variety of bioinorganic process.^{4,5} Thiosemicarbazones commonly act as bidentate ligand through nitrogen and sulphur atoms.^{6,7} The presence of additional donor groups attached to the thiosemicarbazone moiety helps them to behave as tridentate ligands also.^{8,9} Biological activity is shown by thiosemicarbazone derivatives of aldehydes and ketones.^{10,11} Earlier reports show that their metal complexes, due to their ability to form stable chelates with essential metal ions, exhibit enhanced activity.¹²⁻¹⁵ Certain thiosemicarbazones complexes were reported to have applications as nanoprecursor.^{16,17}

The present study reports the synthesis, characterization and biological activities of cobalt, nickel, copper and

zinc complexes of vanillin-4-methyl-4-phenyl-3-thiosemicarbazone. Biological activity was carried out on two Gram-positive bacteria - *Staphylococcus aureus* and *Bacillus cereus*, two-gram negative bacteria - *Escherichia coli* and *Klebsiella pneumonia* and two fungal pathogens - *Aspergillus niger* and *Penicillium* sp.

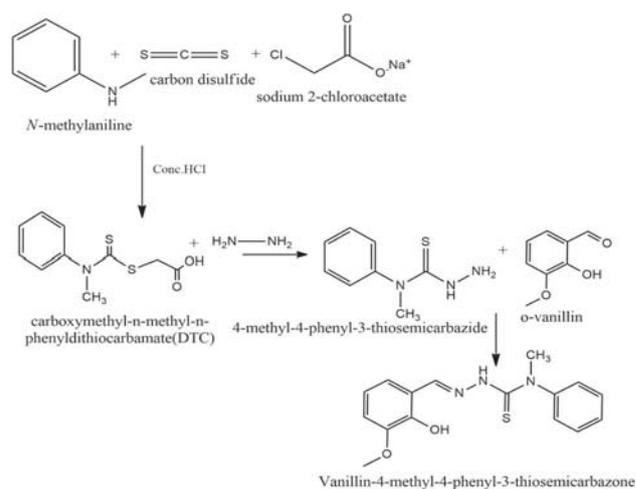
2. Experimental

Analar grade solvents and chemicals were used. Transition metal(II) salts (cobalt/nickel/copper and zinc chlorides), carbon disulfide, N-methyl aniline, sodium hydroxide, sodium chloroacetate, hydrazine hydrate and HCl were purchased from Sigma Aldrich and Merck chemicals. Solvents used for physicochemical measurements were purified by standard methods.

Elemental analysis for C, H, N and S were carried out using ElementarVario EL III CHN analyzer. The magnetic susceptibility measurements were carried out by Gouy's method using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant. Diamagnetic

*For correspondence

corrections were made using Pascal constants. Molar conductance measurements were carried out using 10^{-3} M solutions of the complexes in DMSO solvent at room temperature using digital conductivity meter. Infrared spectra of the ligand and its complexes were recorded using potassium bromide pellets in the range of $4000\text{--}400\text{ cm}^{-1}$ on a Perkin Elmer FT-IR spectrophotometer and the electronic spectra of the ligand and its complexes were recorded using Genesis 10S-UV-VIS spectrophotometer in DMSO solvent. The NMR spectrum was taken in BRUKER Avance –III 400 MHz NMR spectrometer, using DMSO- d_6 as solvent. Powder XRD measurements were conducted using Bruker D.8 Advance X-ray diffractometer. The thermogravimetric analysis was carried out ranging from room temperature to $800\text{ }^\circ\text{C}$ in a Perkin Elmer Diamond TG/DTA at a heating rate of $10\text{ }^\circ\text{C}$.



Scheme 1. Synthesis of ligand.

2.1 Preparation of vanillin 4-methyl-4-phenyl-3-thiosemicarbazone [HVTS]

A mixture of carbon disulfide (12 mL, 0.20 mol) and N-methylaniline (21.6 mL, 0.20 mol) was treated with sodium hydroxide (8.2 g, 0.20 mol) dissolved in 250 mL water. After stirring the solution for 4 h at room temperature, the colour of the solution changed from orange to straw coloured and at this point, sodium chloroacetate (23.2 g, 0.20 mol) was added, stirred and allowed to stand for 24 h. The solution was then acidified with conc. HCl. The resulting solid Carboxymethyl N-methyl-N-phenyl dithiocarbamate was separated by filtration and washed with dil.HCl and dried. Then a mixture of carboxymethyl-N-methyl-N-phenylthiocarbamate, 10 mL of hydrazine hydrate and 5 mL of water was heated on a water bath for half an hour. Purity of the sample was checked by using thin-layer chromatographic technique. The compound separated was filtered, washed with water, dried and recrystallized from ethanol and dried to collect the ligand as white needle-like solid. Yield: 78%, M.p.: $168\text{ }^\circ\text{C}$, $\text{C}_{16}\text{H}_{17}\text{N}_3\text{O}_2\text{S}$, Anal. Found(%): C, 60.91; H, 5.42; N, 13.35; S, 10.16. Calcd. for(%):C, 60.93; H, 5.43; N, 13.32; S, 10.17. IR(KBr, γ/cm^{-1}): (γ_{OH}) 3400, (γ_{NH}) 3438, ($\gamma_{\text{C=S}}$) 824, ($\gamma_{\text{C=N}}$) 1609. ^1H NMR(400 MHz, DMSO- d_6 , TMS): δ 11.32 (1H, s, OH), 2.32 (3H, s, OCH_3), 7.4–8.21 (5H, m, ArH), 6.97–6.9 (3H, m, Ar-H), 8.362 (2H, s, NH_2). ^{13}C NMR(ppm): 181, 147.95, 146.83, 144.54, 144, 129.81, 127.35, 126.49, 121.3, 118.70, 113.16., ESI-MS(m/z): calc: 315.39 Found: 316 (Scheme 1).

2.2 Synthesis of complexes with vanillin 4-methyl-4-phenyl-3-thiosemicarbazone [HVTS]

A hot methanolic solution (30 mL) of vanillin-4-methyl-4-phenyl-3-thiosemicarbazone (0.630 g, 2 mmol) was added dropwise to a hot methanolic solution (30 mL) of 1 mmol cobalt chloride (0.237 g/1 mmol), nickel chloride (0.237 g,

1 mmol)/copper chloride (0.340 g, 2 mmol)/zinc chloride (0.272 g, 2 mmol) with continuous stirring and heated on a water bath at $75\text{ }^\circ\text{C}$ for 4 h. The coloured complexes formed were filtered, washed with methanol to remove unreacted ligand and then dried in vacuum.

2.2a Co(II) complex: Brown solid; Yield; 81%, M.p.; $242\text{ }^\circ\text{C}$, Anal. Found(%): C, 55.86; H, 4.68; N, 12.25; S, 9.37. Calc(%):C,55.89; H,4.69; N, 12.22; S,9.33, IR(KBr, γ/cm^{-1}):(γ_{NH}) 3433, ($\gamma_{\text{C=S}}$)778, ($\gamma_{\text{C=N}}$) 1596, ($\gamma_{\text{M-S}}$) 427, ($\gamma_{\text{M-O}}$) 547, ($\gamma_{\text{M-N}}$) 466.

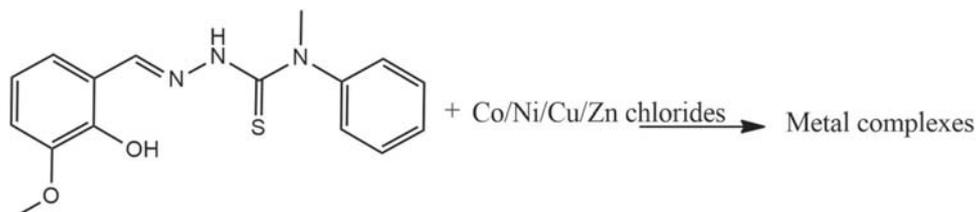
2.2b Ni(II) complex: Black solid; Yield; 82%, M.p.; $162\text{ }^\circ\text{C}$, Anal. Found(%): C,55.93; H, 4.71; N, 12.18; S, 9.35. Calc(%):C,55.91; H,4.69; N, 12.22; S,9.33, IR(KBr, γ/cm^{-1}):(γ_{NH}) 3442, ($\gamma_{\text{C=S}}$)779, ($\gamma_{\text{C=N}}$) 1588, ($\gamma_{\text{M-S}}$) 412, ($\gamma_{\text{M-O}}$) 550, ($\gamma_{\text{M-N}}$) 465.

2.2c Cu(II) complex: Black solid; Yield; 80%, M.p.; $192\text{ }^\circ\text{C}$, Anal. Found(%): C,42.74; H, 4.51; N, 9.36; S, 7.14. Calc(%):C,42.76; H,4.49; N, 9.35; S,7.13, IR(KBr, γ/cm^{-1}):(γ_{NH}) 3446, ($\gamma_{\text{C=S}}$) 777, ($\gamma_{\text{C=N}}$) 1592, ($\gamma_{\text{M-S}}$) 412, ($\gamma_{\text{M-O}}$) 555, ($\gamma_{\text{M-N}}$) 457.

2.2d Zn(II) complex: Light yellow solid; Yield; 76%, M.p.; $206\text{ }^\circ\text{C}$, Anal. Found(%): C,46.61; H, 3.64; N, 10.26; S, 7.53. Calc(%):C, 46.28; H,3.88; N, 10.12; S,7.72, IR(KBr, γ/cm^{-1}):(γ_{NH}) 3404, ($\gamma_{\text{C=S}}$)776, ($\gamma_{\text{C=N}}$) 1595, ($\gamma_{\text{M-S}}$) 421, ($\gamma_{\text{M-O}}$) 564, ($\gamma_{\text{M-N}}$) 446 (Scheme 2).

2.3 Antimicrobial study

Antimicrobial activities of the samples were determined by agar well diffusion method. The media used for the antibacterial test was nutrient broth. The test bacterial strains were inoculated in nutrient broth and incubated at $37\text{ }^\circ\text{C}$ for 24 h. After the incubation period, the culture tubes were compared with the turbidity standard and used. Fresh bacterial culture of 0.1 mL having 108 CFU was spread on the nutrient agar plate using a swab. Wells of 6 mm diameter were punched off into medium with a sterile cork



Scheme 2. Synthesis of complexes.

borer and filled with 50 μ L of the sample by using micropipette in each well in aseptic condition and standard antibiotic was also included as a control. Plates were kept in a refrigerator to allow pre-diffusion of extract for 30 min. Further, the plates were incubated in an incubator at 37 $^{\circ}$ C for 24 h and the antimicrobial activity was evaluated by measuring the zone of inhibition.

Fungal inoculums were prepared by suspending the spores of a fungus (as previously cultured) in saline water, mixed thoroughly, made turbidity standard and used. A spore suspension of fresh fungal inoculums was spread on dextrose agar plates using sterile cotton swabs. After air dried, wells of 6 mm diameter were punched off into medium with a sterile cork borer and filled with 50 μ L (about 50 μ g) of test sample using micropipette in aseptic condition. The plates were kept in a refrigerator to allow pre-diffusion of extract for 30 min and then incubated at 28–37 $^{\circ}$ C for 3–4 days. The activity was evaluated by measuring the zone of inhibition.

3. Results and Discussion

All the complexes were found to be stable at room temperature, insoluble in water and other organic solvents, but soluble in DMSO and DMF. Analytical data of the complexes were found to be in good agreement with their formulation. The molecular formula of the complexes were formulated as $[M(VTS)_2]$ $M=Co(II), Ni(II)$, $[Cu(VTS)Cl] \cdot 2H_2O$, and $[Zn(VTS)Cl]$, $M= Cu(II)$ and $Zn(II)$, HVTS=vanillin-4-methyl-4-phenyl-3-thiosemicarbazide. Cobalt and nickel complexes were found to possess 1:2 metal-ligand stoichiometry while copper and zinc complexes were found to possess 1:1 stoichiometry. The molar conductance values of the complexes in 0.001M DMSO solution lies in the range of 10–21 $\Omega^{-1}cm^2mol^{-1}$ at room temperature. These values confirm the non-electrolytic nature of the complexes.^{18,19}

3.1 ^{13}C -NMR spectrum

The carbon skeleton of the thiosemicarbazone ligand was identified using ^{13}C -NMR spectrum shown in Figure 1. Carbon attached to the C=S group resonates

at downfield shift at 181 ppm.^{20,21} The carbon atom of the phenyl ring attached to the aniline nitrogen also resonates at downward shift at 144 ppm.²² The signals of carbon atoms of the benzene ring attached with methoxy group and a hydroxyl group at 147.91 and 147.95 ppm respectively. The signal of the carbon atom of azomethane at 146.83 ppm. The signal of the carbon atom of the phenyl ring attached to the nitrogen at 144.54 ppm. The carbon atom of the methyl group attached to the nitrogen resonates at 43.89 ppm and methyl group attached to the vanillin derivative resonate at 55.78 ppm. The carbon atoms of the benzene ring were assigned to signal at 127.35 ppm (ortho), 129.810 ppm(meta), 126.49(para) ppm respectively.²³ The carbon atom of the benzene ring of vanillin resonates at 121.37, 118.70, 113.160 ppm respectively.

3.2 1H -NMR spectrum

The proton NMR spectra of the ligand and zinc complex are recorded in d_6 -dimethyl sulphoxide (DMSO- d_6) using trimethylsilane as an internal standard. The chemical shifts of the different types of protons found in the NMR spectrum of the organic ligand is compared with that of the diamagnetic Zn(II) complex. The NMR spectra of the ligand at 11.32 ppm indicate the presence of the phenolic OH group.²⁴ The phenolic OH signal in the spectrum of the ligand is not seen in the spectrum of the zinc complex which indicates that the hydrogen atom of the phenolic group is absent in the complex. The hydrogen atom attached to the nitrogen atom of thiosemicarbazone appears as a singlet at 8.362 ppm. The signal due to azomethane proton gets shifted upon complexation, which is due to the donation of the lone pair of an electron by the nitrogen to the central metal atom resulting in the formation of a coordinate linkage. The protons of the methoxy group attached to the phenolic ring resonate at 2.37 ppm as a singlet.²⁵ The eight aromatic protons resonate in between 7.4–8.21 ppm as multiplet in the ligand.²⁶ The signal due to the aromatic proton and methoxy proton was the same as that of the ligand with a small variation. The proton NMR spectrum of ligand and zinc complex are shown in Figures 2 and 3.

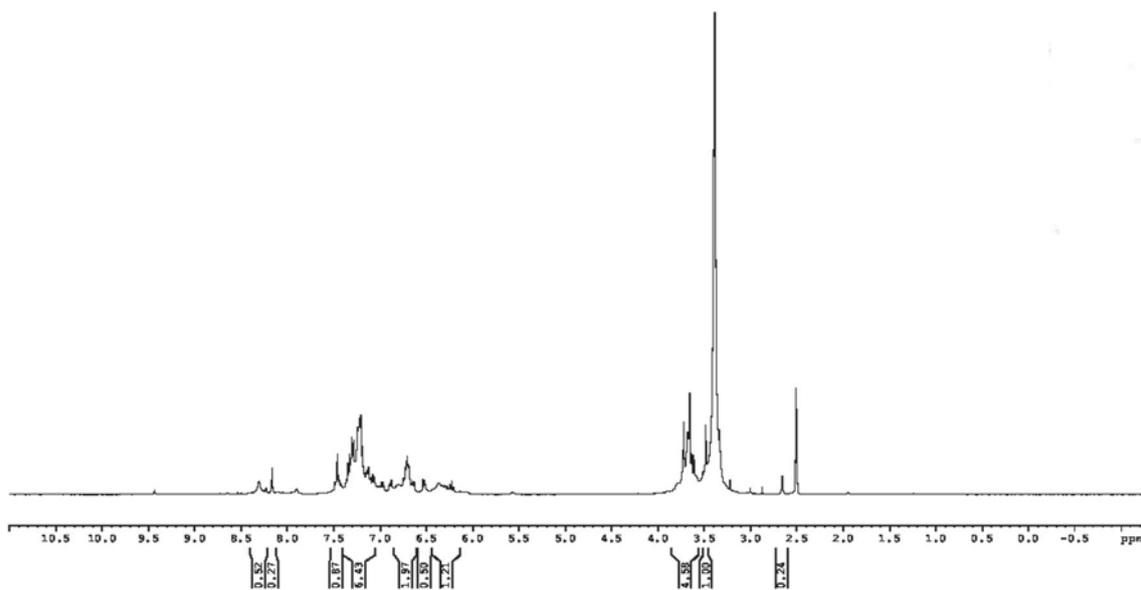


Figure 3. Proton NMR spectrum of $[\text{Zn}(\text{VTS})_2\text{Cl}]$.

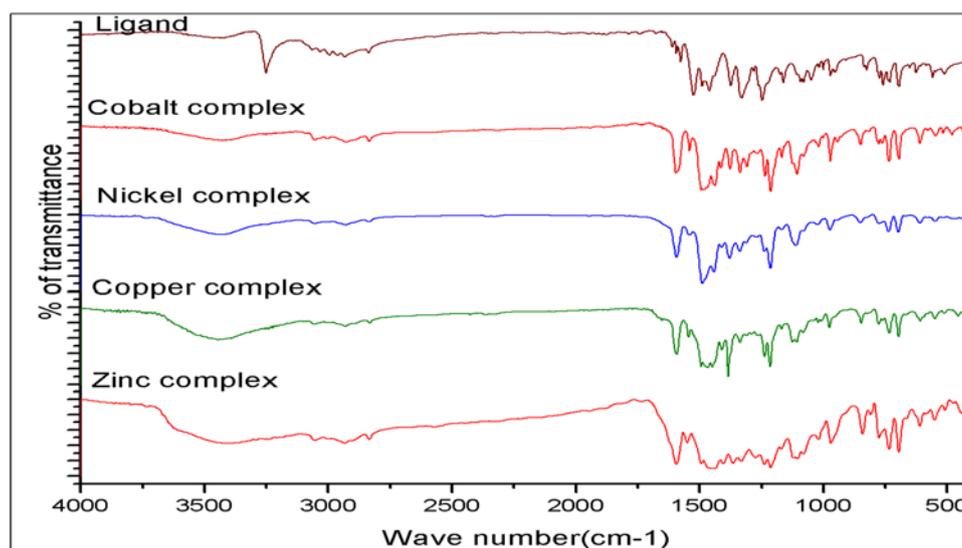


Figure 4. FTIR spectra of ligand and its complexes.

frequency range of $1585\text{--}1592\text{ cm}^{-1}$, indicating bonding of unsaturated nitrogen of azomethane group to the metal ions.²⁸ The thiosemicarbazone ligand shows an intense band at 1162 cm^{-1} and less intense band at 824 cm^{-1} attributed to the $\text{C}=\text{S}$ vibration of the free ligand and absence of a peak at 2500 cm^{-1} indicates that the ligand is present in the thione form in the solid-state. As a result of complex formation, the band due to $\text{C}=\text{S}$ was shifted towards $750\text{--}800\text{ cm}^{-1}$ indicating the involvement of coordination of thio-keto sulphur towards the metal ion.²⁹ In the low-frequency region of complexes some new bands have

been observed in the range of $400\text{--}430\text{ cm}^{-1}$, $450\text{--}480\text{ cm}^{-1}$ and $540\text{--}560\text{ cm}^{-1}$ attributed to the stretching frequency of M-S , M-N and M-O respectively.^{30,31} In the IR spectra of the chloro complexes of copper and zinc, the band corresponding to $310\text{--}350\text{ cm}^{-1}$ regions are tentatively assigned for M-Cl bond.³²

3.4 Electronic spectra

The electronic spectra of ligand and metal complexes were taken in DMSO solvent between $200\text{--}800\text{ nm}$ at 298 K . The vanillin thiosemicarbazone ligand exhibits

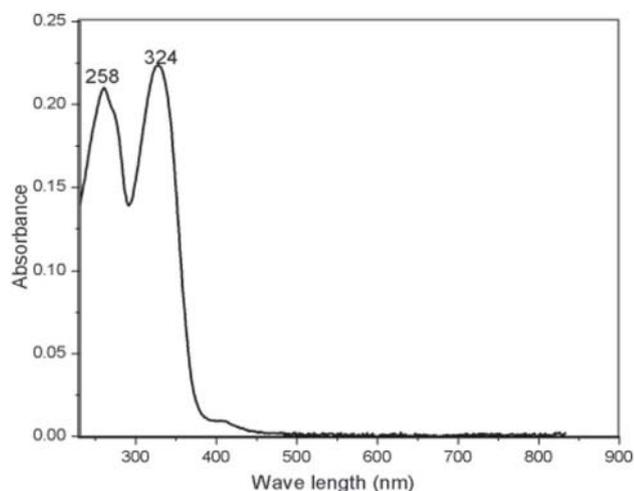


Figure 5. UV spectrum of HVTS.

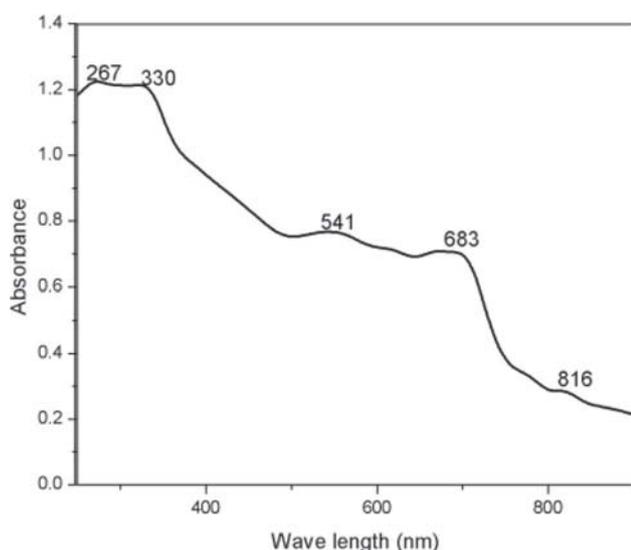


Figure 6. UV spectrum of [Co(VTS)₂].

two bands at 260 and 310 nm. The bands are due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of C=N group in the ligand field structure. On complexation, this band was found shifted to lower wavelength region indicating the coordination of ligand to the central metal ion. The

magnetic moment value of cobalt(II) complex was 4.74 B.M. The electronic spectrum of cobalt complex exhibited three absorption bands at 816 nm, 683 nm and 541 nm assigned to transitions ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, respectively indicating an octahedral geometry around the cobalt ion.³³ Electronic spectrum of Ni(II) complex shows three bands at 590, 656 and 835 nm assignable to be ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions, suggesting an octahedral geometry around the nickel(II) ion. The magnetic moment value of Ni(II) complex was 3.14 B.M., also confirms the octahedral geometry of the Ni(II) complex.³⁴ The copper complex has a magnetic moment of 1.80 BM. It exhibits characteristic bands at 710 nm and 580 nm which are due to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ transitions respectively.³⁵ The magnetic moment along with spectral evidence confirms the square planar structure. The diamagnetic mononuclear Zn(II) complex gave only intra ligand transitions at 281 nm and 352 nm, with a mononuclear tetrahedral geometry around the central metal atom. Zn(II) complex show an absorption band at 485 nm which could be assigned to the ligand to metal charge transfer transitions.³⁶ The electronic spectra of ligand and its complexes are given in Figures 5 to 9.

3.5 Mass spectrum of HVTS and its complexes

The ESI mass spectra of the ligand HVTS and its complexes are given in supplementary information. The mass spectrum of the HVTS shows a peak at 316.1124 [HVTSC+H]⁺. The molecular ion peak (M+1) was found as the base peak in the case of vanillin-4-methyl-4-phenyl-3-thiosemicarbazone. The peak at 338.09434 is due to the adduction [HVTSC+Na]⁺. The observed m/z value of the ligand is in good agreement with the calculated value. The mass spectrum of [Co(VTS)₂] shows a peak at 687.12616 which is due to the molecular ion peak itself. The calculated molecular weight for the Co(II) complex is the same as that of observed one in the

Table 1. XRD data of the VTSC and its complexes.

Ligand/complexes	Lattice constant (Å)			Inter axial angle (°)	Space group	Crystal system
	a	b	c			
HVTS	11.12	6.19	14.32	$\alpha = \gamma = 90, \beta \neq 90$	P2 ₁ /n	Monoclinic
[Co(VTS) ₂]	9.26	14.73	20.19	$\alpha = \gamma = 90, \beta \neq 90$	P2 ₁ /c	Monoclinic
[Ni(VTS) ₂]	7.01	3.23	6.68	$\alpha = \gamma = 90, \beta \neq 90$	C2/m	Monoclinic
[Cu(VTS)Cl].2H ₂ O	4.70	11.29	7.09	$\alpha = \gamma = 90, \beta \neq 90$	P2 ₁ /m	Monoclinic
[Zn(VTS)Cl].	15.29	23.62	6.01	$\alpha = \gamma = 90, \beta \neq 90$	C2/c	Monoclinic

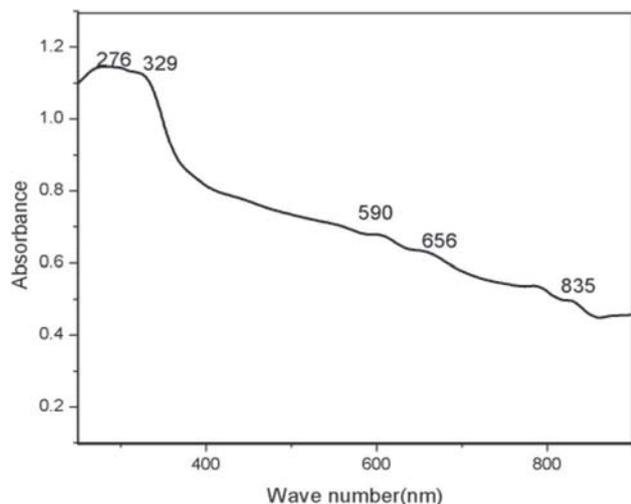


Figure 7. UV spectrum of [Ni(VTS)₂].

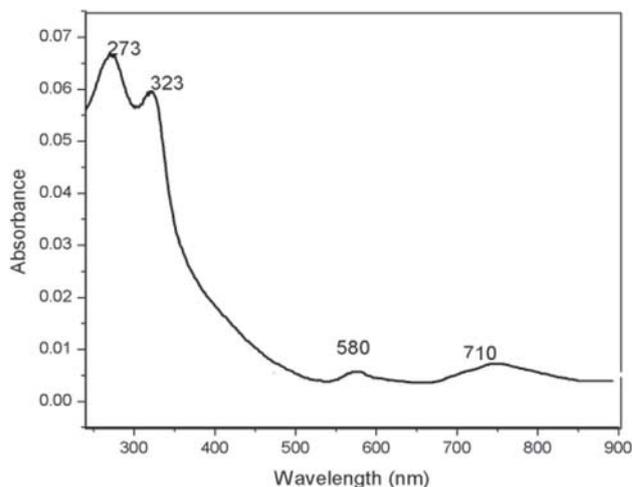


Figure 8. UV spectrum of [Cu(VTS)Cl]·2H₂O.

mass spectrum. Additional peaks present at 314.09658 and 172.07167 is due to the presence of VTS and [VTS-C₈H₈NS+Na]. The mass spectrum of Ni (II) complex was found to show a peak at 687.13831, which is the molecular ion peak itself. The base peak at 373.03333 is due to the [M+VTS]⁺. The value obtained from the mass spectra is the same as that of the calculated value. The mass spectrum of the Cu (II) complex contains peak at 450.06440 due to the molecular ion [M+VTS+Cl+2H₂O]⁺. The base peak at 402.05969 is due to the presence of [M+VTS+Na] and other peaks at 378.03333 and 314.09747 are due to the presence of [M+VTS] and [VTS]. The structure of Cu (II) complex was also confirmed by the mass spectrum. The mass spectrum of the [Zn(VTS)Cl] exhibits a base peak at 415.05303 due to the presence of adduct ion [M+VTS+Cl]⁺. The base peak at 380.02659 is due to the ion [M+VTS]⁺ and the peak at 316.11268 indicates the presence of ligand ion.

From the above studies, the complexes could be formulated as [M(VTSC)₂], M=Co(II),Ni(II), [Cu(VTSC)Cl]·2H₂O and [Zn(VTSC)Cl]. On the basis

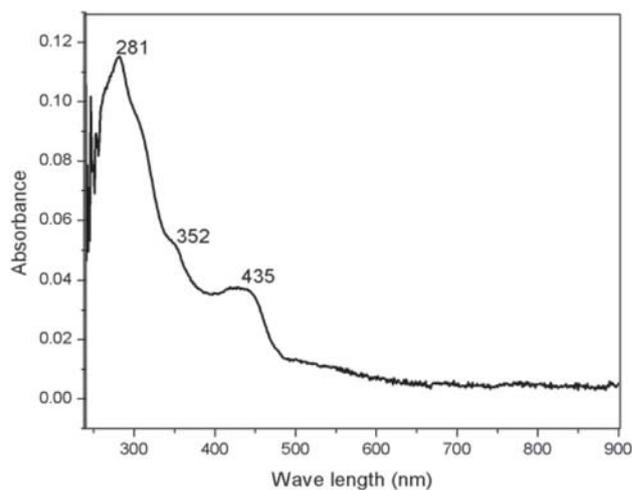


Figure 9. UV spectrum of [Zn(VTS)Cl].

of the previously discussed physicochemical values and spectral data, the structure of the ligand and complexes could be assigned as shown in Figure 10.

Table 2. Antimicrobial studies of ligand and its complexes.

Sample	<i>E. coli</i>	<i>K. pneu</i>	<i>B .cereus</i>	<i>S. Aureus</i>	<i>A. niger</i>	<i>Penicillium sp.</i>
HVTS	14	15	10	8	8	9
[Co(VTS) ₂]	19	17	15	19	10	12
[Ni(VTS) ₂]	20	23	22	26	11	13
[Cu(VTS)Cl] 2H ₂ O	21	27	25	30	10	11
[Zn(VTS)Cl]	28	25	24	26	13	13
Gentamycine	26	28	22	24		
Clotrimazole					20	22

Antibacterial activity: <12 mm-weak activity, 12–16-moderately active: >16-significant activity. Antifungal activity: <7 mm-weekly active; 9–7 mm-moderate active; >10 mm-significant activity.

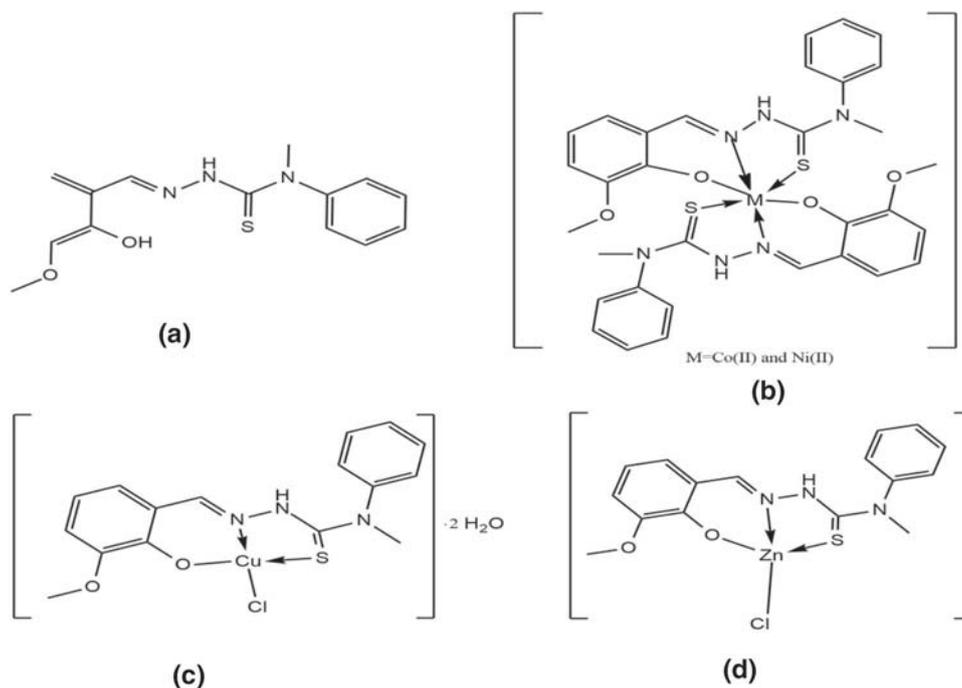


Figure 10. Structure of (a) ligand (b) Co(II) & Ni(II) complexes (c) Cu(II) complex (d) Zn(II) complex.

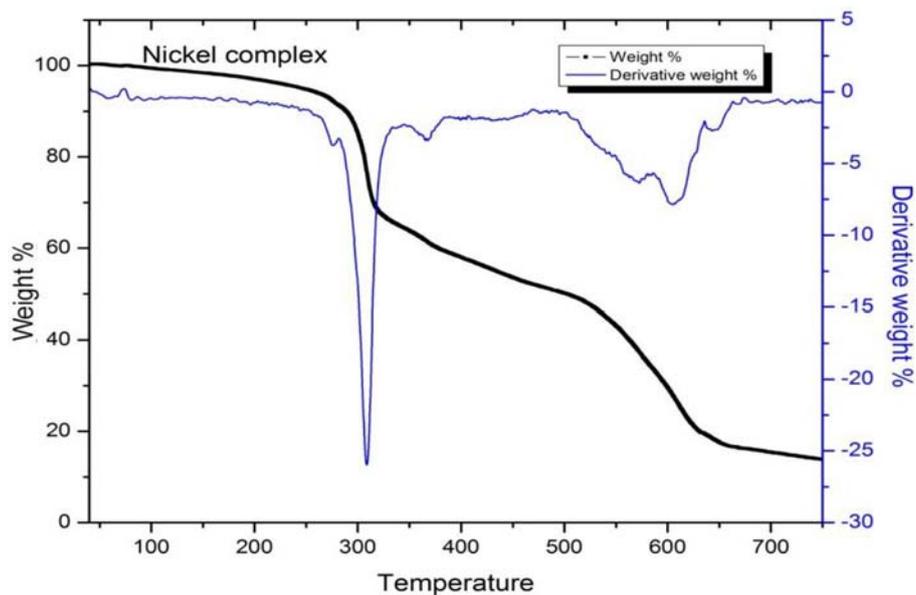


Figure 11. TG-DTG curve of [Ni(VTS)₂].

3.6 Thermogravimetric analysis

The thermal stability of the complex was studied by using thermo gravimetric analysis. Cobalt, nickel and zinc complexes are thermally stable above 275 °C, which indicate the absence of water molecule. These

complexes were found to decompose in a two-step process. The first decomposition for cobalt complex occurs between 280–320 °C with an endothermic peak at 303 °C, and the second decomposition from 600 °C with an endothermic peak at 628 °C. The thermal

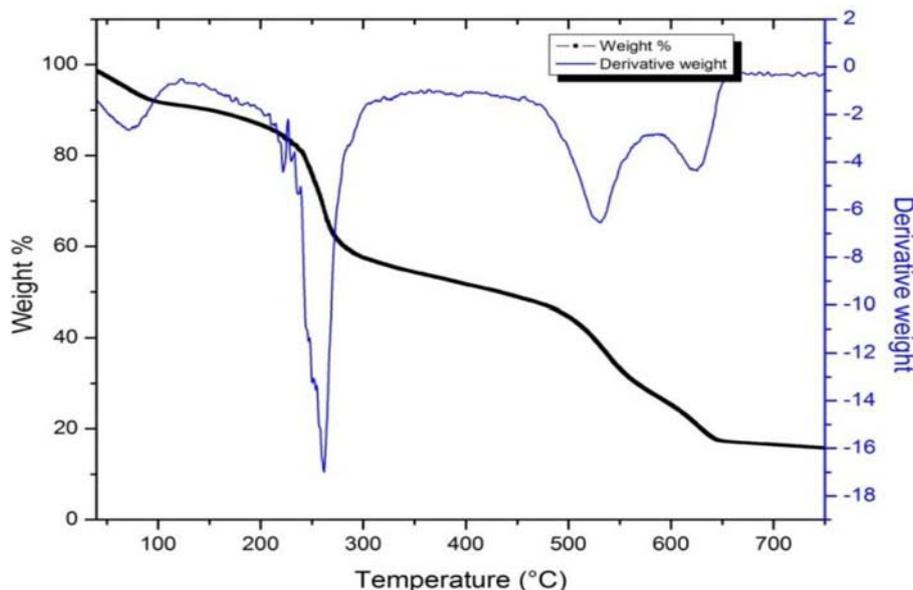


Figure 12. TG-DTG curve of $[\text{Cu}(\text{VTS})\text{Cl}] \cdot 2\text{H}_2\text{O}$.

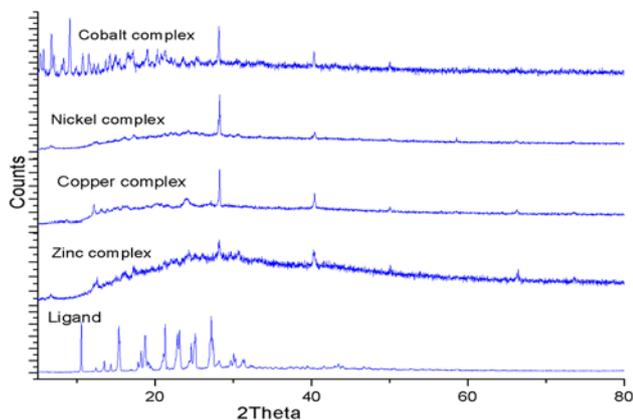


Figure 13. PXRD spectrum of ligand and its complexes.

decomposition of nickel complex starts from 275 °C with an endothermic peak at 308 °C and the second decomposition occurs from 550–670 with an endothermic peak at 570 °C. Copper complex decomposed in between 70–90 °C with an endothermic peak of 81 indicating the presence of lattice water. Spectral data of the complex also confirms the presence of water molecule.³⁷ Second decomposition starts at 220 °C indicating the presence of chloride ion in the complex. The final decomposition occurs above 550 °C.³⁸ All the complexes remained as metal residue above 700 °C.³⁹ The TG-DTG curves of nickel and copper complexes are shown in Figure 11 and Figure 12.

3.7 Powder XRD analysis

The powder X-ray diffraction patterns of the ligand and its complexes were recorded in the range of $2\theta = 5$ to 80°. Sharp crystalline peaks were observed for the ligand and complexes, indicating crystalline behavior of the samples.⁴⁰ All the complexes exhibited sharp peaks in the XRD diagrams. The powder XRD analysis of the ligand and the complexes are shown in Figure 13.

The average grain size of the complexes were calculated using Debye Scherer equation [$d_{\text{XRD}} = 0.9 \lambda / \beta \cos\theta$]. The grain size of the ligand, cobalt, nickel, copper (II) and zinc (II) complexes were 36.1, 81.4, 57.6, 47.6 and 33.4 nm respectively, indicating that the metal complexes fall in the nano regime. The ligand and complexes belong to a monoclinic crystal system with a different space group. The lattice parameters and the space group are given in Table 1.

3.8 SEM analysis

The surface morphology of metal complexes was analyzed using a scanning electron microscope and is shown in Figure 7. SEM images with a magnification value of 3,500X and optimum energy value of 20 kV were used for the analysis. The SEM images of the complexes were found entirely different from that of the ligands. The surface of the ligand seems to have a cylindrical rod-like structure. The cobalt complex exhibits an agglomerated irregular spherical shape

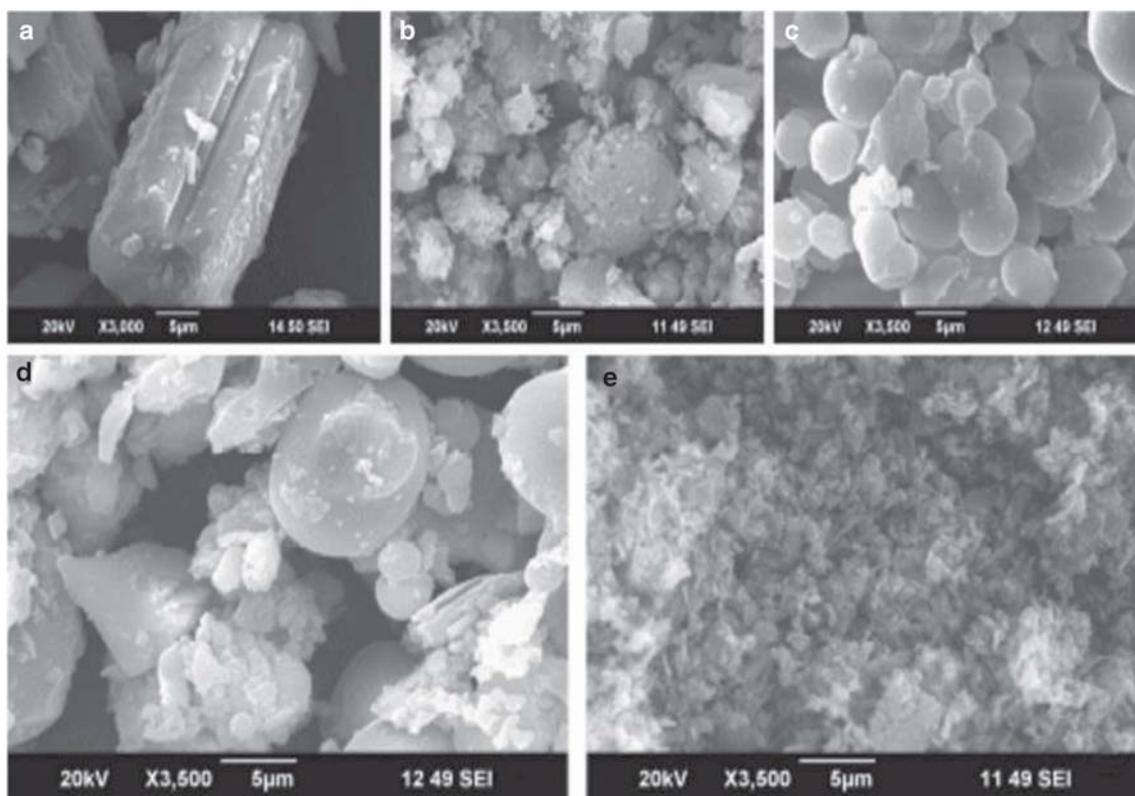


Figure 14. SEM images of (a) ligand (b) Co(II) (c) Ni(II) (d) Cu(II) (e) Zn(II) complexes.

surface morphology while the nickel complex was found to have a homogenous circular plate-like structure. The copper complex contained agglomerated spherical like particles⁴¹ and the zinc complexes had heterogeneous spherical particles. All the complexes are polycrystalline with nano-sized grains.

3.9 Antimicrobial studies

Antimicrobial activities of vanillin-4-methyl-4-phenyl-3-thiosemicarbazone and its complexes were determined by agar well diffusion method. In our study, activities were checked against two Gram-positive bacteria namely- *Staphylococcus aureus* and *Bacillus cereus*, two gram-negative bacteria- *Escherichia coli* and *Klebsiella pneumonia* and two fungal pathogens -*Aspergillus niger* and *Penicillium* sp. The zone of inhibition of samples against different bacteria and fungi are given in Table 2.

The antimicrobial activity data of the thiosemicarbazone and complexes indicates that all the complexes have had better activity than that of the ligand.⁴² The antibacterial activity of the complexes were higher than that of antifungal activity.⁴³ The variation in the

activity of the complexes against different organism depends on the impermeability of the cell of the microbe. The copper and zinc complex show maximum activity against bacteria. The increased activities of the metal complexes than that of free ligand are explained on the basis of chelation theory according to which chelation is considered to reduce the polarity of the metal ions due to the partial sharing of its positive charge with the ligand.⁴⁴ This increases the lipid solubility which favours its permeation into normal cell of the microbes.

4. Conclusions

The vanillin thiosemicarbazone and its cobalt(II), nickel(II), copper(II) and zinc(II) complexes were characterized through elemental analysis, molar conductivity, magnetic moment, electronic spectra, infrared spectra, ¹H, ¹³C NMR spectra, thermogravimetric analysis, powder XRD analysis and SEM analysis. Based on the data, an octahedral geometry was assigned for the cobalt and nickel complex, square planar geometry for copper complex and a tetrahedral geometry for zinc complex. The ligand act as

tridentate coordinating *via* azomethine nitrogen, a sulphur atom and a phenolic oxygen atom. The complexes are non-electrolytic in nature. All complexes except copper complex were stable upto 280 °C. Powder XRD analysis suggests that the ligand and complexes belongs to a monoclinic crystal system with a different space group. The complexes were found to possess crystal size less than 70 nm, which increases the possibility of their use as nano precursors. The surface analysis of the complexes was entirely different from the ligand. Copper and zinc complexes of vanillin thiosemicarbazone were found to possess high antibacterial and antifungal activity as compared with other complexes.

Supplementary Information (SI)

Figures S1–S5 are available as supplementary information at www.ias.ac.in/chemsci.

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