Microwave Synthesis, Spectral, Thermal and Antimicrobial Studies of Some Co(II), Ni(II) and Cu(II) Complexes Containing 2-Aminothiazole Moiety

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Abstract: Some new Schiff base metal complexes of Co(II), Ni(II) and Cu(II) derived from 4-chlorobenzylidene-2-aminothiazole (CAT) and 2-nitrobenzylidene-2-aminothiazole (NAT) have been synthesized by conventional as well as microwave methods. These compounds have been characterized by elemental analysis, FT-IR, FAB-mass, molar conductance, electronic spectra, ESR, magnetic susceptibility, thermal, electrical conductivity and XRD analysis. The complexes are coloured and stable in air. Analytical data revealed that all the complexes exhibited 1:2 (metal: ligand) ratio with coordination number 4 or 6. FAB-mass and thermal data show degradation pattern of the complexes. The thermal behavior of metal complexes shows that the hydrated complexes loses water molecules of hydration in the first step; followed by decomposition of ligand molecules in the subsequent steps. The crystal system, lattice parameter, unit cell volume and number of molecules in unit cell in the lattice of complexes have been determined by XRD analysis. XRD patterns indicate crystalline nature for the complexes. The solid state electrical conductivity of the metal complexes has also been measured. Solid state electrical conductivity studies reflect semiconducting nature of the complexes. The Schiff base and metal complexes show a good activity against the Gram-positive bacteria; *Staphylococcus aureus* and Gram-negative bacteria; *Escherichia coli* and fungi *Aspergillus niger* and *Candida albicans*.

Keywords: Microwave synthesis, 2-aminothiazole, N, S donor, thermal analyses, biological activity.

Introduction

A large number of Schiff bases and their metal complexes have been found to possess important biological and catalytic activity¹. It is well known that N and S atoms play a key role in the coordination of metals at the active sites of numerous metalloproteins². They are used as models for biological systems and find applications in biomimetic catalytic reactions^{3, 4}. Various heterocycles, especially thiazoles, occupy an important place owing to their versatile bioactivities due to the presence of multifunctional groups. 2-aminothiazoles are a remarkably versatile group of compounds that have many biological activities and found recent applications in the drug development. Benzothiazoles are used for production of dyes with photosensitizing properties. Metal complexes with these ligands are becoming increasingly important as biochemical, analytical and antimicrobial reagents in the design of molecular models and material chemistry^{4, 5}. Thiazoles and their derivatives form a part of vitamin B₁ and coenzyme carboxylase. They represent a very interesting class of compounds because of their wide applications as antimicrobial, anti-inflammatory, anti-degenerative and anti-HIV activities^{6, 7}.

Microwave-assisted synthesis is a branch of green chemistry. Microwave-assisted synthesis has gained much attention in recent years. The applications of microwave irradiation are used for carrying out chemical transformations, which are pollution free, eco-friendly, low cost and offer high yields together with simplicity in processing and handling. The salient features of microwave approach are shorter reaction times, simple reaction conditions and enhancements in yields⁸⁻¹². Reports on the synthesis of metal complexes by microwave methods have been comparatively less.

In this study we report the synthesis, physicochemical characterization and biological significances of Co(II), Ni(II) and Cu(II) complexes with ligands derived from 4-chlorobenzylidene-2-aminothiazole (CAT) and 2-nitrobenzylidene-2-aminothiazole (NAT) (Fig. 1). The metal complexes formed with these two new ligands may be used as precursors for the synthesis of new compounds. Some of them may exhibit interesting physical, chemical and biological properties.

Figure 1. Structure of Schiff base ligands.

Experimental

Melting points were taken in open glass capillaries and are uncorrected. Progress of reaction was monitored by silica gel-G coated TLC plates using MeOH:CHCl₃ system (1:9). The spot was visualized by exposing dry plate at iodine vapours chamber. All the used chemicals and solvents were of Anal R grade. All the reagents used for the preparation of the Schiff bases were obtained from Sigma Aldrich. Metal salts were purchased from Loba Chemie. Elemental analyses were performed on an Elemental Vario EL III Carlo Erba 1108 analyzer. FAB-mass spectra were recorded on a JEOL SX 102/DA 6000 Mass Spectrometer using

argon/xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and the spectra were recorded at room temperature. Electronic spectra (in DMSO) were recorded on Perkin Elmer Lambda-2B-spectrophotometer. Molar conductance measurements were conducted using 10^{-3} M solutions of the complexes in DMSO on Elico-CM 82 Conductivity Bridge at room temperature. Magnetic susceptibility measurements were carried out on a Gouy balance at room temperature using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as the calibrant. Diamagnetic corrections were applied in compliance with Pascal's constant. FT-IR spectra were recorded in KBr pellet on a Perkin Elmer RX1 spectrophotometer in wave number region $4000\text{--}400\text{ cm}^{-1}$. X-band EPR spectra were recorded on a Varian E-112 spectrometer at room temperature operating at the X-band region with 100 kHz modulation frequency, 5 mw microwave power and 1 G modulation amplitude using TCNE as the internal standard. Thermogravimetric analysis was carried out under atmospheric condition with a heating rate $10^\circ\text{C min}^{-1}$ on TGA Q500 universal V4.5A TA instrument. Powder X-ray diffraction (XRD) patterns were recorded on a RINT2000 wide angle goniometer. X-ray diffractometer, operated at 40 kV and 30 mA generator using the $\text{CuK}\alpha$ line at $1.54056\text{ \AA}$ as the radiation sources. Sample was scanned between 5° to 90° (2θ) at 25°C . The solid state electrical conductivity has been measured by impedance spectroscopic method using HIOKI 3532-50 LCR Hitester at fixed frequency 1 KHz in the temperature range of 298-413 K. Microwave assisted synthesis were carried out in open glass vessel on a modified microwave oven model 2001 ETB with rotating tray and a power source 230 V, microwave energy output 800W and microwave frequency 2450 MHz. A thermocouple device was used to monitor the temperature inside the vessel of the microwave. The microwave reactions were performed using on/off cycling to control the temperature.

Conventional synthesis of Schiff bases

The Schiff bases (CAT and NAT) have been synthesized by adding the ethanolic solution of 4-chlorobenzaldehyde and 2-nitrobenzaldehyde with ethanolic solution of 2-aminothiazole in equimolar ratio. The reaction mixture was then refluxed on water bath for about 4-6 hours. The condensation product was filtered, thoroughly washed with ethanol and ether, recrystallized and dried in vacuo. The Purity of the synthesized compound was monitored by TLC using silica gel G (Yield: CAT - 83%; NAT – 80%).

Microwave method for the Synthesis of Schiff bases

The equimolar (1:1) ratio of 4-chlorobenzaldehyde and 2-nitrobenzaldehyde with 2-aminothiazole were mixed thoroughly in a grinder. The reaction mixture was then irradiated by the microwave oven by taking 3-4 mL solvent. The reaction was completed in a short time (4-5 min.) with higher yields. The resulting product was then recrystallized with ethanol and finally dried under reduced pressure over anhydrous CaCl_2 in a desiccator. The progress of the reaction and purity of the product was monitored by TLC using silica gel G (yield: 88-90%).

Conventional preparation of Schiff Base Metal Complexes

The metal complexes have been prepared by mixing the ethanolic solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ to the ethanolic solution of Schiff bases (CAT and NAT) in 1:2 molar ratio. The resulting mixture was then refluxed on water bath for about 5-8 hours. A coloured product appeared on standing and cooling the above solution. The complex was filtered, washed with ether and dried under reduced pressure over anhydrous CaCl_2 in a desiccator. It was further dried in an electric oven at $50\text{--}70^\circ\text{C}$.

Microwave method for the Synthesis of metal complexes

The ligand and the metal salts were mixed in 1:2 (metal:ligand) ratio in a grinder. The reaction mixture was then irradiated by the microwave oven by taking 3-5 mL solvent. The reaction was completed in a short time (6-8 min) with higher yields. The resulting product was then recrystallized with ethanol and ether and finally dried under reduced pressure over anhydrous CaCl_2 in a desiccator. The progress of the reaction and purity of the product was monitored by TLC using silica gel G (yield: 78-86%).

Biological activity

The *in-vitro* biological activity of the investigated Schiff base and its metal complexes was tested against the bacteria *Escherichia coli* and *Staphylococcus aureus* by disc diffusion method using nutrient agar as medium and streptomycin as control. The antifungal activities of the compounds were also tested by the Well diffusion method against the fungi *A. niger* and *C. albicans*, on potato dextrose agar as the medium and Miconazole as control. Each of the compounds was dissolved in DMSO and solutions of the concentrations (25, 50 and 100 ppm) were prepared separately. In a typical procedure, a well was made on agar medium inoculated with microorganism. The well was filled with the test solution using a micropipette and the plate was incubated 24 h for bacteria at 37 °C and 72 h for fungi at 30 °C. During this period, the test solution diffused and the growth of the inoculated microorganism was affected. The inhibition zone was developed, at which the concentration was noted.

Results and Discussion

As a result of microwave assisted synthesis, it was observed that the reaction was completed in a short time with higher yields compared to the conventional method. In the microwave method homogeneity of reaction mixture was increased by the rotating of reaction platform tray. The confirming of the results was also checked by the repeating of the synthesis process.

All the metal complexes are coloured, solid and stable towards air and moisture at room temperature. They decompose on heating at high temperature and more or less soluble in common organic solvents. The comparison study data of microwave and conventional methods, with analytical and physical data of the compounds are given in the Table 1. Analytical data show that metal chelates have 1:2 (metal:ligand) stoichiometry. The observed molar conductance of the complexes in DMSO at room temperature are consistent with the non-electrolytic nature of the complexes while Co(II) complex of CAT Schiff base ligand show electrolytic nature.

FAB-mass spectra

The FAB-mass spectra suggested that all the complexes have a monomeric nature. These complexes show molecular ion peaks in good agreement with the empirical formula suggested by elemental analyses.

The FAB mass spectra of the ligand (CAT) and its $[\text{Co}(\text{CAT})_2\text{Cl}_2]2\text{H}_2\text{O}$ and $[\text{Ni}(\text{CAT})_2\text{Cl}_2]2\text{H}_2\text{O}$ complexes were recorded and they are used to compare their stoichiometry composition. The Schiff base (CAT) shows a molecular ion peak at m/z 223 respectively. The $[\text{Co}(\text{CAT})_2\text{Cl}_2]2\text{H}_2\text{O}$ and $[\text{Ni}(\text{CAT})_2\text{Cl}_2]2\text{H}_2\text{O}$ complexes showed a molecular ion peak at m/z 613 and 610 respectively, confirm the stoichiometry of (CAT) and its complexes as ML_2 type. It is good agreement with the microanalytical data^{13, 14}.

Table 1. The comparative results of conventional and microwave methods, analytical, physical data and magnetic moment values of the compounds.

Compound Mol. Wt (Colour)	Reaction period		Yield (%)		Elemental Analysis; Found/(Calcd.)%				μ_{eff} (B.M.)	$^*\Lambda_m$
	CM (h.)	MM (min.)	CM	MM	C	H	N	M		
(C ₁₀ H ₇ N ₂ SCl)CAT 222.54 (Light brown)	4.2	4.9	83.0	88.4	53.76 (53.92)	3.31 (3.14)	12.70 (12.58)	-	-	-
[Co(CAT) ₂ (H ₂ O) ₂]Cl ₂ 611.01(Dark brown)	7.2	6.4	68.1	81.5	39.64 (39.27)	2.39 (2.94)	9.57 (9.16)	9.29 (9.64)	5.09	146.7
[Ni(CAT) ₂ Cl ₂]2H ₂ O 610.79 (Yellowish brown)	6.8	6.8	68.8	84.3	39.63 (39.29)	2.41 (2.94)	9.83 (9.16)	9.14 (9.61)	3.08	45.3
[Cu(CAT) ₂ Cl ₂]2H ₂ O 615.62 (Coffee brown)	6.3	6.1	64.0	83.5	38.63 (38.98)	2.18 (2.92)	9.59 (9.09)	10.07 (10.32)	1.92	43.8
(C ₁₀ H ₇ N ₃ SO ₂) NAT 233.0 (Blackish green)	5.2	5.0	80.2	90.0	51.37 (51.50)	2.82 (3.00)	18.23 (18.02)	-	-	-
[Co(NAT) ₂ Cl ₂]2H ₂ O 631.93 (Leaf brown)	7.9	8.1	66.2	81.2	37.42 (37.97)	2.54 (2.84)	13.63 (13.29)	9.67 (9.32)	5.07	36.3
[Ni(NAT) ₂ Cl ₂]2H ₂ O 631.71 (Marry gold)	7.6	7.2	69.2	83.5	37.57 (37.91)	2.36 (2.85)	13.78 (13.29)	9.94 (9.29)	3.04	32.0
[Cu(NAT) ₂ Cl ₂]2H ₂ O 636.54 (Green)	7.2	7.0	68.0	81.6	37.44 (37.70)	2.37 (2.82)	13.71 (13.19)	9.39 (9.98)	1.93	41.8

CM = Conventional method, time in hours; MM = Microwave method, time in minutes

$^*\Lambda_m = (\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$.

IR spectra

The IR spectra of the complexes were compared with those of the free ligand in order to determine the involvement of coordination sites in chelation. Characteristic peaks in the spectra of the ligand and complexes were considered and compared.

The IR spectra of the ligand CAT exhibits a band at 1602 cm^{-1} due to the azomethine $\nu(\text{C}=\text{N})$ group. This band shifts to lower frequency by $20\text{--}25\text{ cm}^{-1}$ in the complexes, indicating the bonding of nitrogen of the azomethine group to the metal ion and this can be explained by the donation of electrons from nitrogen to the empty d-orbital of the metal atom. A sharp band at 833 cm^{-1} is due to $\nu(\text{C-S-C})$ group. Its position in the complexes has been observed at $818\text{--}822\text{ cm}^{-1}$ indicating the involvement of ring sulphur atom in coordination. An intense band at 1570 cm^{-1} due to $\text{C}=\text{N}$ cyclic of thiazole ring does not shift in the spectra of complexes. This rules out the participation of $\nu(\text{C}=\text{N}$ cyclic) group in coordination. Thus the Schiff base acts as bidentate ligand. The appearance of bands at $3310\text{--}3313\text{ cm}^{-1}$ (stretching mode) supports the presence of water molecules in all the three complexes. However, the appearance of band at 723 cm^{-1} (rocking mode), in cobalt(II) complex suggest the coordinated water molecule. In the low frequency region, the band of weak intensity observed for the complexes in the region $472\text{--}478\text{ cm}^{-1}$ is attributed to $\nu(\text{M-N})$, and that the region $402\text{--}406\text{ cm}^{-1}$ to $\nu(\text{M-S})$.

IR spectrum of the NAT ligand exhibits the $\nu(\text{C}=\text{N})$ band at 1612 cm^{-1} has shifted to lower wave numbers ($1580\pm 10\text{ cm}^{-1}$) in the complexes, suggesting the metal coordination with the azomethine nitrogen. The ligand exhibited a sharp band at 827 cm^{-1} due to $\nu(\text{C-S-C})$ group. Its position in the spectra of complexes has been observed at $803\text{--}807\text{ cm}^{-1}$ indicating the involvement of ring sulphur atom in coordination. An intense band at 1572 cm^{-1} in Schiff base ligand due to $\nu(\text{C}=\text{N}$, thiazole ring), does not alter in the spectra of complexes. This indicates the non-involvement of ring nitrogen in coordination. A band around $3405\text{--}3409\text{ cm}^{-1}$ in the spectra of complexes is assignable to ν_{str} of water. In the low frequency region, the band of weak intensity observed for the complexes in the region $481\text{--}487\text{ cm}^{-1}$ is attributed to $\nu(\text{M-N})$, and that the region $403\text{--}410\text{ cm}^{-1}$ to $\nu(\text{M-S})$ ¹⁵⁻¹⁹.

The IR data of both the Schiff base and its metal complexes show that the Schiff bases (CAT, NAT) are coordinated to the metal ion in bidentate manner with NS donor sites of azomethine nitrogen and thiazole sulfur.

Electronic spectra and magnetic moment

The nature of the ligand field around the metal ion has been deduced from the electronic spectra.

The electronic spectrum of cobalt(II) complex of CAT shows two bands at 17600 and 20181 cm^{-1} which have tentatively been assigned to ${}^4\text{T}_{1\text{g}}(\text{F})\rightarrow{}^4\text{A}_{2\text{g}}(\text{F})$ (ν_2) and ${}^4\text{T}_{1\text{g}}(\text{F})\rightarrow{}^4\text{T}_{1\text{g}}(\text{P})$ (ν_3) respectively. The various ligand field parameters, 10Dq , B , β , ν_2/ν_1 , λ and LFSE have been calculated and the values are as: 9350 cm^{-1} , 869 cm^{-1} , 0.77 , 2.13 , $(-)$ 721 cm^{-1} and 89.33 kJ mol^{-1} respectively. The magnetic moment is 5.09 BM . These findings are in favour of an octahedral geometry for the Co(II) complex. Nickel(II) complex of CAT exhibits three bands at 11235 , 20223 and 26315 cm^{-1} corresponding to transitions ${}^3\text{A}_{2\text{g}}(\text{F})\rightarrow{}^3\text{T}_{2\text{g}}(\text{F})$ (ν_1), ${}^3\text{A}_{2\text{g}}(\text{F})\rightarrow{}^3\text{T}_{1\text{g}}(\text{F})$ (ν_2) and ${}^3\text{A}_{2\text{g}}(\text{F})\rightarrow{}^3\text{T}_{1\text{g}}(\text{P})$ (ν_3) respectively. The values of various ligand field parameters, 10Dq , B , β , ν_2/ν_1 , λ and LFSE are as: 11235 cm^{-1} , 856 cm^{-1} , 0.79 , 1.8 , $(-)$ 248 cm^{-1} and $161.01\text{ kJ mol}^{-1}$ respectively. The magnetic moment is 3.08 B.M. These findings are in favour of an octahedral geometry for the Ni(II)-complex. For the copper (II) complex of CAT shows a single broad band at 13698 cm^{-1} has been observed; this attributes to ${}^2\text{E}_{\text{g}}\rightarrow{}^2\text{T}_{2\text{g}}$ transition. The various ligand field parameters viz. 10Dq , λ and LFSE have been calculated and values are 13698 cm^{-1} , $(-)$ 752 cm^{-1} and 98.15 kJ mol^{-1} respectively. Its magnetic moment is 1.92 B.M. Thus these data suggest the

octahedral geometry for Cu(II) complex. Ligand field parameters and magnetic moment data substantiate the same view.

Table 2. IR bands of Schiff base ligands and their complexes.

Compound	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{N}$ thiazole ring)	$\nu(\text{C}-\text{S}-\text{C})$	$\nu(\text{H}_2\text{O})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{S})$
CAT	1602	1570	833	-	-	-
$[\text{Co}(\text{CAT})_2(\text{H}_2\text{O})_2]\text{Cl}_2$	1582	1569	818	3313, 723	478	402
$[\text{Ni}(\text{CAT})_2\text{Cl}_2]2\text{H}_2\text{O}$	1580	1569	822	3310	470	406
$[\text{Cu}(\text{CAT})_2\text{Cl}_2]2\text{H}_2\text{O}$	1584	1570	820	3312	472	404
NAT	1612	1572	827	-	-	-
$[\text{Co}(\text{NAT})_2\text{Cl}_2]2\text{H}_2\text{O}$	1580	1571	805	3407	485	410
$[\text{Ni}(\text{NAT})_2\text{Cl}_2]2\text{H}_2\text{O}$	1584	1572	807	3405	481	406
$[\text{Cu}(\text{NAT})_2\text{Cl}_2]2\text{H}_2\text{O}$	1587	1571	803	3409	487	403

The electronic spectrum of Co(II) complex of NAT shows two bands at 15510 cm^{-1} and 20538 cm^{-1} which have tentatively been assigned to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ (ν_2) and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ (ν_3) respectively. The various ligand field parameters, 10Dq , B , β , ν_2/ν_1 , λ and LFSE have been calculated and values are as: 8296 cm^{-1} , 960 cm^{-1} , 0.85 , 2.14 , $(-)$ 629 cm^{-1} and 79.26 kJ mol^{-1} respectively. The magnetic moment is 5.07 B.M. These findings are in favour of an octahedral geometry for the Co(II)-complex. Nickel(II) complex of NAT exhibits three bands at 11352 cm^{-1} , 19360 cm^{-1} and 23138 cm^{-1} corresponding to transitions ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ (ν_1), ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ (ν_2) and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ (ν_3) respectively. The values of various ligand field parameters, 10Dq , B , β , ν_2/ν_1 , λ and LFSE are as: 11352 cm^{-1} , 563 cm^{-1} , 0.52 , 1.7 , $(-)$ 211 and $162.69\text{ kJ mol}^{-1}$ respectively. The electronic spectra and magnetic moment data (3.04 B.M.) suggest the octahedral geometry for this complex. In the Cu(II) complex of NAT exhibits a single broad band appears at 13320 cm^{-1} corresponding to transition ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$. The various ligand field parameters viz., 10Dq , λ and LFSE have been calculated and values are: 13320 cm^{-1} , $(-)$ 385 and 95.44 kJ mol^{-1} respectively. Ligand field parameters and magnetic moment (1.93 B.M.) data substantiate for the octahedral geometry of this complex²⁰⁻²³.

ESR spectra

The X-band ESR spectra of Cu(II) complexes were recorded in the solid state at room temperature and their $g_{\parallel}$, $g_{\perp}$, Δg , g_{av} and G have been calculated. The values of ESR parameters $g_{\parallel}$, $g_{\perp}$, g_{av} , Δg and G for Cu(II) complex of CAT are 2.3932 , 2.2724 , 2.3126 ,

0.1208 and 1.4467 respectively. Similarly, the corresponding values for Cu(II) complex of NAT are 2.2145, 2.1995, 2.2045, 0.0150 and 1.0759 respectively.

ESR spectra of the complexes revealed two g values ($g_{\parallel}$ and $g_{\perp}$). Since the $g_{\parallel}$ and $g_{\perp}$ values are closer to 2 and $g_{\parallel} > g_{\perp}$ suggesting a tetragonal distortion around the Cu(II) ion. The trend $g_{\parallel} > g_{\perp} > g_e$ (2.0023) shows that the unpaired electron is localized in $d_{x^2-y^2}$ orbital in the ground state of Cu(II) and spectra are characteristic of axial symmetry.

The exchange coupling interaction between two Cu(II) ions is explained by Hathaway expression $G = (g_{\parallel} - 2.0023)/(g_{\perp} - 2.0023)$. According to Hathaway²⁴, if the value G is greater than four ($G > 4.0$), the exchange interaction is negligible; whereas when the value of G is less than four ($G < 4.0$) a considerable exchange coupling is present in solid complex. The G values for the Cu(II) complexes are less than four indicating, considerable exchange interaction in the complexes²⁵.

Thermal analyses

The thermal behavior of metal complexes shows that the hydrated complexes lose molecules of hydration first; followed by decomposition of ligand molecules in the subsequent steps.

The thermal degradation behavior of the Co(II) complex of NAT has been studied by thermogravimetric analysis. The thermogram of the complex shows a weight loss between 80-130 °C. This corresponds to loss of two lattice water molecules in the complex (Remaining Wt.%, Obs./Calcd., 94.7/94.31). After 260 °C, a gradual weight loss has been observed in general upto 490 °C, corresponding to the loss of partially decomposed ligand part from the complex (Remaining Wt.%, Obs./Calcd., 45.5/41.26). After this temperature a weight loss has been observed up to 620 °C, suggesting the elimination of the remaining part of the ligand. Above 620 °C, a constant weight region has been observed due to metal oxide, as a final pyrolysis product (Remaining Wt.%, Obs./Calcd., 18.6/16.86).

The thermogram of the Ni(II) complex of NAT shows that the complex loss in the weight during the temperature range 80-120 °C, approximately equal to two water molecules, assignable to lattice water in the complex (Remaining Wt.%, Obs./Calcd., 95.5/94.31). On increase in temperature above 240 °C, a speedy weight loss has been observed upto 430 °C, corresponding to the loss of partially decomposed ligand part from the complex (Remaining wt.%, obs./cal., 45.60/44.29). Above this temperature loss in weight has been occurs up to 600°C. This indicates the elimination of the remaining thermally degradable part of the complex. After 600 °C a horizontal curve has been observed which corresponds to a mixture of metal oxide as an ultimate pyrolysis product (Remaining Wt.%, Obs./Calcd., 19.2/17.82)^{26, 27}.

X-ray diffraction study

X-ray diffraction was performed of metal complexes. The XRD patterns indicate crystalline nature for the complexes. X-ray powder diffractogram of the complexes were recorded using $\text{CuK}\alpha$ as source in the range 5°-90° (2 θ). X-ray crystal system has been worked out by trial, error methods for finding the best fit between observed, calculated $\sin^2\theta$. The diffractogram of Co(II) complex of CAT has recorded 23 reflections with maxima at with maxima reflection of $2\theta = 15.684$ which corresponds to $d = 5.6457 \text{ \AA}$. The complex crystallized in cubic system. $\sin^2\theta$ and hkl values for different lattice planes have been calculated. Crystal data for complex, $a = 19.37 \text{ \AA}$; $V = 7267.56 \text{ \AA}^3$, $Z = 9$, $D_{\text{obs}} = 1.3298 \text{ g/cm}^3$, $D_{\text{cal}} = 1.3890 \text{ g/cm}^3$. The observed and calculated values of density and $\sin^2\theta$ show good agreement. The diffractogram of Ni(II) complex of CAT has recorded 10 reflections with maxima at with maxima reflection of $2\theta = 16.046$ which corresponds to $d = 5.5189 \text{ \AA}$. The complex crystallized in cubic system. $\sin^2\theta$ and hkl values for different lattice planes have been calculated. Crystal data for complex, $a = 20.84 \text{ \AA}$; $V = 9052.92 \text{ \AA}^3$, $Z = 13$, $D_{\text{obs}} = 1.4809$

g/cm^3 , $D_{\text{cal}} = 1.5235 \text{ g/cm}^3$. The observed and calculated values of density and $\sin^2\theta$ show good agreement^{28, 29}.

Electrical conductivity

The temperature dependence of the solid state conductivity (σ) of the compounds in their compressed pellet form have been measured at fixed frequency 1KHz in the temperature range 297-413 K. the values of the solid state electrical conductivity of the Schiff base, its complexes increases with increasing temperature, decreases upon cooling over the studies temperature range indicating their semiconducting behavior. The general behavior of electrical conductivity follows the Arrhenius equation:

$$\sigma = \sigma_0 \exp (-E_a / KT)$$

where E_a is the thermal activation energy of conduction, σ_0 is the conductivity constant, K is the Boltzman constant. The lots of σ vs $1000/T$ for all the compounds are found to be linear over a studies temperature range. The room temperature electrical conductivity of all the compounds lies in the range 1.241×10^{-7} - $3.525 \times 10^{-9} \text{ ohm}^{-1}\text{cm}^{-1}$. These values show their semi-conducting nature. The electrical conductivity at room temperature for the complexes of CAT are $\text{Co} > \text{Cu} > \text{Ni}$ and for the metal complexes of NAT are $\text{Co} > \text{Cu} > \text{Ni}$. The activation energy of the compound lies in the range 0.252-0.786^{30, 31}. The confirming of the temperature dependence conductivity of the compounds was also checked by the repeating of the conductivity measurements.

Antimicrobial activities

The *in-vitro* Antimicrobial activity of the synthesized Schiff base ligands and their corresponding metal complexes on selected bacteria *E. coli* and *S. aureus* and two fungi *A. niger* and *C. albicans* was carried out. All of the tested compounds showed good biological activity against microorganism. On comparing the biological activity of the Schiff base and its metal complexes with the standard bactericide and fungicide, it is show that the metal complexes have moderate activity as compared to the standard but all the complexes are more active than their respective ligands. The higher inhibition zone of metal complexes than those of the ligands can be explained on the basis of Overtone's concept and Chelation theory. On chelation, the polarity of the metal ion will be reduced to greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further, it increases the delocalization of π -electrons over the whole chelating ring and enhances the penetration of the complexes into lipid membranes and blocking of the metal binding sites in the enzymes of microorganisms. There are other factors which also increases the activity are solubility, conductivity and bond length between the metal and ligand³²⁻³⁴.

The minimum inhibition values were determined using the filter paper disc diffusion method and the concentrations have been used in ppm. All the synthesized compounds have been screened *in-vitro* for their antibacterial activity against bacteria *E. coli* and *S. aureus* and antifungal activity against two fungi *A. niger* and *C. albicans*. Standards for antibacterial and antifungal activity Streptomycin and miconazole were used respectively. Standards also screened under the similar conditions for comparison. The diameter of the inhibition zones in (mm) are given in Tables 3 and 4.

Table 3. Antibacterial screening data for the ligands and their complexes.

Compound	<i>E. coli</i>						<i>S. aureus</i>					
	Diameter of inhibition zone (mm)			% Activity index *			Diameter of inhibition zone (mm)			% Activity index *		
	25	50	100	25	50	100	25	50	100	25	50	100
CAT	11	13	16	50	54	57	9	12	14	50	55	58
Co(II)	18	21	26	82	88	93	16	20	22	89	91	92
Ni(II)	16	18	22	73	75	79	14	18	20	78	82	83
Cu(II)	18	21	25	82	88	89	15	19	21	83	86	88
NAT	14	16	19	64	67	68	11	13	16	61	59	67
Co(II)	23	26	33	105	108	118	14	18	20	78	82	83
Ni(II)	17	19	22	77	79	79	12	15	18	67	68	75
Cu(II)	22	24	30	100	100	107	17	21	25	94	95	104
Streptomycin (Standard)	22	24	28	100	100	100	18	22	24	100	100	100

$$*\% \text{ Activity Index} = \frac{\text{Zone of inhibition by test compound (diameter)}}{\text{zone of inhibition by standard (diameter)}} \times 100$$

Table 4. Antifungal screening data for the ligands and their complexes.

Compound	Diameter of inhibition zone (mm); Concentration in ppm					
	<i>A. niger</i>			<i>C. albicans</i>		
	25	50	100	25	50	100
CAT	14	17	22	13	17	23
Co(II)	19	23	27	20	24	29
Ni(II)	14	18	25	16	18	23
Cu(II)	18	22	29	17	20	26
NAT	11	14	17	13	15	19
Co(II)	17	21	26	17	19	23
Ni(II)	15	19	23	16	18	22
Cu(II)	16	20	24	18	20	24
Miconazole (Standard)	20	24	30	22	24	29

Conclusion

In the present research studies, our efforts are synthesized of some newly compounds from the conventional as well as microwave methods. These synthesized compounds characterized by various physicochemical and spectral analyses. The synthesized Schiff base ligands bind with the metal ions in a bidentate manner, with SN donor sites of thiophene-S and azomethine-N. FAB-mass and thermal data show degradation pattern of the complexes. Thermogravimetric studied of the complexes also helped to characterize of the complexes. The XRD patterns indicate crystalline nature of the complexes. The antimicrobial data show that the metal complexes to be more biological active compared to those parent Schiff base ligand against all pathogenic species. The compounds also inhibit the growth of fungi and bacteria to a greater extent as the concentration is increased.

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