

Synthesis and characterization of some Schiff bases, their metal complexes and thermal, antimicrobial and catalytic features

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Abstract Two pyridine carboxaldehyde-derived schiff bases and their copper, nickel and manganese complexes have been synthesized, characterized by spectroscopic and thermal analyses. For the antimicrobial activity experiments, the microorganisms *B. megaterium*, *K. pneumoniae*, *E. coli*, *P. aeruginosa*, *S. aureus*, *B. subtilis* and *E. aerogenes* have been used. Nickel and copper complex compounds of ligand L² were recorded as the most effective coordination compounds as antimicrobial. Catalytic activity results revealed that the both manganese and nickel complexes were moderately more effective for the oxidation reactions of cyclohexene and styrene.

Keywords Schiff base · Complex · Thermal · Catalysis · Antimicrobial

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Introduction

Schiff base ligands and their transition metal complexes have captivated the interest of many researches, especially in the application for catalytic reactions including alkane and alkene oxidations [1–4]. Many coordination compounds of different Schiff bases contain different donor sites (e.g., N₂O, N₄, N₂S) in heterocyclic rings, and because of the nature of donor atoms and central metal ions, the transition metal complexes of different Schiff base ligands developed interesting pharmacological activities such as antibacterial, antiviral, antimalarial, antituberculosis and antitumoural agents [5–7]. So far, various pyridine carboxaldehyde-derived Schiff bases and complexes have been synthesized, characterized and examined for their different biological activity [8–10], and recently, some transition metal complexes of these kinds of Schiff bases have been found to be an acetylcholinesterase inhibitor [11]. In addition to above researches, various pyridine-derived Schiff bases and their different complexes have also been examined for their catalytic activities in different organic reactions [12–14]. Our work deals with the synthesis, characterization and thermal, antimicrobial and catalytic features of pyridine-2-carboxaldehyde-derived Schiff bases and their metal complexes.

Experimental

Pyridine-2-carboxaldehyde, *o*-diaminobenzene, 1,2-diaminocyclohexane and acetate salts of copper(II), nickel(II) and manganese(II) were purchased from Sigma-Aldrich. Nuclear magnetic resonance spectra were recorded on a Bruker AV 300 MHz spectrometer in the solvent CDCl₃. Infrared spectra were obtained using KBr

disks on a Shimadzu 8300 FTIR spectrophotometer in the region of 400–4000 cm^{-1} . Ultraviolet spectra were run in ethanol on a Shimadzu UV-160 A spectrophotometer. Mass spectra of the ligand were recorded on a LC/MS APCI AGILENT 1100 MSD spectrophotometer. The oxidation products were analyzed with a gas chromatograph (Shimadzu, GC-14B) equipped with a SAB-5 capillary column and a flame ionization detector. Elemental analyses were performed on a LECO CHNS 932 elemental analyzer, and the metal analyses were carried out on an Ati Unicam 929 Model AA Spectrometer in solutions prepared by decomposing the compounds in aqua regia and subsequently digesting them in conc. HCl. Thermal analyses of synthesized ligand and its metal complexes were carried out on a Perkin-Elmer Thermogravimetric Analyzer TG/DTA 6300 instrument under nitrogen atmosphere between the temperature range 30 and 850 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C min}^{-1}$. Magnetic measurements were taken by the Gouy method using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant. Molar conductances of the Schiff base ligands and their transition metal complexes were determined in MeOH (ca. 10^{-3} M) at room temperature using a Jenway Model 4070 conductivity meter.

Synthesis of the ligands

The two ligands were synthesized from 1:2 equilibrium of the diamine and the pyridine carboxaldehyde. For ligand L^1 , 2 mmol (0.214 g) pyridine-2-carboxaldehyde and 1 mmol (0.114 g) *o*-diaminohexane were mixed in 30 mL ethanol and refluxed for 8 h, and for the ligand L^2 , 2 mmol (0.214 g) pyridine-2-carboxaldehyde and 1 mmol (0.108 g) *o*-diaminobenzene were mixed in 30 mL ethanol and refluxed for overnight. The resulted precipitates were recrystallized from ethanol. Synthesis scheme can be seen in Fig. 1.

L^1 (N^1E,N^2E)- N^1,N^2 -bis(pyridin-2-ylmethylene)cyclohexane-1,2-diamine

Chemical formula: $\text{C}_{18}\text{H}_{20}\text{N}_4$. Yield: 75 %, m.p.: 131 $^{\circ}\text{C}$, Elemental Analysis found % (calculated %): C 74.3(73.9) H 6.1(6.9) N 19.3(19.2). UV-Vis (ethanol) (λ_{max} , nm): 235, 266 FT-IR (KBr, cm^{-1}): 1644 (C=N); 1586, 1466 (Py, Ar-H); 2859, 2926 (CH_2); 617, 666 (Py). Mass spectrum (LC/MS APCI): m/z 293.2 $[\text{M} + \text{H}]^+$. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.53 (2H-1', dd, $J = 3$ Hz, 1 Hz), 7.2 (2H-2', ddd, $J = 6.1$ Hz, 3 Hz, 1 Hz), 7.63 (2H-3', dt, $J = 8$ Hz, 1.7 Hz), 7.87 (2H-4', dd, $J = 8$ Hz, 1 Hz), 3.53 (2H-1, m), 1.5 (2H_a-2, m), 1.81 (4H-3, 2H_b-2, m), 8.3 (CH=N, s). $^{13}\text{C NMR}$ (300 MHz, CDCl_3): δ 73.5 (C-1), 32.7 (C-2), 24.3 (C-3), 149.2 (C-1'), 124.5 (C-2'), 136.4 (C-3'), 121.3 (C-4'), 154.6 (C-5'), 161.4 (CH=N).

L^2 (N^1E,N^2E)- N^1,N^2 -bis(pyridin-2-ylmethylene)benzene-1,2-diamine

Chemical formula: $\text{C}_{18}\text{H}_{14}\text{N}_4$. Yield: 63 %, m.p.: 121 $^{\circ}\text{C}$, Elemental Analysis found % (calculated %): C 74.9(75.5) H 5.1(4.9) N 19.6(19.6). UV-Vis (ethanol) (λ_{max} , nm): 234, 275, 309. FT-IR (KBr, cm^{-1}): 1622 (C=N); 1591, 1500, 1448, 3055 (Py, Ar-H); 2673, 2851, 2920 (CH_2), 621 (Py). Mass spectrum (LC/MS APCI): m/z 287.1 $[\text{M} + \text{H}]^+$. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.48 (2H-1', d, $J = 8$ Hz), 7.25 (2H-2', t, $J = 8$ Hz), 7.8 (2H-3', dt, $J = 7.8$ Hz, 1.7 Hz), 7.87 (2H-4', dd, $J = 7.1$, 1 Hz), 6.3 (2H-2, s), 6.89 (2H-3, d, $J = 8$ Hz), 8.48 (CH=N, overlapped with H-1'). $^{13}\text{C NMR}$ (300 MHz, CDCl_3): δ 142.7 (C-1), 120.1 (C-2), 121.0 (C-3), 149.2 (C-1'), 124.6 (C-2'), 136.8 (C-3'), 122.3 (C-4'), 150.3 (C-5'), 157.4 (CH=N).

Synthesis of the complex compounds

Acetate salts (1 mmol) of Cu(II), Co(II) and Ni(II) were mixed with ethanol solution of our ligand (1 mmol). The resulting mixtures were left refluxing overnight. Complex compounds were crystallized from ethanol.

$\text{Cu}(L^1)(\text{OAc})_2$

($\text{C}_{22}\text{H}_{26}\text{CuN}_4\text{O}_4$), yield: 60 %, m.p.: 167.4 $^{\circ}\text{C}$, Elemental Analysis found % (calculated %): C 55.4 (55.7), H 5.4 (5.5), N 11.9 (11.8), Cu 13.7 (13.4). UV-Vis (ethanol) (λ_{max} , nm): 264, 348, 501. FT-IR (KBr, cm^{-1}): 1628 (C=N), 1472, 3075 (Py, Ar-H), 2932(CH_2), 438 (M-N), 1595 (C-O), 759 (COO), 693 (Py). Λ_{M} ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$): 7.1. μ_{eff} (B.M.): 1.98.

$\text{Mn}(L^1)(\text{OAc})_2$

($\text{C}_{22}\text{H}_{26}\text{MnN}_4\text{O}_4$), yield: 59 %, m.p.: 147.1 $^{\circ}\text{C}$, Elemental Analysis found % (calculated %): C 56.9 (56.8), H 5.8 (5.6), N 11.9 (12.0), Mn 12.4 (11.8). UV-Vis (ethanol) (λ_{max} , nm): 265, 339, 510. FT-IR (KBr, cm^{-1}): 1629 (C=N), 1416, 3020 (Py, Ar-H), 2934, 2862 (CH_2), 413 (M-N), 1577 (C-O), 781 (COO), 632, 686 (Py). Λ_{M} ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$): 12. μ_{eff} (B.M.): 5.85.

$\text{Ni}(L^1)(\text{OAc})_2$

($\text{C}_{22}\text{H}_{26}\text{NiN}_4\text{O}_4$), yield: 65 %, m.p.: 155.2 $^{\circ}\text{C}$, Elemental Analysis found % (calculated %): C 56.7 (56.3), H 6.0 (5.6), N 12.1 (11.9), Ni 12.6 (12.5). UV-Vis (ethanol) (λ_{max} , nm): 246, 341, 468. FT-IR (KBr, cm^{-1}): 1618 (C=N), 1408, 3015 (Py, Ar-H), 2924, 2859 (CH_2), 440 (M-N), 1557 (C-O), 759 (COO), 630, 684 (Py). Λ_{M} ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$): 9.3. μ_{eff} (B.M.): 3.15.

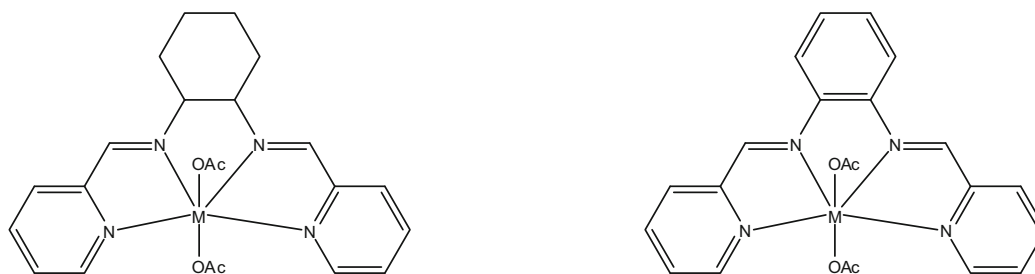
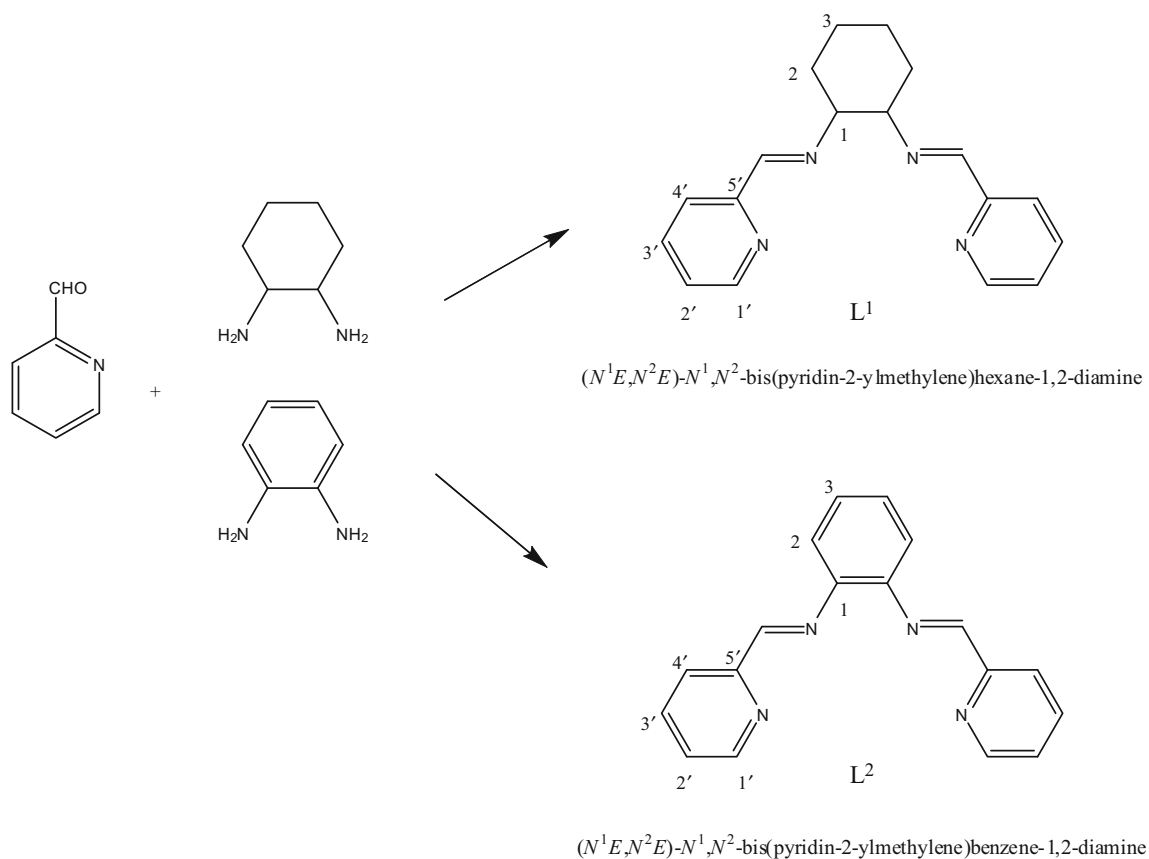


Fig. 1 Reaction scheme for the syntheses and proposed structures of the ligands and their complexes

$Cu(L^2)(OAc)_2$

($C_{22}H_{20}CuN_4O_4$), yield: 55 %, m.p.: 148 °C, Elemental Analysis found % (calculated %): C 56.7 (56.5), H 4.5 (4.3), N 12.1 (11.9), Cu 13.8 (13.6). UV-Vis (ethanol) (λ_{max} , nm): 238, 268, 365, 482. FT-IR (KBr, cm^{-1}): 1600 (C=N), 1428, 1481, 3059 (Py, Ar-H), 2927 (CH_2), 441 (M-N), 1568 (C-O), 748 (COO), 616, 675 (Py). Λ_M ($\Omega^{-1} cm^2 mol^{-1}$): 11.7. μ_{eff} (B.M.): 1.95.

$Mn(L^2)(OAc)_2$

($C_{22}H_{20}MnN_4O_4$), yield: 55 %, m.p.: 173.6 °C, Elemental Analysis found % (calculated %): C 57.9 (57.5), H 4.6 (4.4), N 12.5 (12.2), Mn 12.3(11.9). UV-Vis (ethanol) (λ_{max} , nm): 240, 271, 309, 517. FT-IR (KBr, cm^{-1}): 1598 (C=N), 1476, 1411, 3054 (Py, Ar-H), 2919 (CH_2), 501 (M-N), 1563 (C-O), 743 (COO), 614, 650 (Py). Λ_M ($\Omega^{-1} cm^2 mol^{-1}$): 13.5. μ_{eff} (B.M.): 5.90.

$Ni(L^2)(OAc)_2$

($C_{22}H_{20}NiN_4O_4$), yield: 54 %, m.p.: 131.2 °C, Elemental Analysis found % (calculated %): C 57.2 (57.0), H 4.7 (4.4), N 12.3 (12.1), Ni 12.9 (12.7). UV–Vis (ethanol) (λ_{max} , nm): 242, 340, 379, 448. FT-IR (KBr, cm^{-1}): 1595 (C=N), 1481, 1410, 3063 (Py, Ar–H), 2972 (CH_2), 445 (M–N), 1539 (C–O), 744 (COO), 661 (Py). Λ_M ($\Omega^{-1} cm^2 mol^{-1}$): 7.6. μ_{eff} (B.M.): 3.11.

Oxidation procedure

A mixture of 1×10^{-3} mol catalyst, 20 mL solvent (CH_3CN) and 10 mmol cyclohexene/styrene was stirred under nitrogen atmosphere in a 50-mL round-bottom flask. Then, 20 mmol hydrogen peroxide (30 % in water) was added dropwise. The resulting mixture was vigorously stirred for 8 h at 60 °C. After filtration and washing with solvent, the filtrate was concentrated and then subjected to GC analysis. The yields were recorded as the GC yield based on the starting styrene or cyclohexene. The identity of the oxidation products was confirmed by GC–MS.

Preparation of microorganism culture

The test bacteria kept at 4 °C were injected into Nutrient Buyyon and incubated at 37 °C for 24 h, and the yeasts were incubated in Sabouraud dextrose agar for 24 h at 30–103 °C. Mueller–Hinton agar (MHA) (Oxoid) and Sabouraud dextrose agar (SDA) sterilized in a flask and cooled to 45–50 °C were distributed to sterilized petri dishes with a diameter of 9 cm (15 mL) after injecting cultures (0.1 mL) of bacteria and yeast (106 bacteria per mL and 105 yeasts per mL), and distributing medium in petri dishes homogenously. Dishes injected with extracts were located on the solid agar medium by pressing slightly. Petri dishes were kept at 4 °C for 2 h; placks injected with yeasts were incubated at 25 °C; and the bacteria were incubated at 37 °C for 24 h. At the end of the period, inhibition zones formed on the MHA and SDA were evaluated in millimeters.

Results and discussion

Spectral analysis

Examination of 1H NMR spectrum of L^1 revealed imine protons ($CH=N$) as broad singlet at δ 8.3. The aromatic protons next to nitrogen in the pyridine ring (2H-1') were seen further downfield at δ 8.53 as dd ($J = 1, 3.0$ Hz). 2H-4' was at 7.87 as dd ($J = 8, 1$ Hz), next to this signal at δ 7.63 was a dt (2H-3', $J = 8, 1.7$ Hz). The two hydrogens of

2' para to the imine group were seen furthest upfield at 7.20 ppm as ddd ($J = 3, 6, 1$ Hz), coupling with H-1', H-3' and H-4'. As for the cyclohexane ring, the most deshielded protons were 2H-1 (3.53 ppm, m). Six hydrogens belonging four hydrogens of 3 and two hydrogens of 2 on the cyclohexane ring were seen at 1.81 ppm, and we suspect that the other two hydrogens of 2 (2H_a-2) fall into slight shielding of the lone pair of nitrogen in the imine group or/ and the pyridine rings and show a multiplet at 1.50 ppm [15]. 1H NMR of L^2 [14] revealed the aromatic protons, 2H-2, as a singlet at 6.3 ppm. The other two hydrogens (2H-3) on the benzene ring gave a broad doublet ($J = 8$ Hz) at 6.89 ppm. As for the pyridine ring, 2H-1' gave a doublet ($J = 8$ Hz) at 8.48 ppm. H-2' was observed at 7.25 ppm as a triplet ($J = 8$ Hz). The imine protons were overlapped with the H-1' protons on the pyridine ring at 8.48 ppm. ^{13}C NMR spectra of the ligands gave the imine carbon frequencies at 157.4 ppm for L^2 and at 161.4 ppm for L^1 . Cyclohexane carbons in ligand L^1 were at δ 24.3 (C-3), δ 32.7 (C-2) and at 73.5 (C-1), which is the most deshielded because of the nitrogen in the imine group. Pyridine ring carbons for this ligand were seen between 121.3 and 161.4 ppm. All the aromatic carbons belonging L^2 were observed between 120.1 and 157.4 ppm. The spectral data can be seen in the experimental part.

IR spectra of the ligands revealed the imine stretching frequencies at $1644 cm^{-1}$ (L^1) and at $1622 cm^{-1}$ (L^2). These imine frequencies were considerably redshifted in all of the complexes, which proves the chelation with the metal atoms. The ligands showed pyridine stretching before chelation at $1586 cm^{-1}$, $1466 cm^{-1}$ (L^1) and at $1591 cm^{-1}$, $1448 cm^{-1}$ (L^2); however, all the complexes gave these stretching at bigger wave lengths, respectively, lower wave numbers, frequencies. Additionally, the other known pyridine in plane bendings for the ligands was observed between 616 and 675 nm, which were shifted toward lower or higher frequencies in the spectra of all the complexes [15, 16]. For these kinds of complex compounds, the values of asymmetric and symmetric vibrations of COO^- are important. The IR spectra of all the complexes revealed that asymmetric vibrations [$\nu_{as}(COO^-)$] were observed between 1539 and $1578 cm^{-1}$, whereas symmetric vibrations [$\nu_s(COO^-)$] were observed between 1332 and $1342 cm^{-1}$ range [17, 18]. The sharp bands between 743 and $781 cm^{-1}$ are known to be the characteristic bands for monodentate acetates [17].

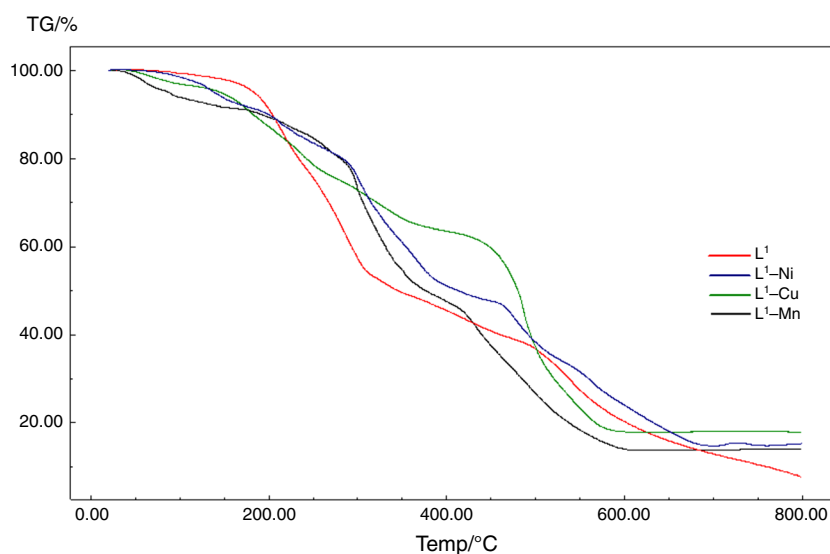
UV–visible spectra of the ligands and the complexes showed absorption bands between 234 and 517 nm. The spectra of the complexes showed some bands in the high-energy region at 309–379 nm which can be assigned to charge-transfer L–M bands [19, 20]. The complex compounds showed dd transitions between 441 and 517 nm.

Table 1 Thermal analysis data for ligand and its complexes

Compound	M.W.	T/°C	Mass loss/% Found (calculated)	Assignment	Residual/ % Found (calculated)
L ¹	292.38	70–306	47.2 (46.5)	C ₈ H ₁₂ N ₂	
		306–	52.7 (53.4)	2(C ₅ H ₄ N)	
Ni(L ¹)(OAc) ₂	469.16	100–300	23.9 (25.2)	2(AcO)	13.6 (12.5) (Ni)
		300–460	30.1 (28.9)	C ₈ H ₁₂ N ₂	
Cu(L ¹)(OAc) ₂	474.01	460–700	34.7 (33.3)	2(C ₅ H ₄ N)	
		50–255	25 (24.9)	2(AcO)	14.99 (13.4) (Cu)
		255–440	15.8 (16.0)	C ₆ H ₄	
Mn(L ¹)(OAc) ₂	465.40	440–600	43.8 (44.3)	2(C ₆ H ₅ N ₂)	
		49–290	24.5 (25.4)	2(AcO)	11.3 (11.8) (Cu)
		290–425	31.4 (29.2)	C ₈ H ₁₂ N ₂	
		425–600	33.0 (33.5)	2(C ₅ H ₄ N)	
L ²		100–190	27.4 (26.5)	C ₆ H ₄	
		190–600	72.5 (73.3)	2(C ₆ H ₅ N ₂)	
Ni(L ²)(OAc) ₂	463.11	49–300	19.6 (25.5)	2(AcO)	13.97 (12.67) (Ni)
		300–400	16.6 (16.4)	C ₆ H ₄	
		400–500	46.5 (45.3)	2(C ₆ H ₅ N ₂)	
Cu(L ²)(OAc) ₂	467.08	60–265	25.1 (25.3)	2(AcO)	12.3 (13.6) (Cu)
		265–348	16.0 (16.3)	C ₆ H ₄	
		348–500	46.5 (44.9)	2(C ₆ H ₅ N ₂)	
Mn(L ²)(OAc) ₂	459.36	118–325	23.1 (25.7)	2(Aco)	9.98 (11.96) (Mn)
		325–390	17.9 (16.5)	C ₆ H ₄	
		390–725	44.9 (45.7)	2(C ₆ H ₅ N ₂)	

All thermal analyses were done under nitrogen atmosphere between the temperature range 30 and 850 °C at a heating rate of 10 °C/min

Fig. 2 TG plots of L¹ and its complexes recorded under nitrogen atmosphere between the temperature range 30 and 850 °C at a heating rate of 10 °C min⁻¹



Magnetic susceptibility studies revealed the geometries of all the complexes to be octahedral. For the copper complexes, the magnetic moments were calculated as 1.95 and 1.98 B.M. [17]. The manganese complexes gave these values as 5.85 and 5.95 B.M. [21]. The nickel complexes

also revealed their characteristic magnetic moment values as 3.11 and 3.15 B.M., suggesting octahedral geometry [21, 22]. Molar conductivities of the ligand and its coordination compounds were between 7.1 and 13.5 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, which proves their nonelectrolyte features [23].

Fig. 3 TG plots of L^2 and its complexes recorded under nitrogen atmosphere between the temperature range 30 and 850 °C at a heating rate of 10 °C min⁻¹

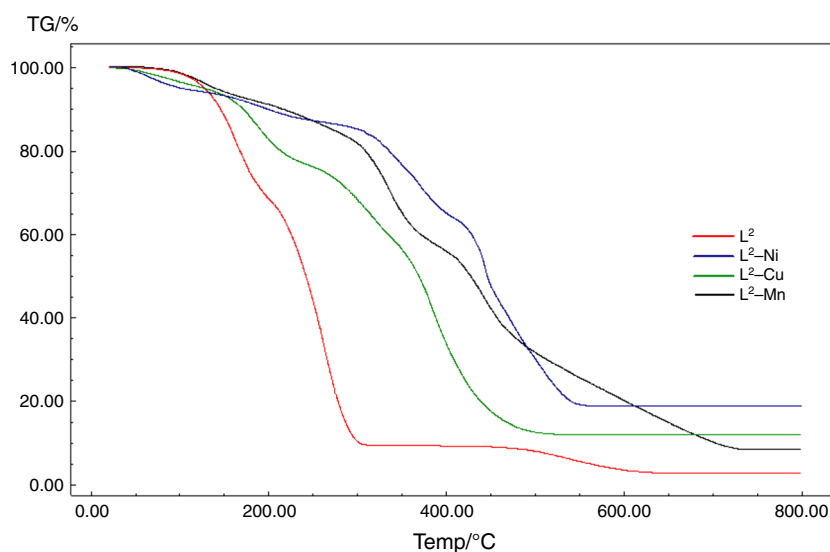


Table 2 Styrene oxidation results

Entry	Catalyst	Styrene conversion/%	Selectivity/%			
			Styrene oxide	Benzaldehyde	Benzoic acid	Others
1	Cu(L ¹)(OAc) ₂	31.5	10.2	65.8	10.4	13.6
2	Mn(L ¹)(OAc) ₂	47.6	22.3	61.4	12.3	4.0
3	Ni(L ¹)(OAc) ₂	64.8	35.0	55.9	5.7	3.4
4	Cu(L ²)(OAc) ₂	28.4	12.9	61.6	11.8	13.7
5	Mn(L ²)(OAc) ₂	71.2	38.6	51.8	7.2	2.4
6	Ni(L ²)(OAc) ₂	35.4	20.7	60.3	12.6	6.4

Others phenylacetaldehyde, 1-phenylethane-1,2-diol

Reaction temperature: 60 °C (333.15 K)

Solvent: acetonitrile

Table 3 Cyclohexene oxidation results

Entry	Catalyst	Cyclohexene conversion/%	Selectivity/%		
			Cyclohexene oxide	2-Cyclohexene-1-ol	Others
1	Cu(L ¹)(OAc) ₂	25.3	9.3	24.5	66.2
2	Mn(L ¹)(OAc) ₂	35.4	15.8	36.6	47.6
3	Ni(L ¹)(OAc) ₂	41.7	20.9	45.6	33.5
4	Cu(L ²)(OAc) ₂	22.5	11.5	28.4	60.1
5	Mn(L ²)(OAc) ₂	55.6	30.1	41.4	28.5
6	Ni(L ²)(OAc) ₂	29.9	17.8	35.7	46.5

Others: 2-cyclohexene-1-one, 2-cyclohexene-1-hydroperoxide

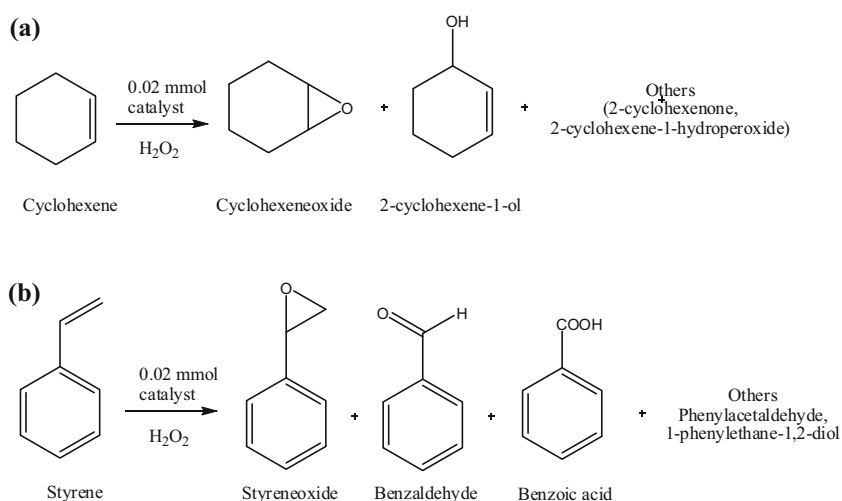
Reaction temperature: 60 °C (333.15 K)

Solvent: acetonitrile

Thermal analysis

Examination of TG graphics of L^1 gives two-step degradation process starting at 70 °C, and the biggest loss was seen at 306 °C with 52.73 % (Calc. 53.4 %), corresponding the two

pyridine units. One can divide the TG graphics of the complexes of L^1 into three degradation steps, the first one of which results in losing the two acetate units. The second and the third steps of degradations in the TG graphics of the coordination compounds Ni(L¹)(OAc)₂ and Mn(L¹)(OAc)₂

Fig. 4 Various oxidation products of cyclohexene (a) and styrene (b)**Table 4** Antimicrobial activity data of L^1 and its complexes

Inhibition zone/mm				
Microorganisms	L^1	$\text{Cu}(\text{L}^1)(\text{OAc})_2$	$\text{Ni}(\text{L}^1)(\text{OAc})_2$	$\text{Mn}(\text{L}^1)(\text{OAc})_2$
<i>B. megaterium</i>	10 ± 1.00	18.6 ± 1.15	13.0 ± 0.00	14 ± 1.15
<i>K. pneumoniae</i>	11 ± 0.57	14.3 ± 0.57	13.3 ± 0.57	14 ± 2.00
<i>E. coli</i>	13 ± 1.52	14.0 ± 1.00	12.3 ± 0.57	15 ± 1.15
<i>P. aeruginosa</i>	11 ± 1.52	15.0 ± 1.00	14.3 ± 0.57	15 ± 1.52
<i>S. aureus</i>	12 ± 2.51	14.3 ± 1.52	13.3 ± 2.08	16 ± 2.51
<i>B. subtilis</i>	10 ± 1.15	13.6 ± 0.57	13.0 ± 1.00	14 ± 1.15
<i>E. aerogenes</i>	12 ± 1.15	14.3 ± 0.57	14.0 ± 1.00	16 ± 2.08

Table 5 Antimicrobial activity data of L^2 and its complexes

Inhibition zone/mm				
Microorganisms	L^2	$\text{Cu}(\text{L}^2)(\text{OAc})_2$	$\text{Ni}(\text{L}^2)(\text{OAc})_2$	$\text{Mn}(\text{L}^2)(\text{OAc})_2$
<i>B. megaterium</i>	13.3 ± 1.52	16.0 ± 1.00	16.0 ± 1.00	17.3 ± 0.57
<i>K. pneumoniae</i>	12 ± 0.00	14.0 ± 0.00	15.0 ± 1.00	14.6 ± 0.57
<i>E. coli</i>	12.3 ± 1.52	13.3 ± 0.57	16.3 ± 0.57	15.6 ± 0.57
<i>P. aeruginosa</i>	12.3 ± 1.15	18.3 ± 0.57	16.6 ± 0.57	16.0 ± 0.00
<i>S. aureus</i>	12.6 ± 1.15	16.6 ± 1.15	16.0 ± 0.00	15.0 ± 3.00
<i>B. subtilis</i>	14.3 ± 0.57	17.0 ± 0.00	16.6 ± 2.08	13.0 ± 1.00
<i>E. aerogenes</i>	13.0 ± 1.00	18.6 ± 1.15	15.6 ± 1.52	13.3 ± 2.51

are assigned to $\text{C}_8\text{H}_{12}\text{N}_2$ (benzene and imine moieties) and $2(\text{C}_5\text{H}_4\text{N})$ (two pyridine moieties), respectively. The copper complex of the same ligand gave the second degradation with a total mass loss of 15.76 % (Calc. 16.03 %), corresponding the benzene moiety only, and the second and the biggest lost occurred over 440 °C with 43.8 % (Calc. 44.3 %), corresponding the pyridine and the imine moieties ($2 \times \text{C}_6\text{H}_5\text{N}_2$).

TG graphics of E6 also gave two steps of degradations: The first step was the loss of benzene [27.42 % (Calc.

26.54 %)], and the second step was recorded and calculated as the pyridine and the imine groups [72.50 % (Calc. 73.34 %)]. All the complexes of L^1 gave three degradation steps: The first of which corresponds to the loss of two acetates, and the second and the third steps belong to the losses of benzene ring and the pyridines with imine groups, respectively.

Among the whole of the complex compounds, the nickel(II) complex of L^1 and the manganese(II) complex of L^2 were more temperature-stable compared to the others,

and all the metal complexes gave their metal percentages as their residual parts. The thermal data can be seen in Table 1, and the Figs. 2 and 3 show the thermal graphics of the synthesized compounds.

Catalytic activity

Both styrene and cyclohexene oxidation reactions gave moderately good results. Among the complex compounds, nickel(II) complex of L^1 and manganese(II) complex of L^2 showed highest performances for these oxidation reactions as catalysts. Since the oxidation reactions are carried out in high temperatures, the performances of these complexes might also be related to the fact that they were thermally the most stable catalysts. The highest performance as a catalyst belongs to the $Mn(L^2)(OAc)_2$ with a styrene conversion percentage of 71.2. For the same reaction, nickel complex of L^1 also showed good conversion with a percentage of 64.8 and resulted in 35 % styrene oxide selectivity. For the cyclohexene oxidation reactions, moderate conversions were observed for all the coordination compounds. Nonetheless, highest conversions among them belong to nickel complex of L^1 and manganese complex of L^2 with percentages of 41.7 and 55.6, respectively, and the cyclohexene oxide selectivities for these complexes were recorded as 20.9 and 30.1 %. For cyclohexene oxidation reaction, moderately highest selectivities were recorded for 2-cyclohexene-1-ol. The rest of the data can be seen in Tables 2 and 3, and the oxidation reaction schemes are given in Fig. 4.

Antimicrobial activity

All the synthesized compounds were examined for their antimicrobial activity against a number of microorganisms. Both ligands L^1 and L^2 were slightly effective against the microorganisms, however, all the complex compounds gave much more effective results compared to their ligands. Between the synthesized ligands, ligand L^2 was slightly more effective toward all microorganisms than L^1 . It is obvious from the results that the coordination compounds of L^2 gave better results than those of L^1 (Tables 4, 5). Especially, nickel and copper complexes of ligand L^2 gave bigger inhibition zones than those of other complexes. The biggest inhibition zones with around 18 mm belong to the copper complexes of both ligands against *P.aeruginosa*, *E. aerogenes* and *B. megaterium*. Among the complex compounds, nickel complex of L^1 was the least effective against most of the organisms. All the inhibition zones for this complex were recorded between 12 and 14 mm, and the latter is the biggest zone seen for the microorganisms *P.aeruginosa* and *E.aerogenes*. Antimicrobial data are given in Tables 4 and 5.

Conclusions

The present work describes the synthesis and characterization of two pyridine-2-carboxaldehyde-derived Schiff bases and their copper(II), nickel(II) and manganese(II) complexes. All spectral data and the thermal analysis supported the proposed structures of all synthesized compounds. Magnetic moment values strongly suggested the geometries of the coordination compounds to be octahedral. Catalytic activity results showed nickel and manganese complexes of the ligands to be better catalysts toward oxidation reactions of styrene and cyclohexene. All the coordination compounds were better antimicrobial agents compared to their ligands.

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