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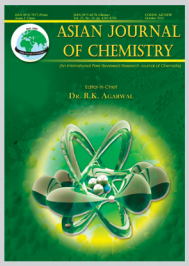

Synthesis, Structural and Biochemical Activity of Pyridine Substituted Pyrrole Ligands and Their Mononuclear Cu(II), Ni(II) and Co(II) Complexes

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Monomeric copper(II), nickel(II) and Co(II) complexes of 6-(2,5-dimethyl-1*H*-pyrrol-1-yl)pyridin-2-amine (dmpypr) and 2,6-*bis*(2,5-dimethyl-1*H*-pyrrol-1-yl)pyridine (tmpypr) were prepared and characterized by elemental analyses, magnetic moments, ^{1}H and ^{13}C NMR, IR, mass spectral studies. The mononuclear metal complexes of dmpypr and tmpypr were found to have a 1:2 metal:ligand ratio. Elemental analyses, stoichiometric and spectroscopic data of metal complexes indicated that the metal ions were coordinated to the -NH_2 and C=N group nitrogen atoms. All of the data obtained from spectral studies supported the structural properties of ligands and their metal complexes. The free ligands and their metal complexes showed antimicrobial activity against *S. aureus* but no antifungal activity was observed against yeast like fungi. Among them, copper complexes and free ligands showed a narrow range of inhibitory activity against *Mycobacterium smegmatis*. Free ligands (**2, 3**), were found to have activity against *Saccharomyces cerevisiae* (Sc).

Key Words: Pyrrole, Pyridin, Metal complexes, Antimicrobial activity.

INTRODUCTION

Pyrroles, one of the classes of heterocycles, are important building blocks in the synthesis of natural products[1] and have different biological activities[2]. These compounds have also been found broadly in application materials chemistry[3]. Despite their importance from a pharmacological, industrial and synthetic point of view, comparatively few methods for their synthesis have been reported[4]. Using Hantzsch[5], Knorr[6] and aza-Witting reactions[7], the Paal-Knorr[8] reaction is one of the simplest methods for the synthesis of N-substituted pyrroles. Many catalysts have been used to promote the Paal-Knorr reaction such as $Ti(OiPr_4)$[9], Al_2O_3[10], $Bi(NO_3)_3$[11], $Bi(OTf)_3$[12], $Sc(OTf)_3$[13] *etc.*[14,15].

In addition, there was a continuing interest in metal complexes of Schiff bases. Because of the presence of both hard nitrogen or oxygen and soft sulphur donor atoms in the backbones of these ligands, they readily coordinated with a wide range of transition metal ions yielding stable and intensely coloured metal complexes, some of which were shown to exhibit interesting physical and chemical properties[16-18] and potentially useful biological activities[19,20]. Many reports were available for the preparation and properties of model copper complexes which mimicked copper-containing metalloproteins such as hemocyanine and tyrosinase[21,22].

In the present paper, novel metal complexes derived from 6-(2,5-dimethyl-1*H*-pyrrol-1-yl)pyridin-2-amine (dmapypr) and 2,6-*bis*(2,5-dimethyl-1*H*-pyrrol-1-yl)pyridine (tmpypr) were reported. Copper(II) nickel(II) and Co(III) complexes were prepared and characterized by elemental analyses, magnetic susceptibilities, IR, UU-VIS, mass spectral studies. The free ligand and metal complexes were tested for bacteria and the free ligands and copper(II) complexes had antibacterial activity against *S. aureus* and *M. smegmatise* was observed.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 spectrometer. DMSO-d_6 and $CDCl_3$ were used as solvent. Chemical shifts (δ) were reported in ppm relative to tetramethyl silane, using the solvent signal as an internal reference. Elemental analyses (C, H, N and S contents) were performed on a Costech 4010 CHNS Elemental analyzer and metal contents were estimated spectrophotometrically. IR spectra were recorded on an ATI Unicam Matson 1000 Model FTIR spectrophotometer and UV/VIS spectra on an ATI Unicam UV2 Model UV/Vis spectrophotometer. Mass spectra (ESI) were recorded on Micromass Quanto LC-MS/MS spectrophotometer. Room temperature magnetic susceptibility measurements were done on a PAR model 155 vibrating sample magnetometer. All

chemicals were of the highest quality available, obtained from local suppliers and used as received.

General procedure for the unsymmetrical pyrroles (2, 3): Here, the synthesized materials are commercially available. However, in a simple way using in present procedures is as below and for the preparation of metal complexes were synthesized. 2,6-Diamino pyridine (1 mmol) and 2,5-hexandione were dissolved in 50 mL of MeOH, then 5 drops of conc. HCl were added into the round bottom flask equipped with a magnetic stirrer and the mixture was refluxed under nitrogen atmosphere, for 24 h with vigorous stirring. After the reaction, the methanol was evaporated. Then, the oily residue was dissolved in diethyl ether (50 mL) and filtered with a filter and ether solution was left for crystallization under room temperature. The crystallized pale orange solid in diethyl ether were filtered and dried over P_4O_{10}.

6-(2,5-Dimethyl-1*H*-pyrrol-1-yl)pyridin-2-amine (dmpypr) (**2**) Anal. calcd. (%) for $C_{11}H_{13}N_3$: C, 70.60, H 6.95, N 22.46; found (%) C 70.55, H 7.05, N 22.50. Yield 60 %, m.p. 124-125 ºC. MS: (ESI) m/z = 188 $[M + 1]^+$ selected IR (KBr, ν_{max}, cm^{-1}): (NH_2): 3474-3300; (C-H_{arom}): 3170; (C-H_{alkyl}): 2900; (C=N): 1626; (C-N): 1560.

2,6-*Bis*(2,5-dimethyl-1*H*-pyrrol-1-yl)pyridine (tmpypr) (**3**) Anal. calcd. (%) for $C_{17}H_{19}N_3$: C 76.95, H 7.22, N 15.84; found (%) C 77.0, H, 7.26, N 15.90. Yield 70 %, m.p. 150 ºC. MS: (ESI) m/z = 266 $[M + 1]^+$ selected IR (KBr, ν_{max}, cm^{-1}): (C-H_{arom}); (C-H_{alkyl}): 3070 2900; (C-N): 1590.

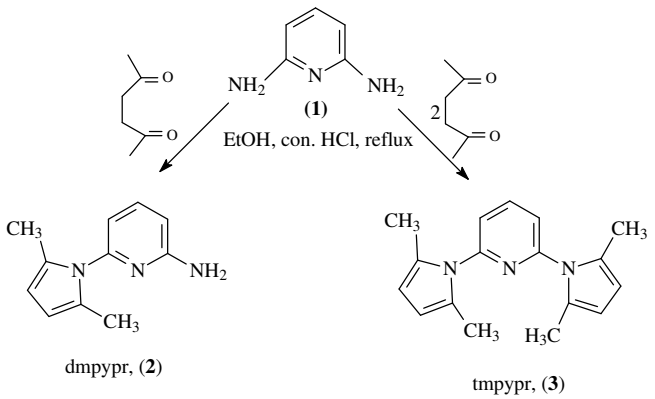
Synthesis of the complexes: Methanolic solution (20 mL) of $M(ClO_4)_2 \cdot 6H_2O$ (here, M = Cu, Ni and Co, 1 mmol) was added to the solution of 6-(2,5-dimethyl-1*H*-pyrrol-1-yl)-pyridin-2-amine (dmpypr) and/or 2,6-*bis*(2,5-dimethyl-1*H*-pyrrol-1-yl)pyridin (tmpypr) (2 mmol) in 20 mL with constant stirring for 2 h then refluxed for 4 h. The precipitate was collected and filtered off, washed with ethanol and then dried diethyl ether and dried over fused calcium chloride *in vacuo* (yield 65-85 %).

Antimicrobial activity assessment: All test microorganisms were obtained from the Hifzissihha Institute of Refik Saydam (Ankara, Turkey) and were as follows: *Escherichia coli* ATCC 25922, *Enterobacter aeroginosa* ATCC 13048, *Yersinia pseudotuberculosis* ATCC 911, *Pseudomonas aeruginosa* ATCC 27853, *Staphylococcus aureus* ATCC 25923, *Enterococcus faecalis* ATCC 29212, *Listeria monositogenes* ATCC 43251, *Bacillus cereus* 709 ROMA, *Mycobacterium smegmatis* ATCC607, *Candida albicans* ATCC 60193, *Candida tropicalis* ATCC 13803 and *Saccharomyces cerevisiae* RSKK 251. All the newly synthesized compounds were dissolved in dimethyl sulphoxide to prepare chemicals stock solution of 20 mg/5 mL.

Agar well diffusion method: Simple susceptibility screening test using agar-well diffusion method[23] as adapted earlier[24] was used. Each bacterium was suspended in Mueller Hinton (MH) (Difco, Detroit, MI) broth. The yeast like fungi was suspended in yeast extracts broth. Then the microorganisms were diluted approximately 10^6 colony forming unit (cfu) per mL. For yeast like fungi, Sabouraud Dextrose Agar (SDA) (Difco, Detriot, MI) were used. Middlebrook 7H10 agar medium (Becton, Dickinson Microbiology Systems) was used for *M. smegmatis*. They were "flood-inoculated" onto the surface of MH and SD agars and then dried. Five mL diameter wells were cut from the agar using a sterile cork-borer and 500 µg/50 µL of the extract substances were delivered into the wells. The plates were incubated for 18 h at 35 ºC. The *Mycobacterium smegmatis* was grown for 3-5 days on Middlebrook 7H10 agar plates at 35 ºC[25]. Antimicrobial activity was evaluated by measuring the zone of inhibition against the test organism. Ampicillin (10 µg), streptomycin (10 µg) and fluconazole (5 µg) were standard drugs. Dimethyl sulphoxide was used as control solvent.

RESULTS AND DISCUSSION

Mononuclear Cu(II), Ni(II) and Co(II) complexes of 6-(2,5-dimethyl-1*H*-pyrrol-1-yl)pyridin-2-amine (dmpypr) and/or 2,6-*bis*(2,5-dimethyl-1*H*-pyrrol-1-yl)pyridine (tmpypr) was prepared and characterized (**Scheme-I**). Metal complexes were verified by elemental analyses and magnetic moment), UV-VIS and IR data (Tables 1-3). In the structures of the ligands N3 units were available for the complexation of metal ions. The corresponding metal complexes (**4-9**) have been prepared with a reaction of the ligand-metal perchlorate salts mixture in ethanol.



Scheme-I: Preparation of ligands

NMR spectra: In the ^{1}H NMR spectra of a $CDCl_3$ solution of compound **2** was seen singlet at 2.13 CH_3-1, 6H), singlet at 5.9 (-HC-3, 2H), doublet at 6.55 (HC-5 and 7, 2H), triplet at 7.55 (HC-6, 1H) ppm (Fig. 1). The ^{1}H NMR spectra of a $CDCl_3$ solution of compound **2** showed broad singlet at 3.35 ppm corresponding to the -NH_2 proton resonance, this signal disappeared on deuterium exchange. The ^{1}H NMR spectrum of compound **3** shows singlet at 2.16 and 2.17 (12H), singlet at 5.90 (4H), multiplet at 7.27 (2H), multiplet at 7.97 (1H) ppm, corresponding to the CH_3, pyrrole, pyridin proton resonances, respectively. In the ^{13}C NMR spectra, resonances were observed as expected which was also consistent with the formula (eight resonance for compound **2** and six resonance for compound **3**). In the ^{1}H NMR spectra, integrated data are consistent with the formula of proposed compounds. The ^{1}H NMR spectral data supports the proposed structure of the pyrroles (**2** and **3**).

Mass spectra: The mass spectra of the pyrroles exhibit molecular ion peaks at m/z 187 M^+, 186 $[M + 1]^+$ and 266 $[M + 1]^+$, indicating formation of the pyrroles **2**, **3**, respectively. The mass spectra (ESI) exhibited the molecular ion at m/z =

TABLE-1
ANALYTICAL DATA, COLOUR, m.p. AND PERCENTAGE YIELD OF THE LIGANDS AND METAL COMPLEXES

Compound	Colour	Yield (%)	Analysis (%) found/(calcd.)			
			C	H	N	M
2	White	60	70.60 (70.56)	6.95 (7.00)	22.55 (22.44)	–
3	Pale white	70	76.88 (76.95)	7.20 (7.22)	15.80 (15.84)	–
4	Dark-brown	65	47.45 (47.57)	5.15 (5.10)	15.15 (15.13)	11.35 (11.44)
5	Red-brown	63	41.74 (41.75)	4.12 (4.15)	13.30 (13.30)	9.15 (9.20)
6	Brown	65	40.65 (40.63)	4.40 (4.34)	12.87 (12.92)	9.10 (9.06)
7	Dark-brown	80	58.75 (58.85)	5.50 (5.52)	12.12 (12.10)	9.10 (9.15)
8	Red-brown	75	51.90 (51.80)	4.90 (4.86)	10.60 (10.66)	7.35 (7.45)
9	Brown	75	51.80 (51.79)	4.80 (4.87)	10.59 (10.66)	7.50 (7.47)

TABLE-2
CHARACTERISTIC IR BANDS (cm^{-1}) OF THE LIGAND AND ITS METAL COMPLEXES

Compound	ν(N-H)	$\nu(C\text{-}H)_{ar}$	ν(C=N)	ν(M-N)	$\nu(M\text{-}H_2O)$	(ClO_4^-)
2	3483-3307	3170	1626	–	–	–
3	–	3160	1590	–	–	–
4	3472-3203	3070	1618	450	3540, 530	1150, 1120, 1079, 1020, 625
5	3367, 3214	3080	1614	430	3545, 540	1080, 1020
6	3310, 3240	3170	1610	425	3554, 520	1070, 1030
7	–	3060	1570	460	3550	1120, 1106, 1070, 1028, 625
8	–	3050	1565	440	3530, 530	1090, 1037,
9	–	3070	1565	430	3540, 580	1078, 1030

TABLE-4
SCREENING FOR ANTIMICROBIAL ACTIVITY OF THE COMPOUNDS (100 µL)

Compound	Stoc. (µg/mL)	Microorganisms and inhibition zone (mm)										
		Ec	Ea	Yp	Pa	Sa	Ef	Li	Bc	Ms	Ca	Ct	Sc
2	37	–	–	–	–	5	–	–	–	10	–	–	25
3	53	–	–	–	–	4	–	–	–	11	–	–	20
4	127	–	–	–	–	12	–	–	–	–	–	–	–
5	125	–	–	–	–	9	–	–	–	–	–	–	–
6	125	–	–	–	–	10	–	–	–	–	–	–	–
7	162	–	–	–	–	15	–	–	–	10	–	–	–
8	158	–	–	–	–	14	–	–	–	–	–	–	–
9	158	–	–	–	–	11	–	–	–	–	–	–	–
Amp.	–	10	10	18	18	35	10	10	15	–	–	–	–
Str.	–	–	–	–	–	–	–	–	–	35	–	–	–
Flu	–	–	–	–	–	–	–	–	–	–	25	25	> 25

Ec: *Escherichia coli* ATCC 25922, Ea: *Enterobacter aeroginosa* ATCC 13048 Yp: *Yersinia pseudotuberculosis* ATCC 911, Pa: *Pseudomonas aeruginosa* ATCC 43288, Sa: *Staphylococcus aureus* ATCC 25923, Ef: *Enterococcus faecalis* ATCC 29212, Li: *Listeria monocytogenes* ATCC 43251, Bc: *Bacillus cereus* 702 Roma, Ms: *Mycobacterium smegmatis* ATCC607, Ca: *Candida albicans* ATCC 60193 Ct: *Candida tropicalis* ATCC 13803, Sc: *Saccharomyces cerevisiae* RSKK 251, Amp.: Ampicillin, Str.: Streptomycin, Flu.: Fluconazole, (–): No activity.

187 M^+ which indicates formation of 6-(2,5-dimethyl-1*H*-pyrrol-1-yl)pyridin-2-amine (**2**). The molecular ion peak ap-peared (m/z, ESI) at 554 M^+ for the $[Cu(dmpypr)_2(H_2O)(ClO_4)]$, at 616 $[M\text{-}3]^+$ for $[Ni(dmpypr)_2(ClO_4)_2(H_2O)]$ at 551 $[M + 1]^+$ for the $[Co(dmapypr)_2(H_2O)(ClO_4)]$, at 696 $[M + 1]^+$ for the $[Cu(tmpypr)_2(ClO_4)(H_2O)]$, at 788 M^+ for $[Ni(tmpypr)_2(ClO_4)_2]$ at 789 $[M + 1]^+$ for the $[Co(tmpypr)_2(ClO_4)_2]$. The mass spectra of the compounds showed the formation of the metal complexes.

Infrared spectra: Characteristic IR bands (cm^{-1}) of the ligands (**2** and **3**) and its metal complexes were given in Table-2. In the IR spectrum compound **2**, the strong band was observed at 1626 cm^{-1} ν(C=N) vibration[26]. In ligands, bands at 2935-2918 cm^{-1} may be assigned to $\nu(C\text{-}H_{alkyl})$ vibration. The ligand exhibited ν(N-H) of primary amine in the region 3484-3300 cm^{-1}. The $-C\text{-}H_{arom}$ stretching bands were observed in the *ca.* 3170 cm^{-1} region. In the IR spectrum compound **3**, the strong band at 1590 cm^{-1} may be assigned to ν(C=N) vibration[26]. In the complexes, ν(C=N), ν(N-H) were shifted to lower frequency by 10-40 cm^{-1}, suggesting coordination of metal *via* nitrogen of pyridine and/or pyrrole. All of the metal complexes show a doublet at *ca.* 1080-1020 cm^{-1}, due to splitting of the $[\nu(T_2)]$ vibration into $[\nu_3(A)]$ and $[\nu_3(E)]$[27]. The presence of these bands shows that the perchlorate is coordinated in the complexes. In the copper(II) complexes (**4**, **7**) were observed to have bands *ca.* at 1140-1120 and 625 cm^{-1} featuring typical characteristics of uncoordinated perchlorates[28-30]. The strong and broad bond at 3472 cm^{-1} indicate the presence of water molecule associated in the complex (**4**)[31] in coordination. In the 460-425 cm^{-1} region, bonds was attributed to ν(M-N)[32]. IR data confirm the binding of the copper(II), nickel(II) and cobalt(II) ions by N_2 donor groups of the present ligands and support the tentative

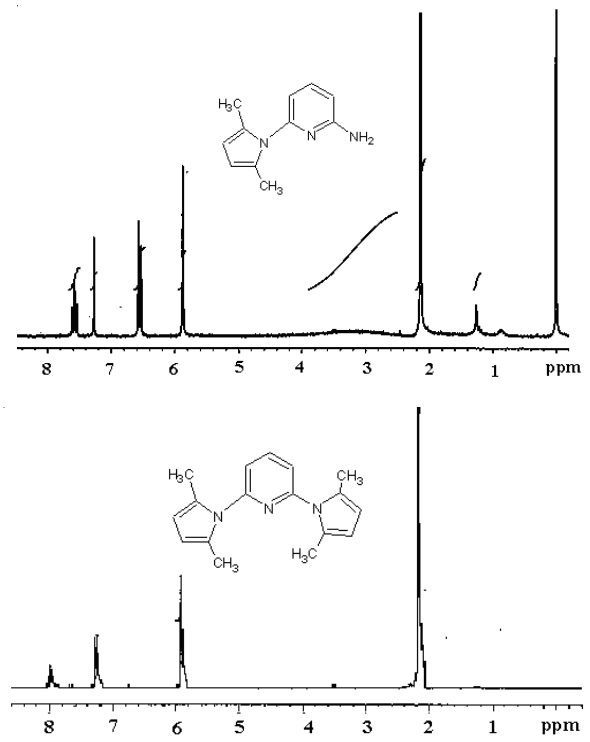


Fig. 1. ^{1}H NMR spectra of the compound **2** and **3**, in $CDCl_3$

structure of the complexes (Fig. 2). The significant shifts in ν(C=N) and ν(N-H) upon complexation are consistent with complex formation and support the concept of coordination of the ligand through the nitrogen.

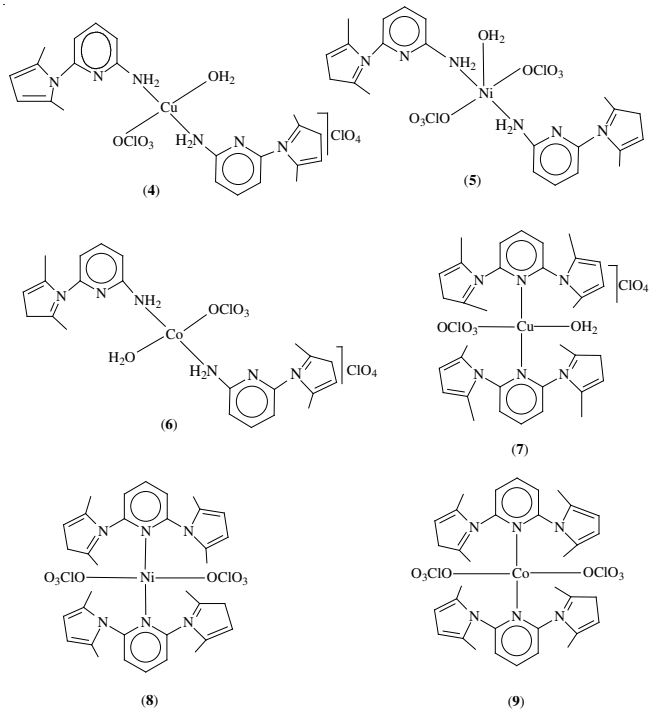


Fig. 2. Proposed structures for the metal complexes

Electronic spectra and magnetic moment: The room temperature magnetic moment data of metal complexes observed at 290 K in the solid state were given in Table-3, including diamagnetic correction. The μ_{eff} values lie within the range normally found for all of the metal complexes.

The electronic spectra of compound **3** were taken in DMSO and recorded in the 200-800 nm regions. The absorption bonds are reported in Table-3. The ligands (**2, 3**) exhibits two characteristic absorptions at 254, 287 nm. These bonds were attributed $\pi\rightarrow\pi^*$ transitions in the pyridine or pyrrole. The band around 310-355 nm was due to the $n\rightarrow\pi^*$ transition of the non-bonding electron present on the pyridine or pyrrole ring[33,34]. The electronic spectra of metal(II) complexes were taken in DMSO. The absorption bands were given in Table-3. The bands arising in the region of 477-510 nm in the solution state could be assigned to the *d-d* transition. The energy of the *d-d* transitions suggests a distorted tetragonal geometry[27,33].

Antimicrobial activity: The free ligand and copper(II) and nickel(II) and cobalt(II) complexes (**4-9**) were tested against morphology of bacteria, a series of the gram negative bacilli (*E. coli*, *E. aeroginosa*, *Y. pseudotuberculosis*, *P. aeruginosa*), gram positive coccus (*S. aureus*, *E. faecalis*), gram positive bacilli (*L. monocytogenes*), gram-positive spore-forming bacteria (*B. cereus*) and *M. smegmatis*, antituberculosis activity. The free ligand and metal complexes were tested for bacteria, only ligand and copper(II) complexes had antibacterial activity against *S. aureus* and *M. smegmatise* observed. The free ligand and metal complexes for antifungal activity against *C. albicans*, *C. tropicalis* and *S. cerevisiae* were tested, but no antifungal activity had been observed against yeast like fungi (Table-4). Free ligands (**2, 3**), were found to have activity against *Saccharomyces cerevisiae* (Sc).

TABLE-3
MAGNETIC MOMENTS AND ELECTRONIC SPECTRAL BANDS OF THE METAL COMPLEXES (IN DMSO)

Comp.	Magnetic moment (BM)	Electronic bands (nm)
Dmpypr, 2	–	254, 287, 355
Tmpypr, 3	–	246, 292, 320
4	1.77	234, 265, 311, 480
5	2.7	241, 275, 312, 477
6	3.9	235, 297, 311, 510
7	1.82	240, 274, 345, 487
8	2.6	242, 257, 290, 477
9	3.7	230, 252, 295, 479

Conclusion

In the present study, we demonstrated the preparation of 6-(2,5-dimethyl-1*H*-pyrrol-1-yl)pyridin-2-amine (dmapypr, **2**) and 2,6-*bis*(2,5-dimethyl-1*H*-pyrrol-1-yl)pyridine (tmpypr) ligand providing N_2 donor array moiety and their three mononuclear copper(II) nickel(II) and cobalt(II) complexes. Although, the nickel(II) complex was diamagnetic, the copper(II) and cobalt(II) complexes were paramagnetic. The metal ion was complexed with nitrogen atoms of ligand or oxygen atoms of water molecules and perchlorate ions. Elemental analyses results were found to be in good agreement (± 0.2 %) with the calculated values. All of the data obtained from spectral data, supported the structural properties of ligands and its Cu(II), Ni(II) and Co(II) metal complexes. The synthesized ligands and their metal complexes showed antibacterial and antifungal properties. In comparison, the copper(II) complex showed more activity against either bacterial or fungal strains, this introducing a novel class of metal-based bactericidal and fungicidal agents.

The free ligand and copper (II), nickel(II) and cobalt(II) complexes showed antimicrobial activity against only *S. aureus* but no antifungal activity was observed against yeast like fungi. Among them, copper complex and free ligand showed a narrow range of inhibitory activity against *Mycobacterium smegmatis*. Free ligands (**2, 3**), were found to have activity against *Saccharomyces cerevisiae*.

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