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RESEARCH ARTICLE

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Synthesis, characterization, and investigation of antibacterial and antifungal properties of salt and metal complexes of 2-amino-5-chloropyridine and 2,6-pyridinedicarboxylic acid

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Abstract

In this study, the salt (**3**) of 2-amino-5-chloropyridine (**1**) and 2,6-pyridinedicarboxylic acid (**2**) and the complexes of the salt ($H\mathbf{1})_x[M(\mathbf{2})_2].nH_2O$, M = Fe (III), x = 1, n = 3 (**4**); M = Co(II), x = 2, n = 4 (**5**); M = Ni(II), x = 2, n = 5 (**6**); M = Cu(II), x = 2, n = 4 (**7**)} were synthesized. The structures of **3-7** were suggested by NMR, AAS, IR, UV, magnetic susceptibility and molar conductivity methods. As a result of spectroscopic analysis, it was observed that all metal complexes had an ionic and octahedral structure. All substances were susceptible to *Candida albicans* (yeast), *Escherichia coli*, *Bacillus subtilis*, *Enterococcus faecalis*, *Pseudomonas aeruginosa*, *Listeria monocytogenes* and *Staphylococcus aureus* bacteria were examined. Antimicrobial activity results were compared with Fluconazole, Ketoconazole, Chloramphenicol, Levofloxacin, Vancomycin and Cefepime. In the activity results, the best values were observed **3**, **5** and **7** in *S. aureus* bacteria, **1** and **5** in *E. coli* bacteria, **1**, **3** and **7** in *P. aeruginoa* bacteria, all compounds in *L. monocytogenes* bacteria, all compounds (except **4**) in *E. faecalis* bacteria, **1** and **3-5** in *B. subtilis* bacteria and **3**, **4** and **7** in *C. albicans* yeast.

Keywords: 2-Amino-5-chloropyridine, 2,6-pyridinedicarboxylic acid, salt, complex, antimicrobial activity.

1. Introduction

Pyridine derivative compounds are widely acknowledged to be found in numerous pharmaceutical formulations exhibiting diverse biological characteristics. Within this category, 2-aminopyridine derivatives have been identified as important precursors for the production of a variety of heterocyclic compounds. The 2-aminopyridine derivatives showcase a wide range of pharmacological activities such as antiparasitic, anti-inflammatory, antihistamine,

antibacterial, antiviral, anticonvulsant, anti-alzheimer, antifungal, antidiabetic, and analgesic properties [1-4]. These derivatives possess the capacity to engage in coordination interactions with metal ions in either a monodentate or bidentate manner, utilizing the pyridine ring and the nitrogen atom located within the amino group [5,6]. Within the modern context, the rise of microbial resistance emerges as a highly complex global challenge, resulting in increasing rates of mortality and morbidity [7], thus emphasizing the critical need for the creation of new compounds that can effectively combat multidrug-resistant microorganisms with a wide spectrum of efficacy.

Pyridine-2,6-dicarboxylic acid (**2**), known for its various biological activities, is a versatile ligand/chelating agent that can coordinate with metal ions, functioning as a bidentate, tridentate, meridian or bridging ligand [8-14].

Our group examine the antibacterial and antifungal properties of salt and metal complexes of 2-aminopyridine derivatives and carboxylic acid derivatives such as 2,6-pyridinedicarboxylic acid [5,6,15,16], salicylic acid [17], 5-sulfosalicylic acid [18], 4-sulfamoylbenzoic acid [19], 2-methoxy-5-sulfamoylbenzoic acid [20-26], 2,4-dichloro-5-sulfamoylbenzoic acid [27], 3-(3/4-sulfamoylphenylcarbamoyl)acrylic acid [28-30].

2. Experimental

2.1. Methods and materials

All chemicals used were analytical reagents and were commercially purchased from Aldrich. Perkin Elmer AAS PinAAcle 900T for AAS analyses, Agilent Premium Compact NMR (600 MHz) spectrometer for NMR spectra studies, Bruker Optics Vertex 70 FT-IR spectrometer for FT-IR spectra, SHIMADZU UV-2550 spectrometer for UV–Vis spectra, Sherwood Scientific Magway MSB MK1 for magnetic susceptibility measurements and WTW Cond 315i/SET Model conductivity meter for molar conductances were used.

*2.2. Preparation of **3-7***

10 mmol (1.2856 g) **1** and 10 mmol (1.6712 g) **2** dissolved in 100 mL of absolute ethanol. The white powder solid (**3**) (2.8090 g, 70% yield) precipitated in the reaction was filtered and dried (Fig. 1).

2 mmol (0.5914) **3** and 2 mmol metal(II) salt [0.556 g $FeSO_4.7H_2O$ or 0.498 g $Co(OAc)_2.4H_2O$ or 0.496 g $Ni(OAc)_2.4H_2O$ or 0.400 g $Cu(OAc)_2.H_2O$] was dissolved in ethanol:water solution (2:1) (100 mL) with stirring one week. Yellow power solid (0.1706 g, 60% yield) for **4**, pink power solid (0.2697 g, 75% yield) for **5**, green power solid (0.2027 g, 55% yield) for **6** and turquoise power solid (0.2172 g, 60% yield) for **7** were obtained from the mixtures (Fig. 1).

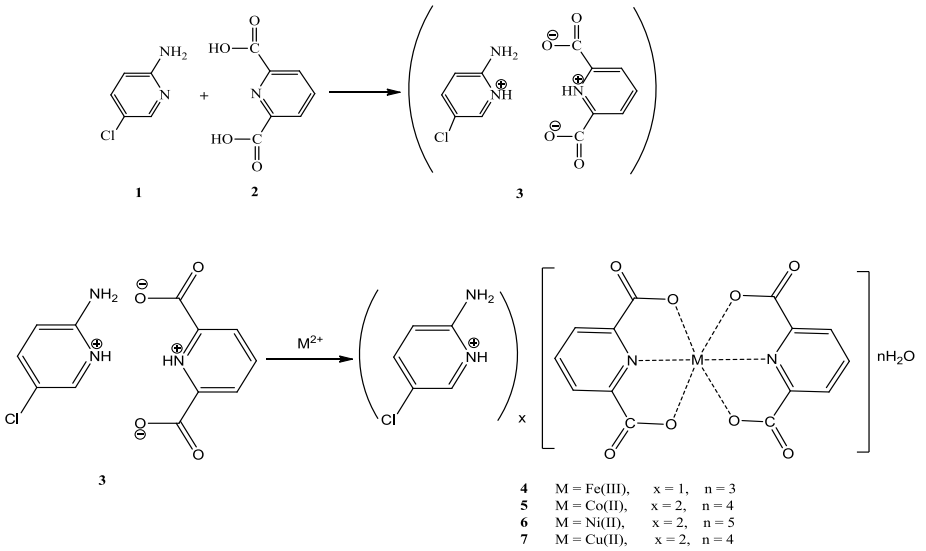


Fig. 1. The structures of **3-7**.

2.3. Antimicrobial study

Candida albicans (ATCC 14053) (yeast), *Staphylococcus aureus* (NRRL-B 767), *Listeria monocytogenes* (ATCC 7644), *Bacillus subtilis*, *Enterococcus faecalis* (ATCC 29212), *Pseudomonas aeruginosa* (ATCC 27853), and *Escherichia coli* (ATCC 25922) bacteria microorganisms were used in this study.

The evaluation of the antimicrobial properties of the substances was conducted through the utilization of a microbroth dilution susceptibility test. Stock solutions were prepared using dimethyl sulfoxide. Each compound, totaling 4 mg, was dissolved in 2 mL of dimethyl sulfoxide. Bacteria and yeast suspensions, grown overnight, were standardized to 10^8 Colony Forming Units/mL using McFarland No. 0.5 standard solution in double-strength Mueller-Hinton broth. Subsequently, 100 µL of each microbe suspension was added to the wells. A well-chain devoid of microbes served as the negative control. The positive growth control was composed of the medium along with sterile distilled water. The determination of the minimum inhibitory concentration (MIC) was based on the observation of the first well exhibiting no turbidity following an incubation period of 18-24 hours at 37 °C.

3. Results and discussion

3.1. Elemental analysis and AAS results

Elemental analysis was conducted for **3-7**, while AAS was carried out for **4-7**. The obtained results indicated a the **1**:**2** ratio for **3** and the metal:**1**:**2** ratios for **4-7** were observed to be 1:1 for **3**, 1:1:2 for **4** and 1:2:2 for **5-7** (Table 1).

Table 1. Elemental analysis and AAS results of **3-7**.

Compound	Formula	Found% Anal. Cald.%			
		C	H	N	M
3	$C_{12}H_{10}ClN_3O_4$	48.75(48.74)	3.45(3.41)	14.20(14.21)	-

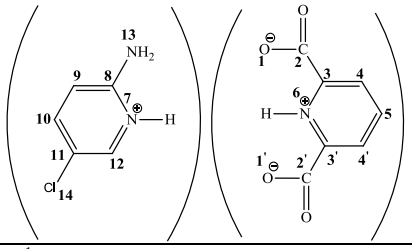
4	$C_{19}H_{18}ClFeN_4O_{11}$	40.10(40.06)	3.20(3.18)	9.90(9.84)	9.90(9.80)
5	$C_{24}H_{26}Cl_2CoN_6O_{12}$	40.00(40.02)	3.65(3.64)	11.65(11.67)	9.90(9.84)
6	$C_{24}H_{26}Cl_2NiN_6O_{13}$	39.00(39.05)	3.80(3.82)	11.45(11.39)	8.00(7.95)
7	$C_{24}H_{26}Cl_2CuN_6O_{12}$	39.80(39.76)	3.60(3.61)	11.50(11.54)	8.80(8.77)

*3.2. NMR result of **3***

In ^{1}H NMR spectrum in d_6-DMSO of **3** (Table 2, Fig. 2), the protons were observed at 6.42 ppm (H^9, doublet, $^3J_{H9\text{-}H10}$= 9.00 Hz) with 1H intensity, 7.36 ppm (H^{10}, doublet-doublet, $^3J_{H10\text{-}H9}$ = 9.00 Hz ve $^4J_{H10\text{-}H12}$ = 2.40 Hz) with 1H intensity, 7.84 ppm (H^{12}, doublet-doublet, $^4J_{H12\text{-}H10}$ = 2.40 Hz) with 1H intensity, 6.06 ppm (H^{13}, singlet) with 2H intensity, 8.21 ppm (H^4 and $H^{4'}$, doublet, $^3J_{H4/H4'\text{-}H5}$ = 7.80 Hz) with 2H intensity and 8.14 ppm (H^5, triplet, $^3J_{H5\text{-}H4,H3}$ = 7.80 Hz) with 1H intensity.

^{13}C NMR spectrum in d_6-DMSO of **3** (Table 2, Fig. 3), the carbon peaks were observed at 165.898 ppm (C^2, $C^{2'}$), 148.555 ppm (C^3, $C^{3'}$), 127.902 ppm (C^4, $C^{4'}$), 117.790 ppm (C^5), 158.878 ppm (C^8), 145.976 ppm (C^9), 109.741 ppm (C^{10}), 137.168 ppm (C^{11}) and 139.647 ppm'de (C^{12}).

Table 2. Results of NMR spectra (ppm).



	^{1}H-NMR		^{13}C-NMR
H^4, $H^{4'}$	8.21 (2H, d) [$^3J_{H4/H4'\text{-}H5}$ = 7.80 Hz]	C^2, $C^{2'}$	165.898
H^5	8.14 (1H, t) [$^3J_{H5\text{-}H4,H4'}$ = 7.80 Hz]	C^3, $C^{3'}$	148.555
H^6	-	C^4, $C^{4'}$	127.902
H^7	-	C^5	117.790
H^9	6.42 (1H, d) [$^3J_{H9\text{-}H10}$ = 9.00 Hz]	C^8	158.878
H^{10}	7.36 (1H, dxd) [$^3J_{H10/H9}$ = 9.00 Hz. $^4J_{H10\text{-}H12}$ = 2.40 Hz]	C^9	145.976
H^{12}	7.84 (1H, d) [$^4J_{H12\text{-}H10}$ = 2.40 Hz]	C^{10}	109.741
H^{13}	6.06 (2H, s)	C^{11}	137.168
		C^{12}	139.647

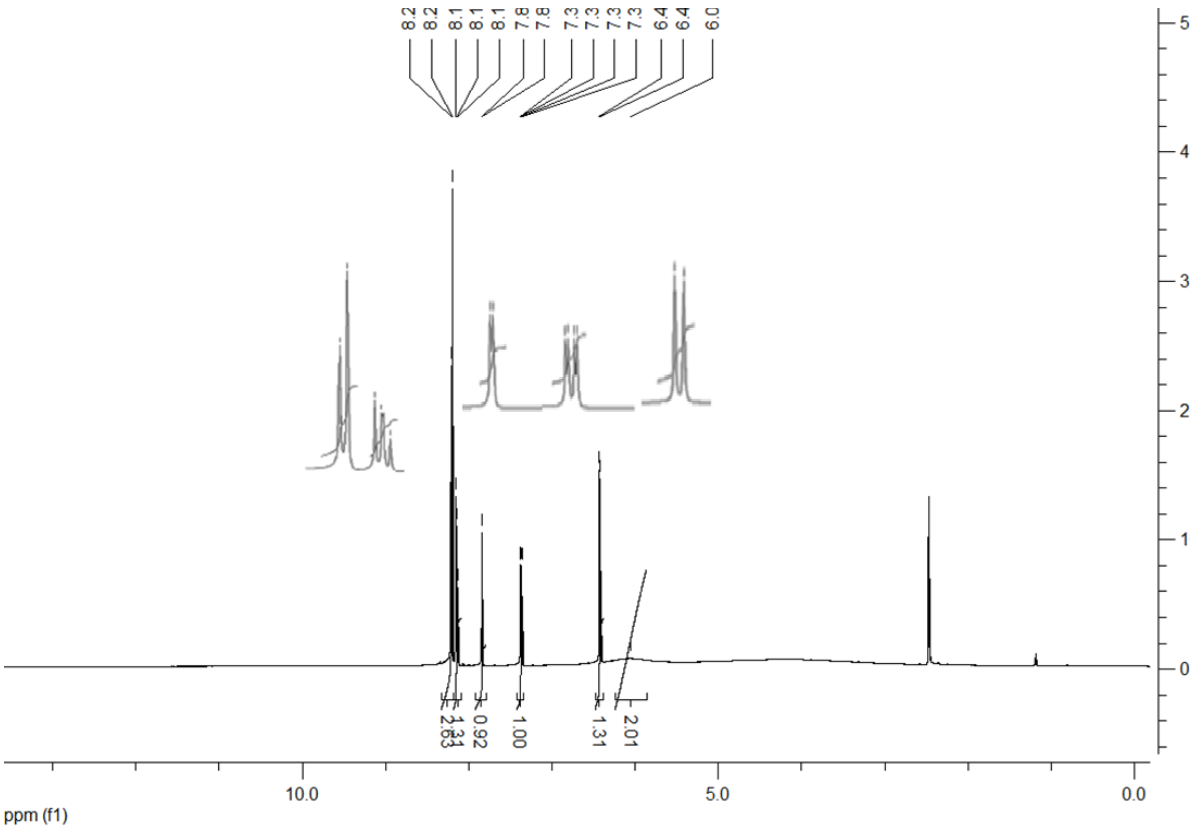


Fig. 2. ^{1}H NMR spectrum of **3**.

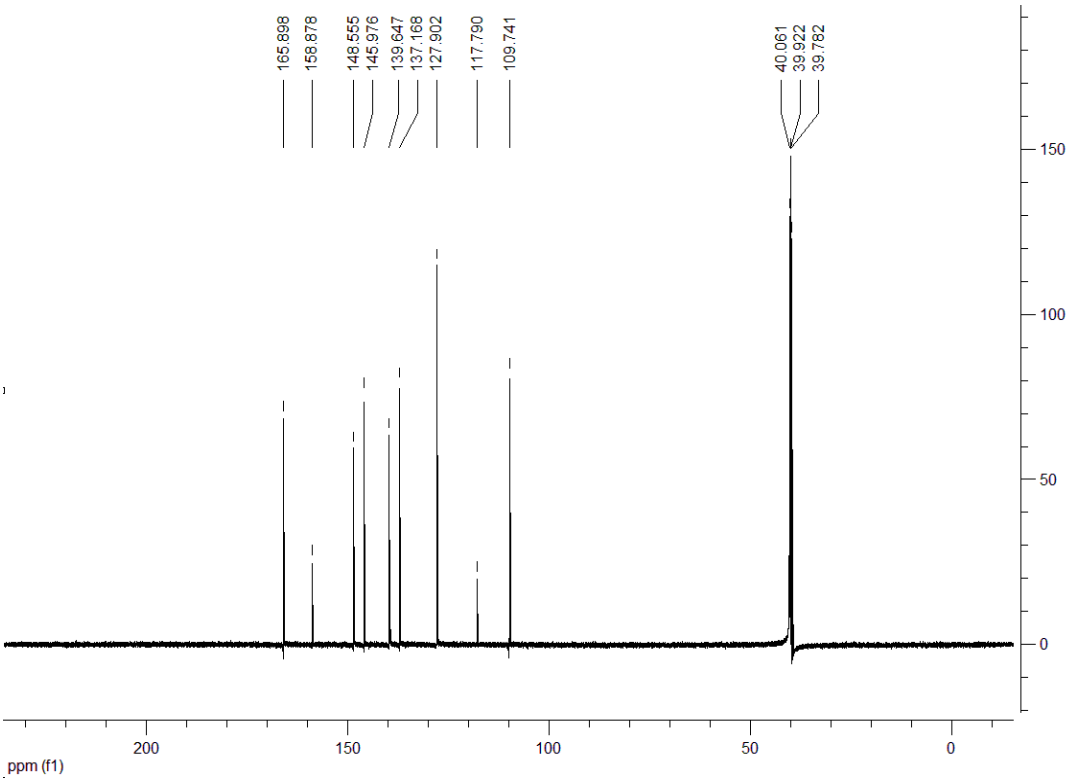


Fig. 3. ^{13}C NMR spectrum of **3**.

3.3. FT-IR results

The FT-IR results of **3-7** are given in Table 3. The water molecules in the structure of **4-7** were the cause of the ν(O-H) vibrations, which were seen as wide bands between 3416 and 3569 cm^{-1}. The ν(N-H) vibrations of **3-7** are responsible for bands that appear at 3432 and 3317, 3408 and 3239, 3356 and 3236, 3349 and 3238 and 3379 and 3210 cm^{-1}, respectively. The ν(N^{+}-H) vibrations observed in the range 2549-2773 cm^{-1} for **3-7** [31]. These peaks observation shows that the **1** molecule is present in the complexes as a complimentary ion outside of coordination. The binding of the COO^{-} group to the metal ion is indicated by the difference in the lengths of its asymmetric and symmetric oscillations (Δυ). The results of **4-7** were calculated to be 195 (1662 and 1467 cm^{-1}), 191 (1660 and 1469 cm^{-1}), 200 (1665 and 1465 cm^{-1}) and 200 (1679 and 1479 cm^{-1}), respectively. These findings imply that the carboxylate group forms a monodentate bond with the metal ion [32]. The absorption bands in the region of 3076-3107 cm^{-1} for aromatic *ν*(C-H), 1419-1685 cm^{-1} for *ν*(C=N)/*ν*(C=C), 1070-1394 cm^{-1} for *ν*(C=O), 748-770 cm^{-1} for *ν*(py), 588-598 cm^{-1} for *ν*(M-O) (except **3**) and 469-506 cm^{-1} for *ν*(M-N) (except **3**) are found for all compounds.

3.4. Results of UV/Vis measurements

The electronic spectra of **3-7** (as shown in Fig. 4, dissolved in DMSO at a concentration of 1.10^{-3} molL-1) exhibit both π-π* and n-π* transitions, which are detected at 298 nm (27100 Lmol^{-1}cm^{-1}) and 272 nm (2700 Lmol^{-1}cm^{-1}) for **1**, 290 nm (30180 Lmol^{-1}cm^{-1}) for **2**, 322 nm (28730 Lmol^{-1}cm^{-1}) for **3**, 292 nm (32380 Lmol^{-1}cm^{-1}) and 266 nm (10110 Lmol^{-1}cm^{-1}) for **4**, 318 nm (34370 Lmol^{-1}cm^{-1}) and 292 nm (24070 Lmol^{-1}cm^{-1}) for **5**, 314 nm (26810

$Lmol^{-1}cm^{-1}$) and 292 nm (24150 $Lmol^{-1}cm^{-1}$) for **6** and 274 nm (27000 $Lmol^{-1}cm^{-1}$) and 254 nm (22300 $Lmol^{-1}cm^{-1}$) for **7**. The d-d transitions of metal atoms with octahedral structure occurred at wavelengths of 688 nm (310 $Lmol^{-1}cm^{-1}$) for **5**, 702 nm (290 $Lmol^{-1}cm^{-1}$) for **6** and 782 nm (350 $Lmol^{-1}cm^{-1}$) for **7** [15,16].

Table 3. IR data of all compounds (cm^{-1})

	3	**4**	**5**	**6**	**7**
ν(O-H)	-	3504(br)	3569(br)	3466(br)	3416(br)
ν(N-H)	3432(m)	3408(m)	3356(m)	3349(m)	3379(m)
	3317(m)	3239(m)	3236(m)	3238(m)	3210(m)
$\nu(C\text{-}H)_{Ar}$	3090(w)	3107(w)	3076(w)	3089(w)	3095(w)
$\nu(N^{+}\text{-}H)$	2703(w)	2773(w)	2733(w)	2677(w)	2708(w)
	2575(w)	2549(w)	2571(w)	2524(w)	2528(w)
ν(C=O)	1762(s)	1662(s)	1660(s)	1665(s)	1679(s)
	1478(s)	1467(s)	1469(s)	1465(s)	1479(s)
ν(C=N)	1685(s)	1622(s)	1637(s)	1639(s)	1655(s)
ν(C=C)	1626(s)	1605(s)	1609(s)	1610(s)	1609(s)
	1562(s)	1577(s)	1563(s)	1585(s)	1555(s)
	1545(s)	1437(s)	1499(s)	1563(s)	1502(s)
	1428(s)		1436(s)	1500(s)	1419(s)
				1437(s)	
ν(C-O)	1385(s)	1384(s)	1394(s)	1394(s)	1374(s)
	1229(s)	1278(s)	1281(s)	1282(s)	1267(s)
	1070(s)	1073(s)	1074(s)	1077(s)	1077(s)
ν(py)	748(s)	770(s)	767(s)	764(s)	770(s)
ν(M-O)	-	597(w)	588(w)	596(w)	598(w)
ν(M-N)	-	494(w)	469(w)	506(w)	490(w)

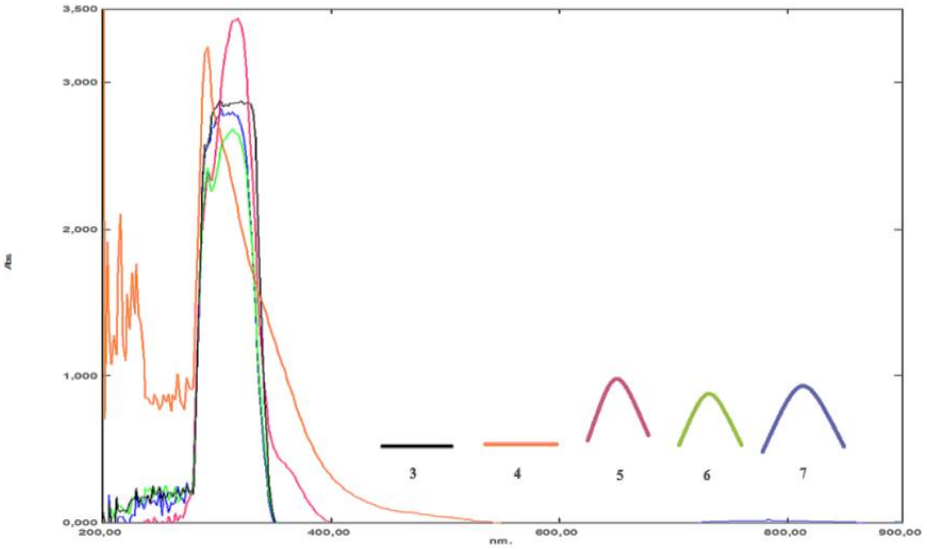


Fig. 4. UV–Vis spectra of **3-7**.

3.5. Magnetic susceptibilities

Magnetic susceptibility results of **4-7** were found between 5.84, 3.80, 2.72 and 1.69 BM. These values say that there are five, three, two and one unpaired electrons in the complexes, respectively. The magnetic moment for the metal ion obtained in the octahedral geometry is also consistent with this value [15,16].

3.6. Molar Conductivity

Conductivity measurements of **4-7** (in DMSO) were observed as 68.90 for **4**, 51.50 for **5**, 50.50 for **6** and 59.20 µS/cm for **7** and these results are 1:1 ionic for **4** and 2:1 ionic for **5-7** [33].

3.7. Antimicrobial activity

The antimicrobial activity of **1-7**, Vancomycin, Levofloxacin, Cefepime, Chloramphenicol, Ketoconazole and Fluconazole were investigated by microdilution method. MIC values of all compounds showing activity against bacteria and yeast are given in Table 4. The observed activity results are similar to 2-aminopyridine derivatives, salt and metal complexes found in the literature [5,6,15,18].

The antifungal drugs (Ketoconazole and Fluconazole) and **1-7** have activity against *C. albicans* when MIC values are compared. Compounds **3** and **4** showed greater activity than according to Ketoconazole and Fluconazole while compounds **1**, **5** and **6** showed equal effective. Compound **2** was found to have a lower degree of action.

Table 4. MIC values of compounds (µg/mL)

	C. albicans	***L. monocytogenes***	***E. coli***	***B. subtilis***	***S. aureus***	***E. faecalis***	**P. aeruginoa**
Ketoconazole	62.50	-	-	-	-	-	-
Fluconazole	62.50	-	-	-	-	-	-

Vancomycin	-	125.00	62.50	250.00	31.25	31.25	62.50
Levofloxacin	-	31.25	62.50	62.50	31.25	31.25	31.25
Cefepime	-	31.25	31.25	62.50	62.50	62.50	31.25
Chloramphenicol	-	62.50	62.50	62.50	62.50	62.50	125.00
1	62.50	62.50	31.25	31.25	62.50	62.50	31.25
2	125.00	62.50	62.50	62.50	62.50	62.50	62.50
3	31.25	62.50	62.50	31.25	31.25	62.50	31.25
4	31.25	62.50	62.50	31.25	62.50	125.00	62.50
5	62.50	62.50	31.25	31.25	31.25	62.50	62.50
6	62.50	62.50	62.50	62.50	62.50	62.50	62.50
7	31.25	62.50	62.50	62.50	31.25	62.50	31.25

All antibacterial drugs (Vancomycin, Levofloxacin, Cefepime and Chloramphenicol) and **1-7** have activity against *L. monocytogenes* when MIC values are compared of all compounds indicated greater activity than according to Vancomycin. All compounds showed equally activity according to Chloramphenicol while all compounds showed lower activity according to Levofloxacin and Cefepime.

All compounds showed greater activity *E. coli* than according to Vancomycin. While compounds **1** and **5** showed equally effective, the other compounds were found to have a lower degree of according to Cefepime. Compounds **1** and **5** showed greater activity than according to Vancomycin, Levofloxacin and Chloramphenicol while the other compounds showed equally effective.

All compounds showed greater activity *B. subtilis* than according to Vancomycin. **1** and **3-5** showed greater activity than according to Levofloxacin, Chloramphenicol and Cefepime the other compunds showed equally effective.

While **3**, **5,** and **7** showed equally effective *S. aureus*, the other compounds were found to have a lower degree of according to Vancomycin and Levofloxacin. **3**, **5,** and **7** showed greater activity than according to Chloramphenicol and Cefepime while the other compounds showed equally effective.

All compounds showed greater activity *E. faecalis* than according to Vancomycin and Levofloxacin. While all compounds (except **4**) showed equally effective, the other compounds were found to have a lower degree of according to Chloramphenicol and Cefepime.

All compounds showed greater activity *P. aeruginosa* than according to Chloramphenicol. **1**, **3,** and **7** showed greater activity than according to Vancomycin while the other compounds equally effective. While **2** and **4-6** showed equally effective, the other compounds were found to have a lower degree of according to Levofloxacin and Cefepime.

4. Conclusions

In this study, the salt (**3**) of 2-amino-5-chloropyridine (**1**) and 2,6-pyridinedicarboxylic acid (**2**) and the metal complexes of the salt $\{(H\mathbf{1})_x[M(\mathbf{2})_2].nH_2O$, M = Fe (III), x = 1, n = 3 (**4**); M = Co(II), x = 2, n = 4 (**5**); M = Ni(II), x = 2, n = 5 (**6**); M = Cu(II), x = 2, n = 4 (**7**)} were synthesized. The structures of **3-7** were suggested by AAS, IR, UV, NMR (for compound **3**), magnetic susceptibility, and molar conductivity methods. As a result of spectroscopic analysis, it was observed that all metal complexes had an ionic and octahedral structure. All compounds exhibited antimicrobial efficacy against both bacterial and fungal microorganisms. In the activity results, the best values were observed **1** and **5** in *E. coli* bacteria, **3**, **5**, and **7** in *S. aureus* bacteria, all compounds in *L. monocytogenes* bacteria, **1**, **3**, and **7** in *P. aeruginoa* bacteria, all compounds (except **4**) in *E. faecalis* bacteria, **1** and **3-5** in *B. subtilis* bacteria and compounds **3**, **4**, and **7** in *C. albicans* yeast.

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Author contribution statements

Author 1 Investigation, Writing –review & editing, Author 2 Investigation, Author 3 Investigation, Author 4 Investigation, Author 5 Writing –original draft.

References

[1] M. Marinescu, "2-Aminopyridine - a classic and trendy pharmacophore," *Int. J. Pharma Bio. Sci.*, vol. 8, no. 2, pp. 338-355, 2017, doi: 10.22376/ijpbs.2017.8.2.p338-355.
[2] R. N. Rao and K. Chanda "2-Aminopyridine – an unsung hero in drug discovery," *Chem. Commun.*, vol. 58, pp. 343-382, 2022, doi: 10.1039/D1CC04602K.
[3] K. J. Orie, R. U. Duru and R. I. Ngochindo "Syntheses, complexation and biological activity of aminopyridines: a mini-review," *Am. J. Het. Chem.*, vol. 7, no. 2, pp. 11-25, 2021, doi: 10.11648/j.ajhc.20210702.11.
[4] P. Sharma and P. Sinha, "Recent advancements in multicomponent reactions of substituted 2- aminopyridines synthesis: a decade review," *Cur. Chinese Chem.*, vol. 3, e061223224235, pp. 18, 2023, doi: 10.2174/0126660016267259231012105113.
[5] C. Yenikaya, M. Poyraz, M. Sarı, F. Demirci, H. İlkimen and O. Büyükgüngör, "Synthesis, characterization and biological evaluation of a novel Cu(II) complex with the mixed ligands 2,6-pyridinedicarboxylicacid and 2-aminopyridine," *Polyhedron*, vol. 28, no. 16, pp. 3526-3532, 2009, doi: 10.1016/j.poly.2009.05.079.
[6] C. Yenikaya, N. Büyükkıdan, M. Sarı, R. Keşli, H. İlkimen, M. Bülbül and O. Büyükgüngör, "Synthesis, characterization and biological evaluation of novel Cu(II) complexes with proton transfer salt of 2,6-pyridinedicarboxylic acid and 2-amino-4-methylpyridine," *J. Coord. Chem.*, vol. 64, no. 19, pp. 3353-3365, 2011, doi: 10.1080/00958972.2011.620608.
[7] Centers for Disease Control and Prevention Facts about Antibiotic Resistance and Antibiotic Prescribing: Attitudes, Behaviors, Trends, and Cost. [(accessed on 21 April 2022)]; Available online: http://www.cdc.gov/getsmart/community/about/fast-facts.html
[8] M. M. Khalil and A. E. Attia, "Potentiometric studies on the binary and ternary complexes of copper(II) containing dipicolinic acid and amino acids," *J. Chem. Eng. Data*, vol. 44, no. 2, pp. 180-184, 1999, doi: 10.1021/je980185d.
[9] S. Xiang, D. X. Bao, J. Wang, Y.C. Li and X.Q. Zhao, "Luminescent lanthanide coordination compounds with pyridine-2,6-dicarboxylicacid," *J. Lumin.*, vol. 186, pp. 273–282, 2017, doi: 10.1016/j.jlumin.2017.02.037
[10] M. J. Celestine, J.L. Bullock, S. Boodram, V. H. Rambaran and A.A. Holder, "Interesting properties of p-, d-, and f-block elements when coordinated with dipicolinic acid and its derivatives as ligands: their use as inorganic pharmaceuticals," *Rev. Inorg. Chem.*, vol. 35, vol. 2, pp. 57-67, 2015, doi: 10.1515/revic-2014-0004
[11] A. M. Kirillov and G. B. Shul'pin, "Pyrazinecarboxylic acid and analogs: highly efficient co-catalysts in the metal-complex-catalyzed oxidation of organic compounds," *Coord. Chem. Rev.*, vol. 257, pp. 732-754, 2013, doi: 10.1016/j.ccr.2012.09.012
[12] M. V. Kirillova, M. F. C. Guedes da Silva, A. M. Kirillov, J. J. R. Frausto da Silva and A. J. L. Pombeiro, "3D hydrogen bonded heteronuclear CoII, NiII, CuII and ZnII aqua complexes derived from dipicolinic acid," *Inorg. Chim. Acta*, vol. 360, pp. 506-512, 2007, doi: 10.1016/j.ica.2006.07.087.
[13] N. Büyükkıdan, "Proton transfer salts and their complexes and mixed-ligand complexes of pyridine dicarboxylic acids and piperazines: a short review," *J. Sci. Rep. A*, vol. 49, pp. 198-235, 2022.
[14] H. Aghabozorg, F. Manteghi and S. Sheshmani, "A brief review on structural concepts of novel supramolecular proton transfer compounds and their metal complexes," *J. Iran. Chem. Soc.*, vol. 5, pp. 184-227, 2008, doi: 10.1007/BF03246111.
[15] H. İlkimen, S. G. Salün, A. Gülbandılar and M. Sarı, "The new salt of 2-amino-3-methylpyridine with dipicolinic acid and its metal complexes: Synthesis, characterization and antimicrobial activity studies," *J. Mol. Struct.*, vol. 1270, pp. 133961, 2022, doi: 10.1016/j.molstruc.2022.133961.
[16] H. İlkimen, S. G. Salün, A. Gülbandılar and M. Sarı, "Synthesis, characterization, antimicrobial activity studies of a novel salt of dipicolinic acid with 2-amino-5-methylpyridine and their metal complexes," *Pharm. Chem. J.*, 2024, (in press).
[17] H. İlkimen and A. Gülbandılar, "Synthesis, characterization, anti-microbial activity studies of salicylic acid and 2-aminopyridine derivatives salts and their Cu(II) complexes," *J. Sci. Rep. A*, vol. 56, pp. 94-104, 2024.
[18] H. İlkimen, C. Yenikaya and A. Gülbandılar, "Investigation of the antimicrobial activities of proton transfer salts of 5-sulfosalicylic acid and 2-aminopyridine derivatives," 3rd International Conference on Innovative Academic Studies, September 26-28, 2023, Konya, Türkiye, pp. 779-783. ISBN: 978-625-6530-66-9.
[19] H. İlkimen, N. Türken and A. Gülbandılar, "Synthesis, characterization, antimicrobial and antifungal activity of studies of two novel aminopyridine-sulfamoylbenzoic acid salts and their Cu(II) complexes," *J. Iranian Chem. Soc.*, vol. 18, no. 9, pp. 1941-1946, 2021, doi: 10.1007/s13738-021-02157-4.

[20] H. İlkimen and A. Gülbandılar, "Synthesis, characterization, anti-microbial activity studies of 2-methoxy-5-sulfamoylbenzoic acid and 2-amino-5/6-picoline salts and their Cu(II) complexes," *Uşak Univ. J. Sci. Nat. Sci.*, 2024, (in press).
[21] H. İlkimen, C. Yenikaya and A. Gülbandılar, "Synthesis, characterization and investigation of antimicrobial activities of salts of 2-aminopyridine derivatives and 2-methoxy-5-sulfamoylbenzoic acid," *Selcuk Univ. J. Sci. Fac.*, vol. 49, no. 2, pp. 53-63, 2023, doi: 10.35238/sufefd.1315568.
[22] H. İlkimen and A. Gülbandılar, "Synthesis, characterization, anti-microbial activity studies of 2-methoxy-5-sulfamoylbenzoic acid and 2-aminopyridine derivatives salts and their Cu(II) complexes," *Pamukkale Univ. J. Eng. Sci.*, 2024, doi. 10.5505/pajes.2024.48196
[23] H. İlkimen, C. Yenikaya and A. Gülbandılar, "Synthesis, characterization, investigation of antimıicrobial properties of proton transfer salt andCu(II) complex of 2-metoxy-5-sulfamoilbenzoic acid and 2,3-diaminopyridine derivatives," III. Baskent International Conference On Multidisciplinary Studies, September 23-25, 2022, Ankara, Türkiye, pp. 105-119, ISBN - 978-625-8246-04-9.
[24] H. İlkimen, C. Yenikaya and A. Gülbandılar, "Synthesis, characterization and investigation of antimicrobial and antifungal activities of 2-methoxy-5-sulfamoylbenzoic acid and 2-aminonitropyridine derivatives," 3rd International Conference on Innovative Academic Studies, September 26-28, 2023, Konya, Türkiye, pp. 784-793. ISBN: 978-625-6530-66-9.
[25] H. İlkimen and A. Gülbandılar, Synthesis, characterization, and investigation of antimicrobial and antifungal activities of 2-Amino-5-substituted epipyridine derivatives and proton transfer salts of 2-methoxy-5-sulfamoylbenzoic acid," 2nd International Conference on Contemporary Academic Research ICCAR 2023, November 4-5 2023, Konya, Türkiye, pp. 40-47. ISBN: ISBN: 978-625-6530-69-0
[26] H. İlkimen, C. Yenikaya and A. Gülbandılar, "2-Amino-6-substitüepiridin türevleri ile 2-metoksi-5-sulfamoyilbenzoik asitin proton transfer tuzlarının sentezi, karakterizasyonu, antimikrobiyal ve antifungal aktivitelerinin incelenmesi," 2nd International Conference on Contemporary Academic Research ICCAR 2023, November 4-5 2023, Konya, Türkiye, pp. 48-55. ISBN: ISBN: 978-625-6530-69-0.
[27] H. İlkimen and A. Gülbandılar, "Synthesis, characterization, antimicrobial and antifungal activity studies of four novel 2-aminopyridine and 2,4-dichloro-5-sulfamoylbenzoic acid salts and their Cu(II) complexes," *Kuwait J. Sci.*, vol. 50, no. 3A, pp. 1-11, 2023, doi: 10.48129/kjs.19163.
[28] H. İlkimen, C. Yenikaya and A. Gülbandılar, "Antimicrobial activity of (E)-3-(4-sulfamoylphenylcarbamoyl)acrylic acid derivatives," *J. Sci. Rep. A*, vol. 52, pp. 365-375, 2023, doi: 10.59313/jsr-a.1126888.
[29] H. İlkimen, C. Yenikaya and A. Gülbandılar, Synthesis, characterization and investigation of antimicrobial activities of metal complexes of (E)-4-oxo-4-(3-sulfamoylphenyl)amino)but-2-enoic acid," *Bayburt Univ. J. Sci.*, vol. 6, no. 1, 12-19, 2023, doi: 10.55117/bufbd.1137044.
[30] H. İlkimen, C. Yenikaya and A. Gülbandılar, "Antimicrobial activity of proton salts of 3-(sulfamoylphenylcarbamoyl) acrylic acid derivatives with aminopyridine derivatives. *J. Sci. Rep. A*, vol. 54, no. 2, pp. 264-272, 2023, doi: 10.59313/jsr-a.1311495.
[31] D. Cook, "Vibrational spectra of pyridinium salts," *Canadian J. Chem.*, vol. 39, no. 10, 2009-2024, 1961, doi: 10.1139/v61-271.
[32] K. Nakamoto, "Infrared and raman spectra of inorganic and coordination compounds," 5th ed. NewYork: Wiley-Interscience, pp. 232 (1997).
[33] W. J. Geary, "The use of conductivity measurements in organic solvents for the characterisation of coordination compounds," *Coord. Chem. Rev.*, vol. 7, no. 1, pp. 81-122, 1971, doi: 10.1016/S0010-8545(00)80009-0.