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Proton Transfer Salt and Metal Complexes of 4,4'-Ethylenedipyridine and 2,3-Pyrazinedicarboxylic Acid: Synthesis, Structural Characterization and Biological Activity

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Keywords:

4,4'-Ethylene dipyridine, 2,3-Pyrazine dicarboxylic acid, Metal complex, Antimicrobial activity

Abstract

In this study, a new salt {(H_2BPE)(PDA), **1**} synthesized from 4,4'-ethylenedipyridine (BPE) with 2,3-pyrazinedicarboxylic acid (H_2PDA) and its complexes Fe(III) {(H_2BPE)[Fe_2(PDA)(H_2O)$_4$]$_n$, **2**} and Ni(II) {[Ni(PDA)(BPE)$_2$(H_2O)$_2$]$_n$.H_2O, **3**}, were synthesized and defined by using ^{1}H and ^{13}C NMR, TG-DTA, IR, UV-Vis, elemental analysis, magnetic susceptibility techniques. In addition, antibacterial and antifungal activities of starting materials and synthesized compounds against *Candida albicans* yeast *and Bacillus subtilis*, *Staphylococcus aureus*, *Enterococcus faecalis*, *Pseudomonas aeruginosa*, *Escherichia coli* and *Listeria monocytogenes* bacteria were investigated using the microdilution method and compared with existing antibiotics (Cefepime, Vancomycin, Levofloxacin and Fluconazole). Compounds **1-3** were observed to have activity against yeast and bacteria. In particular, compound **3** (7.80 µg/mL) against *E. faecalis*, compounds **3** (7.80 µg/mL) against *B. subtilis* bacteria, and compound **1** (15.60 µg/mL) against *C. albicans* yeast. showed better activity than control compounds.

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1 INTRODUCTION

2,3-Pyrazinedicarboxylic acid (PDA) is a heterocyclic carboxylic acid and is used in the synthesis of coordination compounds [1]. Compared to pyridine dicarboxylic acids, 2,3-pyrazinedicarboxylic acid has certain advantages as it has richer coordination modes, hydrogen bond acceptors and donors [2,3]. It is one of the most sought-after ligands, especially in the formation of lattice-structured compounds [4,5]. These compounds have a wide range of uses such as material sciences, medicine, industrial catalysis, luminous characteristics, and molecular recognition processes in biological systems [6-9]. PDA and its deprotonated anions have six potential coordination sites containing nitrogen atoms of the pyrazine ring and oxygen atoms of carboxylic groups and act as multifunctional ligands to act as bridging ligands in metal complexes [10,11]. Structures constructed between PDA ligands and d-block transition metals are generally in 1D and 2D [12-17] coordination modes, whereas PDA ligands and lanthanidines generally have 3D architectures [18-20].

Bidentate and flexible ligands, like 4,4’-ethylenedipyridine (BPE) can produce polymetallic coordination networks with intriguing supramolecular solid-state topologies [21,22]. While BPE ligand coordinates to the metal in Co(II) [23] and Cu(II) [24] complexes synthesized previously by our research group, it is present as a complementary ion in the newly synthesized Fe(II) complex.

In this study, a novel salt {(H_2BPE)(PDA), **1**} synthesized from 4,4’-ethylenedipyridine (BPE) with 2,3-pyrazinedicarboxylic acid (H_2PDA) and its complexes, Fe(III) {(H_2BPE)[Fe_2(PDA)(H_2O)$_4$]$_n$, **2**}, and Ni(II) {[Ni(PDA)(BPE)$_2$(H_2O)$_2$]$_n$.H_2O, **3**}, were synthesized and described by NMR, TG-DTA, IR, UV-Vis, elemental analysis and magnetic susceptibility techniques. In addition, the antibacterial and antifungal activities of the initial materials and newly obtained metal complexes were investigated against *E. faecalis*, *P. aeruginosa*, *B. subtilis*, *S. aureus*, *L. monocytogenes* and *E. coli* bacteria and *C. albicans* yeast by microdilution method. Antimicrobial results of the compounds were compared with existing antibiotics (Vancomycin, Levofloxacin, Cefepime and Fluconazole).

2 MATERIALS AND METHODS

2.1 Methods and materials

All of the chemicals were bought from Abcr. For the purpose of figuring out compound structures, equipment like the Elementar Vario III EL (for elemental studies), Perkin Elmer SII Exstar 6000 TG/DTA 6300 (for thermal analysis), BRUKER OPTICS VERTEX 70 (for IR analysis), SHIMADZU UV-2550 (for UV-Vis), and Sherwood Scientific Magway MSB MK1 (for magnetic moment measurements) were used.

2.2 Synthesis of 1-3

30 mL of pure ethanol were used to dissolve 10 mmol of H_2PDA (1.0814 g) and 10 mmol of BPE (1.6712 g). The mixture was refluxed while being stirred for two hours, producing **1** as a white powder (90% yield) (Figure 1).
Proton transfer salt (**1**) (1 mmol, 0.253g) and metal salt, {1 mmol $FeSO_4.7H_2O$ (0.249 g) for **2** and 1 mmol $Ni(CH_3COO)_2.4H_2O$ (0.248 g) for **3**}, were dissolved in 20 mL of water. After stirring for one day at room temperature, the mixture was filtered and left to crystallize. Following one week, compounds **2** (ivy, 75% yield) and **3** (green, 65% yield) were obtained as powder (Figure 1).

Anal. Calcd. for **1** {$C_{18}H_{16}N_4O_4$, M = 352,34 g/mol}, C, 61.36%; H, 4.58%; N, 15.90%. Found: C, 61.42%; H, 4.60%; N, 15.95%. for **2** {$C_{18}H_{26}Fe_2N_4O_9$, M = 554.11 g/mol}, 39.02%; H, 4.73%; Fe, 20.16%; N, 10.11%. Found: 39.00%; H, 4.75%; Fe, 20.20%; N, 10.10%. for **3** {$C_{18}H_{20}N_4NiO_7$, M = 462.07 g/mol}, C, 46.69%; H, 4.35%; N, 12.10%; Ni, 12.67%. Found: 46.65%; H, 4.30%; N, 12.15%; Ni, 12.60%.

2.3 Antimicrobial study

The minimal amount of an active ingredient required to prevent the development of tested microorganisms is known as the minimum inhibitory concentration, or MIC. When compared to the reference medications, every evaluated molecule exhibited antibacterial and antifungal action (Table 1). The antibacterial evaluation showed that the compounds had a considerable amount of action. Generally, the MIC values fall between 7.80 to 125.00 μg/mL for every strain that has been assesse.

The microdilution testing technique yielded the MIC values [24] DMSO was used to create the chemical stock solutions. The usual antibacterial agents were vancomycin, levofloxacin, and cefepime; the typical antifungal drug was fluconazole. Table 1 provides the observed data on the antibacterial activity of the compounds and control medications as MIC values, in µg/mL.

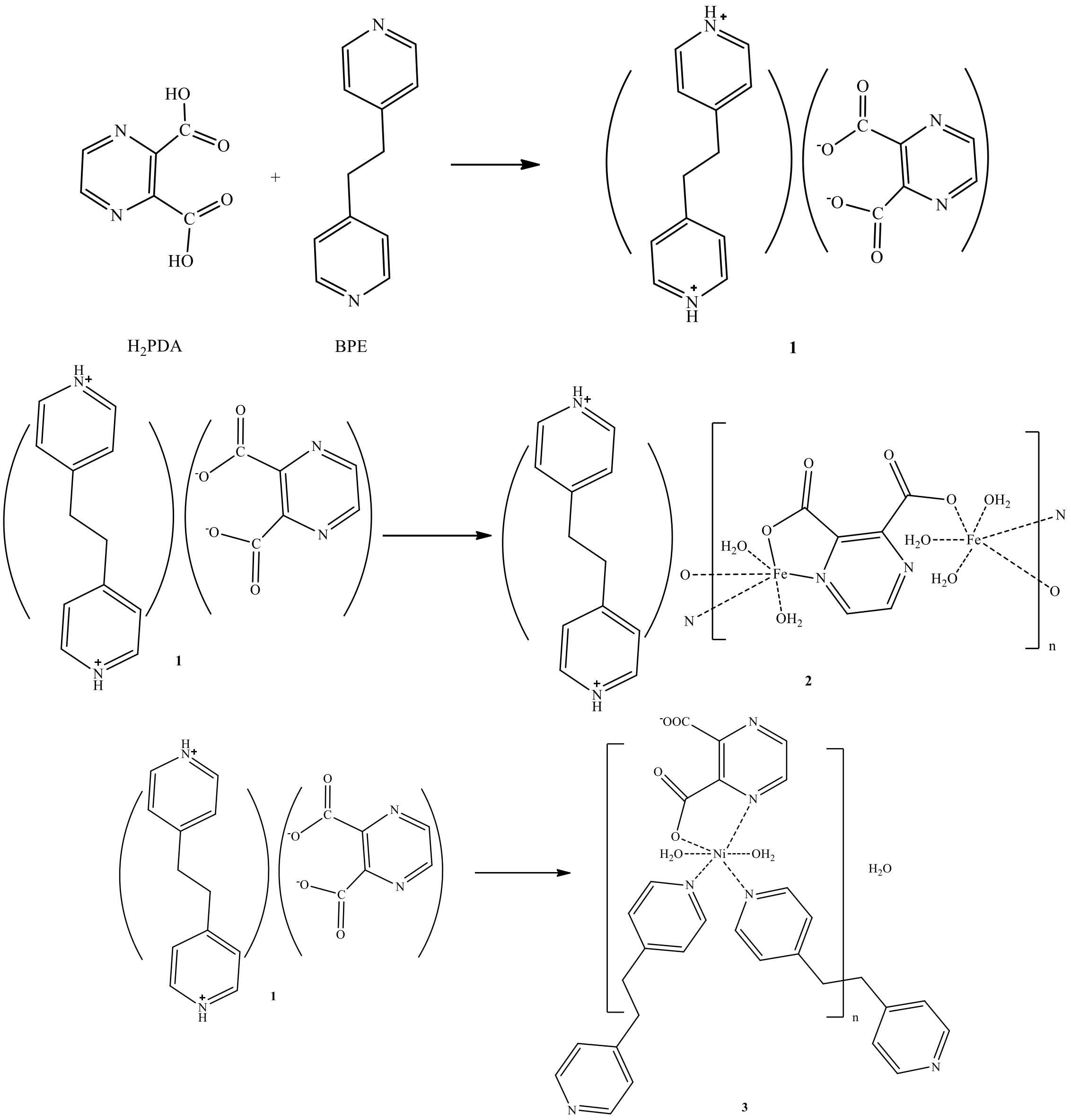


Figure 1. The structures of compounds **1-3**

2.3.1 Microdilution method

The compounds' antibacterial efficacy was assessed using the Microbroth Dilution Susceptibility Assay. The samples were produced as stock solutions in dimethylsulfoxide. In 2 milliliters of DMSO solution, 4 milligrams of synthesized chemicals and 4 milligrams of antibiotics were dissolved.

Using McFarland No. 0.5 standard solution, overnight-grown bacterial and yeast suspensions in double-strength Mueller-Hinton broth were standardized to 10^8 Colony Forming Units/mL. Next, 100 milligrams of each suspension of microorganisms was put to each well. As a negative control, the last well-chain devoid of any microorganism was employed. The medium and sterile distilled water functioned as a positive growth control. The MIC was established by determining the first well that remained turbidity-free after incubation at 37 °C for 18–24 hours.

Table 1. Antimicrobial activity results of all compounds (µg/mL)

Compound	***S. aureus***	***B. subtilis***	***P. aeruginosa***	***L. monocytogenes***	***E. coli***	***E. faecalis***	***C. albicans***
Vancomycin	31.25	250	62.50	125.00	31.25	62.50	-
Levofloxacin	31.25	62.50	31.25	31.25	31.25	62.50	-
Cefepime	62.50	62.50	31.25	31.25	62.50	31.25	-
Fluconazole	-	-	-	-	-	-	62.50
BPE	62.50	62.50	62.50	31.25	31.25	62.50	62.50
H_2PDA	31.25	15.60	31.25	31.25	31.25	15.60	62.50
1	62.50	31.25	62.50	62.50	62.50	62.50	15.60
2	62.50	7.80	31.25	62.50	62.50	62.50	62.50
3	62.50	7.80	62.50	62.50	62.50	7.80	62.50

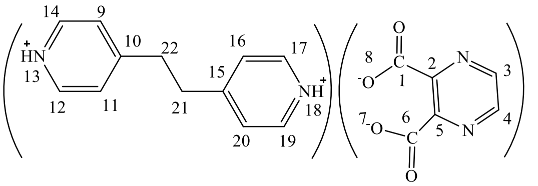
3 RESULTS AND DISCUSSION

3.1 NMR spectra of 1

In the ^{1}H NMR spectrum of **1** (Fig. 2, Table 2), the protons $H^{9,11}$, $H^{16,20}$ ($^3J_{H9,11\text{-}H16,20}$-$^3J_{H12,14\text{-}H17,19}$ = 8,40 Hz) and $H^{12,14}$, $H^{17,19}$ ($^3J_{H12,14\text{-}H17,19}$-$^3J_{H9,11\text{-}H16,20}$ = 8,40 Hz) were observed as doublet at 7.29 ppm and 8.44 ppm, each 4H intensity, while the H^3 and H^4 with an intensity of 2H and H^{21} and H^{22} with an intensity of 4H were seen as singlets at 8.83 and 2.95 ppm, respectively.

^{13}C-NMR spectrum of **1** exhibits seven signals (Fig. 3, Table 2). Carboxylate carbons (C^1 and C^6) were observed at 166.76 ppm. Carbons of PDA^{2-} ring were seen at 145.89 ppm for C^2 and C^5, at 150.96 ppm for C^3 and C^4. H_2BPE^{2+} ring carbons were monitored at 124.76 ppm ($C^{9,11,16,17}$), 146.17 ppm ($C^{10,15}$), 149.53 ppm ($C^{12,14,17,19}$) and 35.00 ppm ($C^{21,22}$).

Table 2. Results of NMR for **1** (ppm)



	^{1}H NMR	^{13}C NMR	
H^3, H^4	8.83 (2H, s)	C^1, C^6	166.76
$H^{9,11}$-$H^{16,20}$	7.29 (4H, d) ($^3J_{H9,11\text{-}H16,2\text{-}}$$^3J_{H12,14\text{-}H17,19}$ = 8.40 Hz)	C^2, C^5	145.89
$H^{12,14}$-$H^{17,19}$	8.44 (4H, d) ($^3J_{H12,14\text{-}H17,19\text{-}}$$^3J_{H9,11\text{-}H16,20}$ = 8.40 Hz)	C^3, C^4	150.96
H^{13}-H^{18}	-	$C^{9,11}$, $C^{16,20}$	124.76
H^{21}, H^{22}	2.95 (4H, s)	C^{10}, C^{15}	146.12
		$C^{12,14}$, $C^{17,19}$	149.53
		C^{21}, C^{22}	35.00

3.2 Thermal analyses of 2 and 3

TG-DTG and DTA curves and values of 2 and 3 are given in Figs 4 and 5 and Table 3.

Compound 2 thermally decomposed in three steps. A loss of five moles of water was observed in endothermic first step (DTG_{max} = 173 °C). The endothermic second stage and exothermic third stage are consistent with the loss of H2BPE (DTG_{max} = 302 °C) and PDA (DTG_{max} = 395 and 407 °C) fragments, respectively. The final product left undecomposed is FeO.

Compound 3 thermally decomposed in two steps. The endothermic first stage corresponds to the loss of three moles of water molecules (DTG_{max} = 81 °C for 3). In the second exothermic step, it was observed that BPE+PDA units detached (DTG_{max} = 237, 282, 342, 441 and 488 °C). The final undecomposed products are NiO.

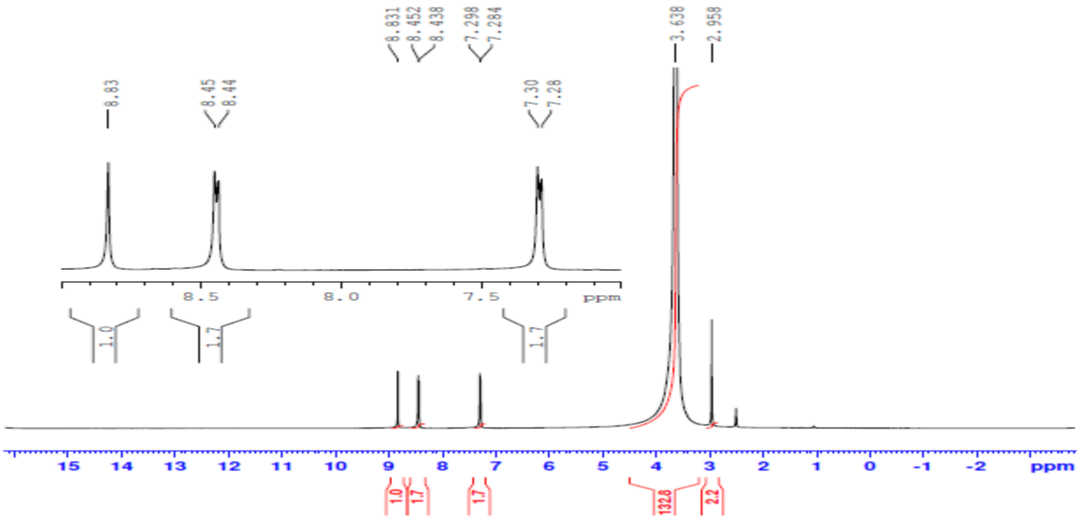


Figure 2. ^{1}H NMR spectrum of **1**

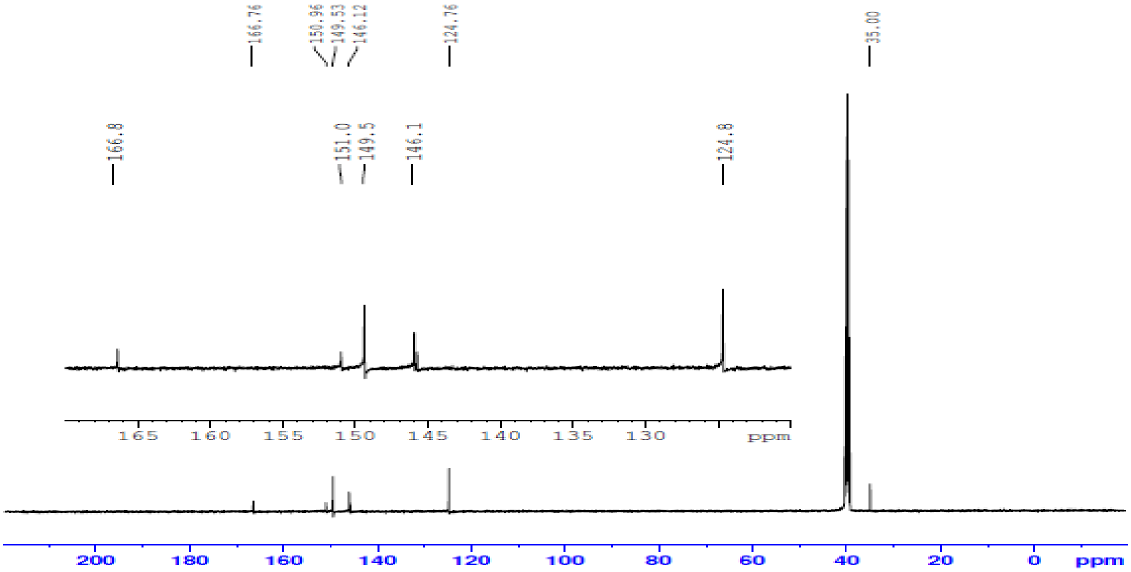


Figure 3. ^{13}C NMR spectrum of **1**

Table 3. Thermal analyses results of compounds **2** and **3**

Compound	Temperature (°C)	DTG$_{max}$ (°C)	Leaving Group	Found (%)	Calculated (%)
2	30-200	173	5 H_2O	16.25	16.20
	200-345	302	H_2BPE	33.62	33.70
	345-900	395, 407	PDA	29.97	30.00
	-		Fe	20.16	20.10
3	30-150	81	3 H_2O	11.67	11.70
	150-900	237, 282, 342, 441, 488	BPE + PDA	75.71	75.
	-	-	Ni	12.62	12.60

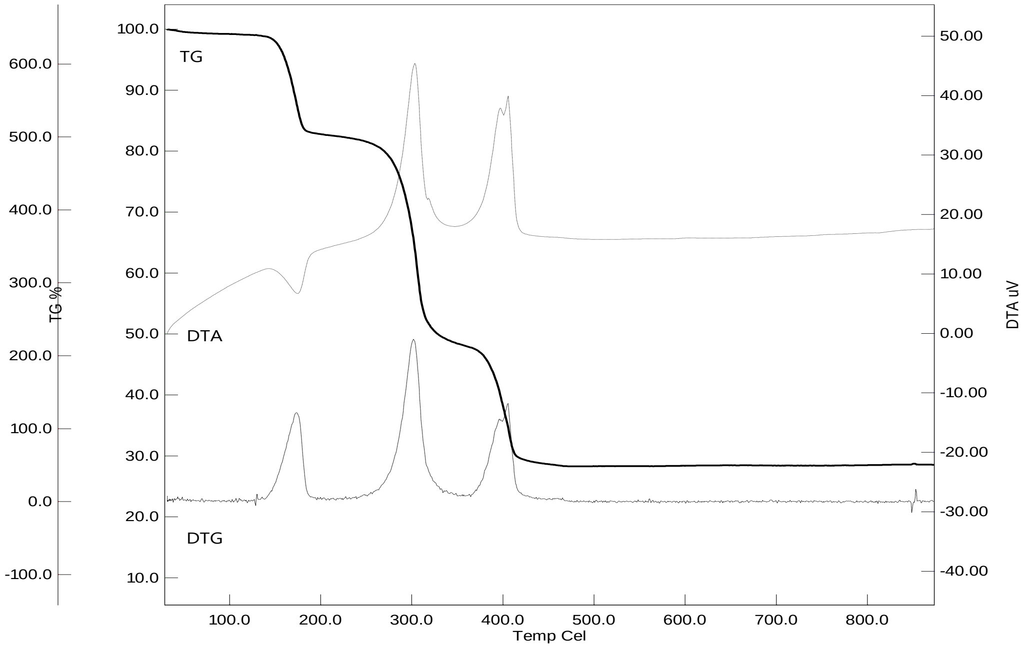


Figure 4. TG-DTG and DTA curves of **2**

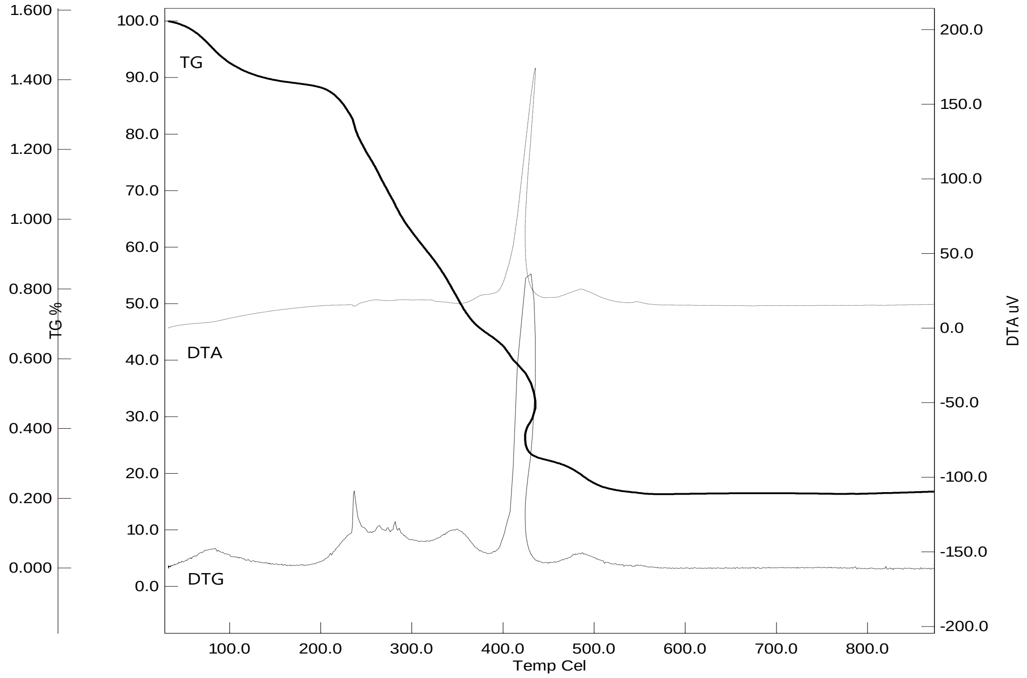


Figure 5. TG-DTG and DTA curves of **3**

3.3 FT-IR results of 1-3

The FTIR spectra of **1-3** and data are given in Figs 6-8 and Table 4, respectively. The broad vibration peaks between 3500 and 3200 cm^{-1} indicate ν(OH) vibrations of **2** and **3**. Within the range of 2562–2463 cm^{-1}, broad and weak ν(N$^+$-H) bands for **1** and **2** were seen [25]. The difference (Δν) between the extensions of the asymmetric and symmetric vibrations of the COO$^-$ group shows how it coordinates to the metal ion. The differences of **2** and **3** were calculated 204 (1637 and 1433 cm^{-1}) and 248 (1699 and 1451 cm^{-1}) respectively. According to these data, the carboxylate group is bound to the metal ion as a monodentate ligand [26]. The peaks at the range of 3079-3033 cm^{-1}, 2946-2860 cm^{-1}, 1645-1427 cm^{-1}, 754-741 cm^{-1}, 547-538 cm^{-1} and 450-434 cm^{-1} for compounds (**1-3**) are assigned aryl ν(C-H), aliphatic ν(C-H), ν(C=N)/ν(C=C), ν(py), ν(M-O) and ν(M-N), respectively.

Table 4. IR data of all compounds (cm^{-1})

	1	**2**	**3**
ν(O–H)	-	3421-3199(br)	3445-3200(br)
ν(C–H)$_{\text{aro.}}$	3072(w)	3033(w)	3079(w)
ν(C–H)$_{\text{alp.}}$	2919(w)	2946(w) 2860(w)	2931(w) 2868(w)
ν(N^{+}–H)	2513(w)	2500(w)	-
ν(C=O)$_{\text{asym}}$	1708(s)	1637(s)	1699(s)
ν(C=O)$_{\text{sym}}$	1340 (s)	1433(s)	1451(s)
ν(C=N)/ν(C=C)	1596(s) 1522(s)	1600(s) 1570(s) 1505(s) 1459(s) 1433(s)	1645(s) 1573(s) 1503(s) 1451(s) 1427(s)
ν(py)	754(s)	750(s)	741(s)
ν(M–N)	-	434(s)	450(s)
ν(M–O)	-	538(s)	547(s)

s: strong, br: broad, w: weak

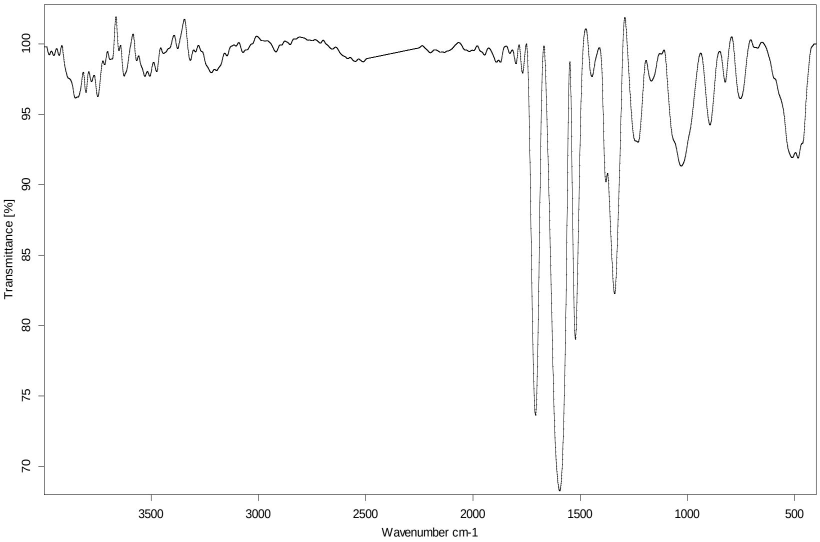


Figure 6. FT-IR spectrum of **1**

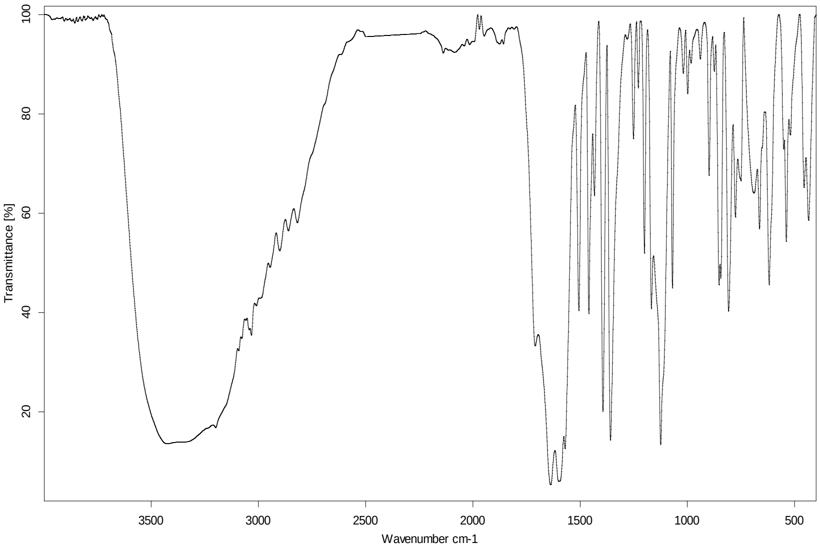


Figure 7. FT-IR spectrum of **2**

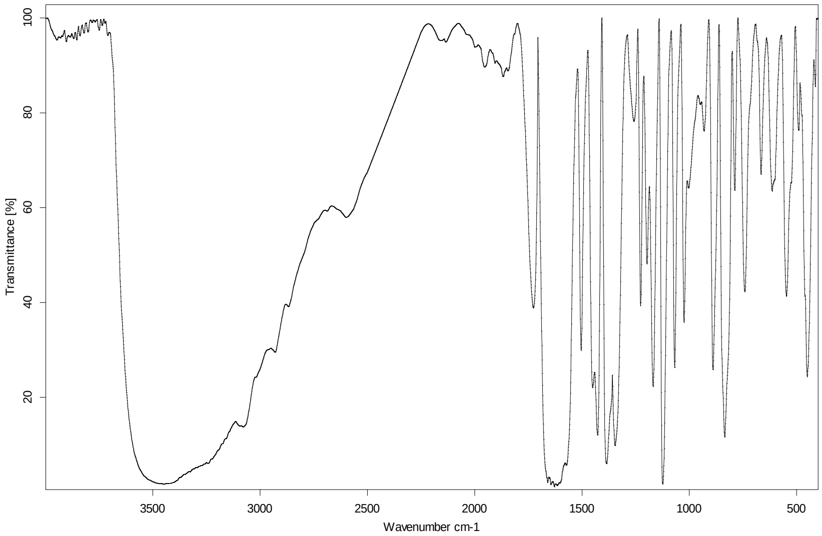


Figure 8. FT-IR spectrum of **3**

3.4 UV-Vis spectra

The ultraviolet-visible spectra of **1-3** (Fig 9) were recorded in DMSO (1x10^{3-} M). The π-π* and n-π* transitions (λ{ε_0(Lmol^{-1}cm^{-1})}) were monitored in the spectra at 295(27560) and 317(26530) nm for **1**, 290(32050), 295(32740) and 298(32150) nm for **2** and 290(20900) and 295(21190) nm for **3**. The d-d transitions bands, indicating an six coordinated metal ions, were found at 778(540) for **2** [27] and 603(1260) for **3** [28].

3.5 Magnetic susceptibilities

The calculated magnetic moment values are based on spin only and do not include orbital contribution. For this reason, some differences can be observed between the calculated and experimentally found magnetic moment values. Each Fe(II) ion in complex **2** has a magnetic moment value of 3.34 B.M, indicating that the complex has an octahedral structure with high spin due to the presence of four unpaired electrons [29]. The magnetic moment of **3** is 3.22 B.M agree with the expected values (2.8-3.4 BM) for octahedral Ni(II) ions with two unpaired electrons [30,31].

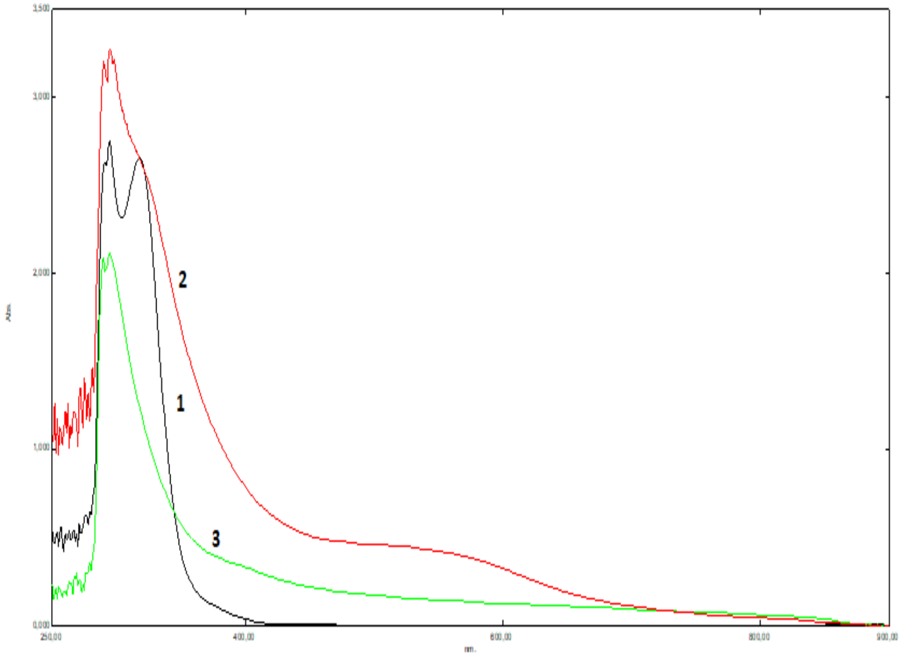


Figure 9. UV-Vis spectrum of **1-3.**

3.6 Antimicrobial results of compounds

In this work, antibacterial and antifungal activities of BPE, H_2PDA and synthesized **1-3** were were assessed using the microdilution technique. The minimum inhibitory concentration (MIC) values for each compound are presented in Table 1. Analysis of the MIC values revealed the presence of antibacterial and antifungal properties in all the tested compounds.

Against *E. coli* bacteria, BPE and H_2PDA were found to have similar effects when compared with control compounds Vancomycin and Levofloxacin. Against *E. coli* compounds **1-3** have similar effects with Cefepime as control compound. Against *E. faecalis* bacteria, complex **3** and H_2PDA had higher activity than all control compounds. The other compounds have similar effects with Vancomycin and Levofloxacin while have less effect for Cefepime. Against *P. aeruginosa* bacteria, BPE, **1** and **3** were determined to have similar effects with Vancomycin while H_2PDA and **2** exhibited equal effect with Levofloxacin and Cefepime. Against *L. monocytogenes*, all compounds were found to have higher efficacy against this bacterium than the Vancomycin while BPE and H_2PDA were showed similar effects with as Levofloxacin and Cefepime. The other compounds showed less activity than Cefepime and Levofloxacin. Against *S. aureus* bacteria, **1-3** showed less effect than the control compounds. The BPE and **1-3** were determined to have equal effects with Cefepime while H_2PDA exhibited higher effect than Cefepime. Compound H_2PDA was determined to have similar effects with Vancomycin and Levofloxacin while the others displayed less activity than Vancomycin and Levofloxacin. Against *B. subtilis* bacteria, **2**, **3**, H_2PDA and **1** exhibited higher effect than the control drugs. The other compounds were determined to have similar effects with Levofloxacin and Cefepime while all compounds more effective than Vancomycin. Against *C. albicans* yeast species, **1**, showed a higher effect than the control antibiotics Fluconazole while BPE, H_2PDA, **2** and **3** had similar effects with Fluconazole.

4 CONCLUSIONS

In this study, a new salt (H_2BPE)(PDA) (**1**) and its metal complexes (H_2BPE)[Fe_2(PDA)(H_2O)$_4$]$_n$ (**2**) and [Ni(PDA)(BPE)$_2$(H_2O)$_2$]$_n$.H_2O (**3**) were synthesized. The structures of amorphous compounds (**2** and **3**) were suggested according to the analysis results. All compounds were found to have activity against fungi (*C. albicans*) and bacteria (*P. aeroginosa*, *S. aureus*, *E. faecalis*, *B. subtilis*, *L. monocytogenes*, *E. coli*). Particularly, compound **3** (7.80 g/mL) against *E. faecalis,* compounds **3** (7.80 g/mL) against *B. subtilis* bacteria, and compounds **1** (15.60 g/mL) against *C. albicans* yeast, demonstrated superior activity than control compounds. As a result, the **1-3** obtained can be assessed for use in the synthesis of novel antibacterials. The various applications of the produced chemicals should be investigated.

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Author Contributions

Nurgün BÜYÜKKIDAN: Conceptualization, Methodology, Software, Formal analysis, Investigation, Writing - Original Draft, Writing - Review & Editing, Project administration, Funding acquisition
Seher KAYA: Conceptualization, Methodology, Software, Formal analysis, Investigation, Writing - Original Draft, Writing - Review & Editing
Halil İLKİMEN: Conceptualization, Methodology, Software, Formal analysis, Investigation, Writing - Original Draft, Writing - Review & Editing
Aysel GÜLBANDILAR: Methodology, Formal analysis, Writing - Original Draft, Writing - Review & Editing

All authors read and approved the final manuscript.

Conflict of interest

No conflict of interest was declared by the authors.

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