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Synthesis, Characterization, and Antimicrobial Activity of a Novel Proton Salt and Its Cu(II) Complex[1]

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Abstract—A novel proton transfer compound $(H_2Ppz)(HDipic)_2$ (**I**) obtained from 2-(piperazin-1-yl)ethanol (Ppz) and pyridine-2,6-dicarboxylic acid (H_2Dipic) and its Cu(II) complex $(H_2Ppz)[Cu(Dipic)_2] \cdot 6H_2O$ (**II**) have been prepared and characterized by elemental, spectral (^1H and ^{13}C NMR, IR and Uv-Vis) and thermal analyses. Magnetic measurement and single crystal X-ray diffraction methods have also been applied for compound **II**. The molecular structure of **II** consists of one 1-(2-hydroxyethyl)piperazine-1,4-diium cation, one bis(pyridinium-2,6-dicarboxylate)Cu(II) anion and six uncoordinated water molecules. In complex **II**, the copper ion coordinates to two oxygen and one nitrogen atoms of two pyridine-2,6-dicarboxylate molecules forming an octahedral conformation. Furthermore, the synthesised compounds (**I** and **II**) were screened for their antimicrobial activities against Gram (–) (*Escherichia coli* and *Pseudomonas aeruginosa*) and Gram (+) (*Staphylococcusaureus* and *Bacillus cereus*). The results were reported, discussed and compared with the corresponding starting materials (H_2Dipic and Ppz).

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INTRODUCTION

Pyridine-2,6-dicarboxylic acid (or dipicolinic acid) (H_2Dipic) forms stable chelates with simple metal ions and oxometalcations and can display widely varying coordination behaviour, functioning as a multidentate ligand. Dipicolinates (Dipic) commonly coordinate to transition metals by either carboxylate bridges between metal centers, to form polymeric or dimeric complexes [1–3], or by tridentate (O,N,O') chelation to one metal ion [4, 5]. The dipicolinic ligand with Cu^{2+} ions commonly has one or two coordination modes. In one coordination mode, a single planar Dipic ligand binds in the equatorial plane of a Cu^{2+} cation and other ligands such as H_2O or pyridine based heterocycles occupy the remaining sites, thereby forming a square planar or square pyramidal coordination geometry [6]; or two planar Dipic molecules coordinate perpendicularly generating a distorted octahedral coordination geometry [7].

In the antimicrobial agent production in the recent studies, metal ions, such as Cd^{2+}, Pd^{2+}, Pt^{2+}, Ag^{+}, Au^{+}, and bio cations, such as Co^{2+}, Ni^{2+}, Cu^{2+}, Fe^{3+}, Cr^{3+}, Mn^{3+}, Zn^{2+}, were determined and shown high activity to inhibit the development of bacterial resistance [8, 9]. Many papers that describe antimicrobial properties of H_2Dipic have appeared in recent years [8, 10–12]. Metal complexes of H_2Dipic and some of their derivatives have also been used for new pharmaceutical compounds [13, 14]. Metal ions have an effect by exchange of the metals or by disturbing to the internal and external coordination of active region to the structural integrity of enzymes. Metal ions compared to an organic antimicrobial agent provide longer time interaction through strong covalent or ionic bonds with target molecules [15]. The antimicrobial activity of the metal complexes generally depends on the chelation ability of the ligand, the nature of nitrogen donor ligands, the total charge of the complex, the existence and the nature of the metal ion neutralizing the ionic complex and the nuclearity of the metal center in the complex [16]. Cu(II) and Ni(II) complexes of H_2Dipic can act as effective DNA cleaving agents. Also it has been observed that the activity of Mn(II), Fe(II) and Co(II) complexes is lower than that of Cu(II) complex [17]. Antimicrobial activities of a novel macrocyclic ligand derived from the reaction of H_2Dipic with homopiperazine and its Co(II), Ni(II), Cu(II), and Zn(II) complexes were also studied [18].

In this paper we report the structures of a novel proton transfer salt obtained from the reaction of pyridine-2,6-dicarboxylic acid and 2-(piperazin-1-yl)ethanol (Ppz), formulated as $(H_2Ppz)(HDipic)_2$ (**I**) and its Cu(II) complex formulated as $(H_2Ppz)[Cu(Dipic)_2] \cdot 6H_2O$ (**II**). They are characterized by the spectral and thermal analyses. Furthermore, the biological evaluation of these compounds has been studied.

[1] The article is published in the original.

EXPERIMENTAL

Materials and general methods. All chemicals used were analytical reagents and were commercially purchased from Aldrich. $Cu(CH_3COO)_2 \cdot H_2O$, Ppz, and H_2Dipic were used as received. ^{1}H NMR spectra were recorded with 500 MHz UltraShield NMR spectrometer (D_2O, 25°C; $SiMe_4$ as internal standard and 85% H_3PO_4 as an external standard). Elemental analyses for C, H, N, and S were performed on a Leco CHNS-932 instrument. IR spectra were recorded on a Bruker Optics, vertex 70 FT-IR spectrometer using ATR techniques. Thermal analyses were performed on SII Exstar 6000 TG/DTA 6300 model using platinum crucible with 10 mg sample. TG/DTA measurements were taken in the static air, within 30–700°C temperature range. The UV-Vis spectra were carried out with a SHIMADZU UV-2550 spectrometer in the range 900–200 nm. Magnetic susceptibility measurements at room temperature were taken using a Sherwood Scientific Magway MSB MK1 model magnetic balance by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant.

Synthesis of I. A solution of Ppz (0.946 g, 726 mmol) in ethanol (10 mL) was added dropwise to the solution of H_2Dipic (1.214 g, 726 mmol) in ethanol (10 mL) with stirring. White precipitate was filtered, washed with water and dried in air. The yield was 95%.

For $C_{20}H_{24}N_4O_9$ (**I**) ($M = 464.15$)

anal. calcd., %:	C, 51.72;	H, 5.21;	N, 12.06.
Found, %:	C, 51.82;	H, 5.42;	N, 12.16.

Synthesis of II. A solution of $Cu(CH_3COO)_2 \cdot H_2O$ (0.68 g, 340 mmol) in water (10 mL) was added to an aqueous solution of **I** (0.10 g, 340 mmol, 10 mL). The blue crystals of complex **II** suitable for X-ray analysis were obtained after 2 days from reaction solution. The yield was 60%.

For $C_{20}H_{34}CuN_4O_{15}$ (**II**) ($M = 633.15$)

anal. calcd., %:	C, 37.77;	H, 5.70;	N, 8.81.
Found, %:	C, 38.11;	H, 5.45;	N, 9.06.

X-ray structure determination of II. H atoms were positioned geometrically and refined using a riding model. The final difference Fourier maps showed no peaks of chemical significance. For the crystal structure determination, the single-crystal of complex **II** was used for data collection on a four-circle Rigaku R-AXIS RAPID-S diffractometer (equipped with a two-dimensional area IP detector). The graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å) and oscillation scans technique with $\Delta\omega = 5°$ for one image were used for data collection. The lattice parameters were determined by the least-squares methods on the basis of all reflections with $F^2 > 2\sigma(F^2)$. Integration of the intensities, correction for Lorentz and polarization effects and cell refinement was performed using CrystalClear [19] software. The structures were solved by direct methods using SHELXS-97 [20] and refined by a full-matrix least-squares procedure on F^2 using the program SHELXL-97 [20]. One of the water molecules was disordered and we could not locate the hydrogen atoms of it, other water H atoms were located in the difference Fourier map. All other hydrogen atoms were added at calculated positions and refined using a riding model. Anisotropic thermal displacement parameters were used for all non-hydrogen atoms. The final difference Fourier maps showed no peaks of chemical significance. Crystal data and structure refinement parameters of compound **II** were given in Table 1. Supple-

Table 1. Crystal data and structure refinement for compound **II**

Paramerter	Value
Formula weight	632.0
Temperature, K	293(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions:	
a, Å	12.0754(2)
b, Å	17.9239(2)
c, Å	13.3694(4)
β, deg	113.16(3)
Volume, Å^3	2658.89(1)
Z	4
ρ_{calcd}, mg/cm^3	1.58
Absorption coefficient, mm^{-1}	0.902
$F(000)$	1316
Crystal	Block
Crystal size, mm	0.12 × 0.13 × 0.21
θ Range for data collection, deg	2.2–26.4
Index ranges	$-15 \le h \le 15$, $-22 \le k \le 17$, $-16 \le l \le 16$
Reflections collected	15707
Independent reflections	5405 ($R_{int} = 0.075$)
Completeness to θ = 26.24, %	99.9
Data/restraints/parameters	3400/0/352
Goodness-of-fit on F^2	1.052
Final R indices ($F^2 > 2\sigma(F^2)$)	$R_1 = 0.066$, $wR_2 = 0.144$
R indices (all data)	$R_1 = 0.113$, $wR_2 = 0.169$
Largest diff. peak and hole, e Å^{-3}	0.343 and −0.499

mentary material has been deposited with the Cambridge Crystallographic Data Centre (no. 824573; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

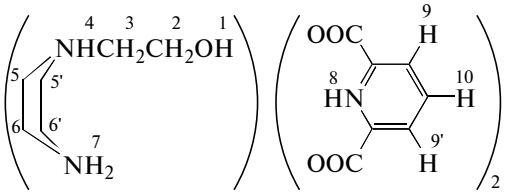
Antimicrobial activity studies. *Escherichia coli* ATCC 25922, *Pseudomonas aeruginosa* ATCC 27853, *Staphylococcus aureus* ATCC 6535, and *Bacillus cereus* ATCC 7064 were used for the antimicrobial assays. Antimicrobial activity tests were carried out using the broth dilution method as described by the NCCSL standards [21]. All stock solutions of the compounds were prepared in pure water according to the needed concentrations for experiments. H_2Dipic was prepared in ethanol and controlled effect on microorganism.

For the broth dilution method, cultures were grown in nutrient agar (Merck) at 37°C for 18 h. These cultures were used as starter cultures. Initial bacterial concentrations (approximately 5×10^5 cfu mL^{-1}) were estimated for the cultures at 600 nm by matching with 0.5 McFarland turbidity standards. Nutrient broth containing microorganisms were transferred 1 mL in test tubes, and made 2-fold serial dilution in nutrient broth from 3000 to 23.4 μg mL^{-1}. Growth inhibition was determined by measuring MICs (as the lowest concentration in which microbial growth was prevented) as indicated by the lack of turbidity after 24 h of incubation at 37°C. The ethanol was also tested for antimicrobial activity.

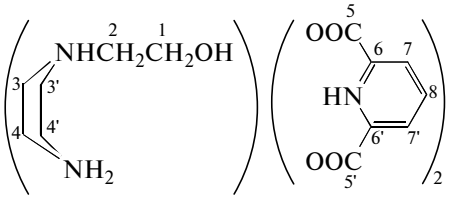
RESULTS AND DISCUSSION

The NMR spectra displayed two characteristic sets of resonances indicative of the presence of H_2Ppz^{2+} and $HDipic^-$ with a molar ratio of 1 : 2. The numbering scheme of ^1H and ^{13}C NMR chemical shifts for compound **I** are given below:

^{1}H NMR



^{13}C NMR



The first, well separated set, corresponding to H_2Ppz^{2+} has been located at 3.35, 3.60, and 3.95 ppm while the second set for $HDipic^-$ at 8.35 and 8.57 ppm. Two sets of triplets for the protons H-3 and H-2 with both 2H intensity are observed at 3.35 ppm ($^3J_{H2-H3}$ = 5.22 Hz) and 3.95 ppm ($^3J_{H2-H3}$ = 5.22 Hz), respectively. All H_2Ppz^{2+} ring protons (H-5, H-5' and H-6, H-6') are observed as a broad singlet at 3.60 ppm with 8H intensity [22]. A doublet for H-9 and H-9' protons with 4H intensity and a triplet for proton H-10 with 2H intensity of the two $HDipic^-$ ring are observed at 8.35 ppm ($^3J_{H9,9'-H10}$ = 7.84 Hz) and 8.57 ppm ($^3J_{H9,9'-H10}$ = 7.83 Hz), respectively. In addition, a singlet at 4.85 ppm is assigned to the H-1 (OH), H-4 (NH) and H-7 (NH_2) protons of H_2Ppz^{2+} ring and H-8 (NH) proton of two $HDipic^-$ rings.

^{13}C NMR spectrum of **I** exhibits eight resonances. Four peaks out of eight at 43.64 (C-3, C-3', 2C), 51.52 (C-4, C-4', 2C), 58.03 (C-2, 1C), and 61.23 ppm (C-1, 1C) could be assigned to the carbons of H_2Ppz^{2+} moiety. The other set of four peaks at 129.92 (C-7, C-7', 4C), 148.43 (C-6, C-6', 4C), 149.66 (C-8, 2C), and 168.50 ppm (C-5, C-5', 4C) are due to the carbons of $HDipic^-$ moiety.

The IR spectrum of **I** shows broad band at 3230 cm^{-1}, which is assigned to ν(OH) vibration. In the IR spectrum of **II**, the ν(OH) vibration associated with free water molecules is observed as very strong and broad band in the 3466–2900 cm^{-1} region. Its broadening to lower energy up to ca. 2900 cm^{-1} and its high intensity is indicative of an extensive H-bonding. The ν(NH) vibrations are observed at 2751–2476 cm^{-1} for **I** and at 2757–2490 cm^{-1} for **II** due to protonated amine groups [23].

The relatively weak bands at 3031 and 2997 cm^{-1} for **I** are due to the aromatic and aliphatic ν(CH) stretching vibrations, respectively. The aromatic ν(CH) vibrations are observed at 3096 and 3019 cm^{-1} but aliphatic ν(CH) stretching vibrations are not observed for compound **II** due to overlapping with the broad ν(OH) vibration band. In **I**, asymmetric $\nu_{as}(COO^-)$ and symmetric $\nu_s(COO^-)$ vibration bands of the carboxylate group are observed at 1613 and 1587 cm^{-1}, respectively. Complex **II** exhibits characteristic bands of coordinated carboxylate groups arised at 1611 cm^{-1} for the asymmetric vibration and 1571 cm^{-1} for the symmetric vibration [24]. The strong absorption bands due to ν(C=C) vibrations are located in the regions 1587–1465 and 1470–1425 cm^{-1} for compound **I** and **II**, respectively [8]. The weak bands

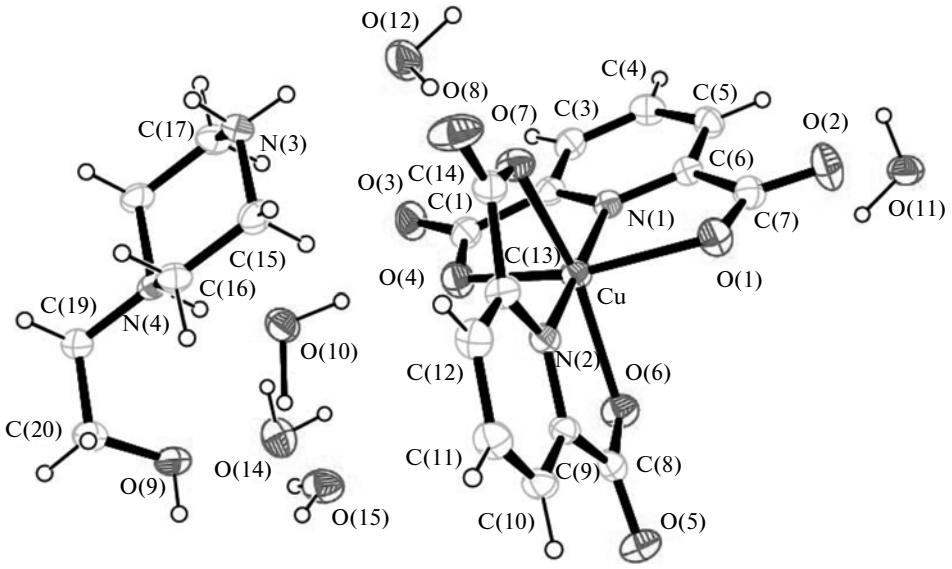


Fig. 1. The molecular structure of **II** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level. For the clarity disordered water molecule was not shown in the figure.

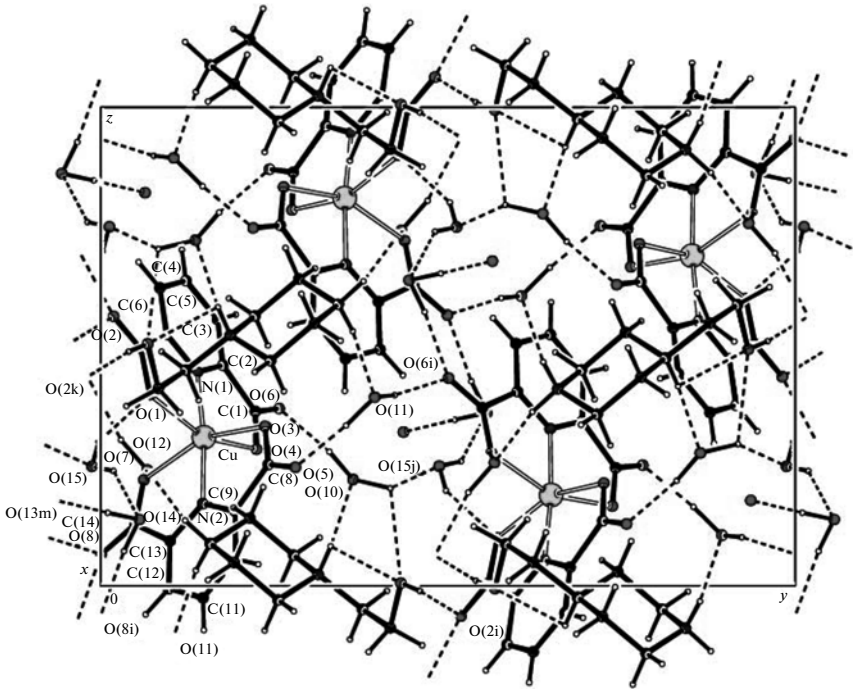


Fig. 2. The crystal packing of **II** viewed down the *x* axis. Dashed lines indicate extensive H bonding with the water molecules. For the disordered water atom, only O atom was shown.

at 590 and 425 cm^{-1} are due to Cu–O and Cu–N vibrations, respectively, of complex **II**.

X-ray diffraction analysis of **II** was undertaken. The molecular structure of **II** with an atom numbering scheme is given in Fig. 1. Packing diagram is shown in Fig. 2. Relevant bond distances and angles are given in Table 2. Structure of **II** consists of one H_2Ppz^{2+} cation, one $[Cu(Dipic)_2]^{2-}$ anion and six uncoordinated water molecules. In complex **II**, the copper ion coordinates to two oxygen and one nitrogen atoms of two pyridine-2,6-dicarboxylate molecules forming an octahedral conformation. Both primary carboxylate O atoms from Dipic occupy the *trans*-apical positions of the Cu(II) coordination polyhedron, with bond lengths 2.18 and 2.21 Å and define the lowest *trans*-angle of **II**

Table 2. Selected bond lengths (Å) and angles (deg) for complex **II**

Bond	*d*, Å	Bond	*d*, Å
Cu–N(2)	1.935(4)	Cu–N(1)	1.927(4)
O(9)–C(20)	1.419(7)	Cu–O(1)	2.178(4)
O(5)–O(4)	2.189(6)	Cu–O(7)	2.175(4)
Cu–N(1)	1.927(4)	Cu–O(6)	2.210(4)
O(2)–C(7)	1.233(7)	O(7)–C(14)	1.260(6)
O(6)–C(8)	1.253(6)	O(8)–C(14)	1.222(7)
O(1)–C(7)	1.258(6)	O(4)–C(1)	1.258(6)
Angle	ω, deg	Angle	ω, deg
CuN(2)C(9)	119.1(3)	O(1)Cu O(4)	156.3(3)
CuN(2)C(13)	120.0(4)	O(7)Cu O(6)	155.6(3)
C(9)N(2)C(13)	120.8(4)	N(1)Cu N(2)	174.0(3)
CuN(1)C(2)	119.3(3)	Cu N(1)C(6)	119.8(3)
C(2)N(1)C(6)	120.9(4)		

Table 3. Geometric parameters of hydrogen bonds for complex **II***

Contact D–H···A	Distance, Å		Angle DHA, deg
	H···A	D···A	
N(3)–H(3*A*)···O(12)	1.85	2.75(4)	161
N(3)–H(3*B*)···O(11)^{i}	1.92	2.804(5)	168
N(4)–H(4*A*)···O(10)	1.85	2.727(5)	161
O(9)–H(9)···O(2)^{ii}	1.91	2.729(6)	174
O(10)–H(10*A*)···O(3)	1.71	2.658(5)	153
O(10)–H(10*B*)···O(9)	2.45	3.063(5)	107
O(10)–H(10*B*)···O(15)^{ii}	1.66	2.806(5)	150
O(11)–H(11*A*)···O(5)	1.70	2.730(5)	173
O(11)–H(11*B*)···O(8)^{ii}	1.86	2.789(5)	159
O(12)–H(12*A*)···O(7)	1.89	2.713(4)	157
O(12)–H(12*B*)···O(2)^{iii}	1.85	2.849(5)	165
O(14)–H(14*A*)···O(8)^{iv}	1.89	2.799(5)	171
O(14)–H(14C)···O(13)^{v}	1.79	2.753(6)	170
O(15)–H(15C)···O(1)	2.15	2.778(6)	149
O(15)–H(15D)···O(14)	2.07	2.789(5)	146
C(5)–H(5)···O(7)^{iii}	2.46	3.267(6)	145
C(12)–H(12)···O(15)^{iv}	2.56	3.443(6)	159
C(15)–H(15*B*)···O(4)	2.57	3.520(6)	165
C(16)–H(16*A*)···O(3)^{vi}	2.38	3.183(7)	140
C(17)–H(17*B*)···O(14)^{vii}	2.55	3.239(7)	128
C(18)–H(18*A*)···O(6)^{i}	2.52	3.436(6)	158

* Symmetry transformations used to generate equivalent atoms: ^{i} $-1+x, 1/2-y, -1/2+z$; ^{ii} $1-x, 1/2+y, 1/2-z$; ^{iii} $1-x, -y, 1-z$; ^{iv} $1-x, -y, -z$; ^{v} $1-x, -1/2+y, 1/2-z$; ^{vi} $x, 1/2-y, -1/2+z$; ^{vii} $-1+x, y, z$.

(~155°). The *trans*-angle O(Pdc)CuO(Pdc) also has a significantly low value (~156°). Both OCuO *trans*-angles of **II** reveal the rather rigid structures of such tridentate ligands, which are roughly planar (0.0037 Å). In contrast, the NCuN *trans*-angle is much more close to 180° (174°) and the dihedral angle defined by the mean planes of two Pdc ligands is 87.1°, showing that they fall perpendicular. The Cu–N and Cu–O bond distances lies within expected range of 1.92–1.93 and 2.17–2.21 Å, respectively (Table 2). In all essential details, the geometry of the molecule regarding bond lengths and angles of the compound are in good agreement with the values observed in similar Cu(II) complexes [8, 24, 25].

In the 1-(2-hydroxyethyl)piperazine-1,4-diium cation the piperazine group is protonated at both N atoms and adopts a chair conformation with puckering parameters *Q*, θ, and φ of 0.575(5) Å, 0.0(5)°, respectively, and 139.0(3)° [26] (Fig. 1). For an ideal chair θ has a value of 0 or 180°.

N–H···O_w cation-water and water-anion hydrogen bonds link the cation and anions and extensive H-bonding geometry with the water molecules indicates the molecular packing (Fig. 2 and Table 3).

The electronic spectra of **I**, **II** and the free ligands (Ppz and H_2Dipic) were recorded in water and DMSO solutions at a $1 \times 10^{3-}$ M concentration at room temperature (Fig. 3). The electronic spectra of all compounds display strong absorption bands in water solution (λ, nm (ε, M^{-1} cm^{-1})): (283 (232) for H_2Dipic, 296 (3169) for Ppz, 290 (3274) and 295 (3562) for **I** and 285 (2149) for **II**) and in DMSO solution (286 (1986) for H_2Dipic, 302 (4340) for Ppz, 289 (3072) for **I** and 283 (1712) and 353 (974) for **II**) which are assigned to π–π* transitions. The broad absorption band is observed for complex **II** at 777 (34) in water solution and at 793 (7) in DMSO solution due to *d–d* transition [27].

The room temperature magnetic moment of the Cu(II) complex is 1.67 μ_B indicating the presence of one unpaired electron.

Figure 4 shows the TG–DTG and DTA curves of compound **II**. The first stage, an endothermic peak (DTG_{max} = 69 and 97°C) between 35 and 104°C, corresponds to the loss of the 6 moles of hydrate water molecules (found 16.6%, calcd. 17.0%). The second endothermic stage (DTG_{max} = 256°C), between 104 and 278°C, corresponds to the loss of the H_2Ppz^{2+} together with two moles of $C_5H_3NO_2$ group of the

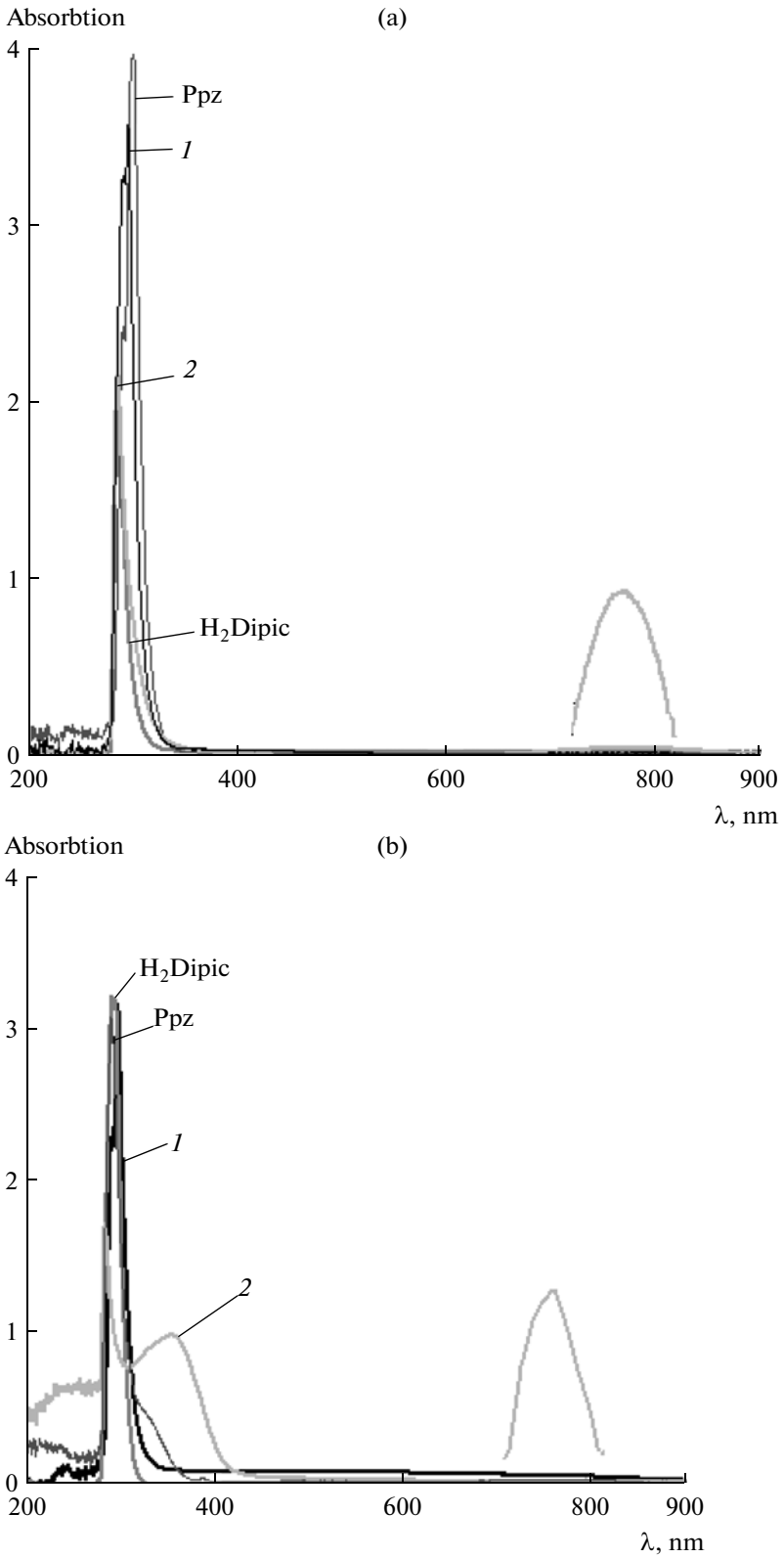


Fig. 3. UV-Vis spectra of free ligands, H_2Dipic, Ppz, **I**, and complex **II**: in water (a) and DMSO (b).

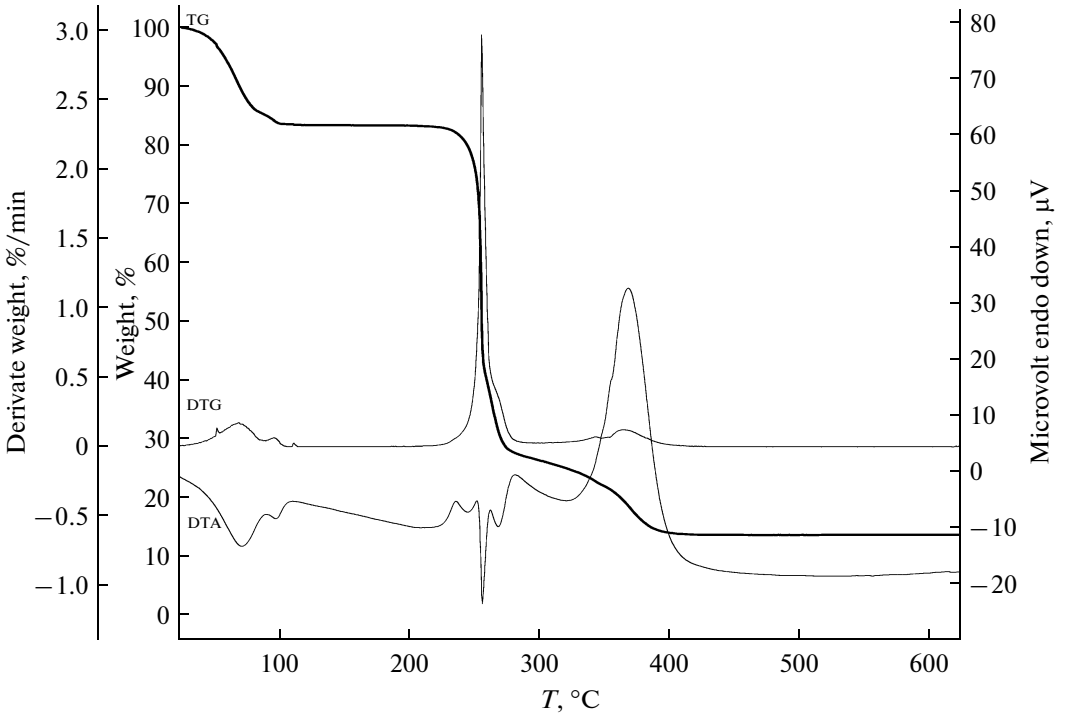


Fig. 4. The TG–DTG and DTA curves of **II**.

$Dipic^{2-}$ (found 55.5%, calcd. 55.2%). In the third stage, loss of C_4O_3 of $Dipic^{2-}$ residue is observed between 278 and 425°C with DTG_{max} at 343 and 365°C (found 14.7%, calcd. 15.1%). The final decomposition product was CuO identified by IR spectroscopy (found 13.2%, calcd. 12.7%).

The compound **I** and its Cu(II) complex **II** have been screened for antibacterial activities along with the free ligands H_2Dipic and Ppz (Table 4). According to the antimicrobial screening data, while the MIC value of H_2Dipic exhibited approximately 500 μg mL^{-1}, Ppz showed antibacterial activities at 3.125–6.25 μL mL^{-1}. The MIC values of **I** and **II** increased according to main matter H_2Dipic and Ppz. The compound **I** has more effective on Gram (+) (especially *B. cereus*) than Gram (–). But **II** showed effect at high concentration (>3000 μg mL^{-1}) without distinguishing Gram (+) and Gram (–). The MIC value of **I** showed more effective on *B. cereus* according to other bacteria. *B. cereus* is a endospore bacterium and H_2Dipic is a basic component of endospore and one of the most suitable ligand systems for modeling potential pharmacologically active compounds because of the low toxicity, amphophilic nature and diverse biological activities [14, 28].

Table 4. The MIC value of H_2Dipic, Ppz, **I** and **II** on bacteria

Compound	Gram (–)		Gram (+)	
	μg mL^{-1}			
	E. coli	*P. aeruginosa*	*S. aureus*	*B. cereus*
H_2Dipic	500	500	500	250
Ppz	3.125	6.25	3.125	6.25
$(H_2Ppz)(HDipic)_2$ (**I**)	1500	1500	750	187.5
$(H_2Ppz)[Cu(Dipic)_2] \cdot 6H_2O$ (**II**)	>3000	>3000	>3000	>3000

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