

**SYNTHESIS, STRUCTURE DETERMINATION, AND BIOLOGICAL ACTIVITY  
OF BIS-(3, 5-DIAMINO-1, 2, 4-TRIAZOLIUM-BIS (PYRIDINE-2,6-  
DICARBOXYLATO)-ZINCATE(II)TETRAHYDRATE  
[(C<sub>2</sub>H<sub>6</sub>N<sub>5</sub>)<sub>2</sub><sup>+</sup> ZN (DIPIC)<sub>2</sub><sup>2-</sup>].4H<sub>2</sub>O**



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### ABSTRACT

A new supramolecular compound of Zn (II) ( $[(C_2H_6N_5)_2^+Zn(dipic)_2^{2-}].4H_2O$ ) was synthesised by the reaction of ZnCl<sub>2</sub> with pyridine-2,6-dicarboxylic acid (dipicH<sub>2</sub>) and 3, 5-diamino-1,2,4-triazole (Hdatrz) and was characterised by elemental analysis, FTIR spectroscopy, UV-Vis spectroscopy, mass spectrometry, <sup>1</sup>H-NMR, thermal analysis and single crystal X-ray diffraction method. In the title compound, the Zn<sup>II</sup> ion is coordinated by four oxygen atoms and two nitrogen atoms from the tridentate chelating rings of (dipic)<sup>2-</sup> anions. The geometry of the resulting ZnN<sub>2</sub>O<sub>4</sub> coordination can be described as distorted octahedral. To balance the charges, two protonated triazolium (C<sub>2</sub>H<sub>6</sub>N<sub>5</sub>)<sup>2+</sup> cations are present. In the crystal structure, extensive O—H...O and N—H...O hydrogen bonds involving HdatrzH<sup>+</sup>, the complex anion and uncoordinated water molecules form a three-dimensional network. Analysis of the <sup>1</sup>H-NMR spectrum of the complex shows that the Zn<sup>II</sup> ion is coordinated to the dipicolinate ions. ESI-MS spectrum of the compound indicates the presence of both the carboxylate and the triazolium moieties in the complex. The *in vitro* antibacterial and antifungal activities of compound **I** were evaluated. The zinc complex, (C<sub>2</sub>H<sub>6</sub>N<sub>5</sub>)<sub>2</sub>[Zn(dipic)<sub>2</sub>].4H<sub>2</sub>O showed that compound **I** exhibited good inhibitory effect against the two bacteria, with inhibition zones of 28 and 30mm for *E. Coli* and *S. aureus*, respectively, a moderate effect against *A. niger* but non against *C. albicans*.

### INTRODUCTION

During the past decade, studies involving pyridine-2, 6-dicarboxylic acid (dipicolinic acid) have attracted scientists in the field of coordination, inorganic and bioinorganic chemistries. Dipicolinic acid and its anions (Hdipic<sup>-</sup>, dipic<sup>2-</sup>) are suitable for the building of multidimensional frameworks, due to the presence of two adjacent oxygen atoms of carboxylate groups as substituent on the *N*-heterocyclic pyridine ring (Çolak, *et al.*, 2009). Dipicolinic acid exhibits different coordination modes including monodentate (Gourdon and Launay, 1995), bidentate (Buglyo *et al.*, 2005), tridentate (Okabe and Oya, 2000,) and bridging, in transition metal-dipicolinate complexes depending on whether the divalent anionic (dipic<sup>2-</sup>), monoprotonated anionic (Hdipic<sup>-</sup>) or diprotonated (H<sub>2</sub>dipic) forms are coordinated to metal ions (Alper *et al.*, 2009). Complexes of pyridine-2,6-dicarboxylic acid have potential applications in the fields of aqueous chemistry, catalysis, biochemistry, antitumor activity, bactericidal compositions and development of more effective anti-HIV agents (Moghimi *et al.*, 2007, Park *et al.*, 2007). On the other hand, Schiff bases of triazoles show antibacterial as well as antifungal activity (Rao *et al.*, 2000). Triazole and its derivatives are attractive ligands for the design of novel hybrid materials because they integrate the coordination geometry of both pyrazoles and imidazoles with respect to the arrangement of their three heteroatoms (Ding *et al.*, 2005). Substituted 1, 2, 4-triazoles can be protonated to form triazolium cations (Yesilel *et al.*, 2008; Myskiva and Goreshnik 2010). Since some organic groups

are capable of metal ion complexation and hydrogen bond formation, it is interesting to link them to metal ions and obtain inorganic self-assembled systems. The approach we have employed in the preparation of these systems is the one-pot synthesis involving proton transfer from carboxylic acids to derivatives 1, 2, 4-triazole (Johnson *et al.*, 2015, Atim *et al.*, 2013, Yousuf *et al.*, 2011). In these metal complexes hydrogen bonding plays a major role in stabilizing the crystal structure into a 3 dimensional network. In continuation of our work, here, we report the complexation behaviour of Zn (II) with pyridine -2, 6-dicarboxylic acid and 3,5-diamino-1,2,4-triazole and its antimicrobial activity.

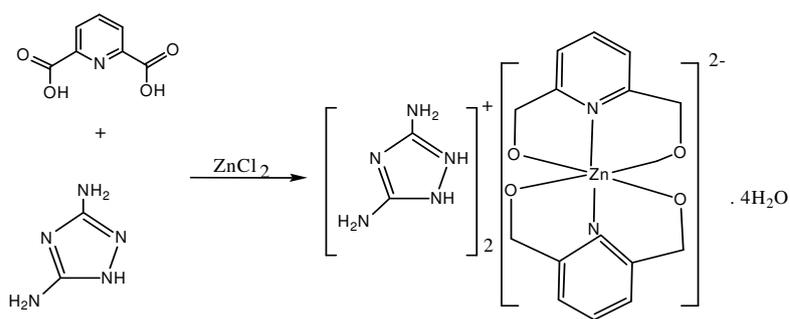
## MATERIALS AND METHOD

All chemicals and reagents were of analytical grade, obtained commercially and used as received. Pyridine-2, 6-dicarboxylic acid (dipicolinic acid, H<sub>5</sub>C<sub>7</sub>NO<sub>4</sub>) and zinc chloride (ZnCl<sub>2</sub>) were from Merck while 3,5-diamino-1,2,4-triazole (C<sub>2</sub>H<sub>5</sub>N<sub>5</sub>) was from Molekula.

Fourier Transform Infrared (FT-IR) spectra (4000-400 cm<sup>-1</sup>) of the solid samples were recorded in KBr pellets using a Shimadzu-8900 spectrometer. Microanalyses were performed on a Perkin-Elmer automated model 2400 Series II CHNS/O analyzer. Electronic absorption spectra in the UV-Visible region were recorded on a Hitachi U-3200 Spectrometer between 190nm-450 nm in DMSO. Melting points were obtained by using a Buchi 535 melting point apparatus. <sup>1</sup>H-NMR spectra were acquired on a Bruker AC-300 MHz spectrometer at ambient temperature in D<sub>2</sub>O. All chemical shifts are given in ppm relative to tetramethylsilane. Mass spectra of the ligands were obtained by Electron Ionization on JEOL-MS Route -600A by direct inlet probe while that of the complex was obtained by the soft technique; Electro spray ionization (ESI-MS) on QSTAR Excel MS/MS system. Room temperature Magnetic susceptibility measurement was made on powdered sample using a Sherwood Scientific magnetic susceptibility balance. Corrections for diamagnetism were estimated from Pascal's constants. Thermogravimetric analysis of the supramolecular complex was carried out using SDT Q600 thermal analyzer at a heating rate of 10°C min<sup>-1</sup> in a nitrogen atmosphere.

### Synthesis of the Title Compound [(C<sub>2</sub>H<sub>6</sub>N<sub>5</sub>)<sub>2</sub><sup>+</sup> (Zn(dipic)<sub>2</sub><sup>2-</sup>].4H<sub>2</sub>O (1)

To a mixture of methanol/water solution (1:10 mL) were added 1 mmol (0.099 g) of 3, 5-diamino-1,2,4-triazole and 1 mmol of dipicolinic acid (0.167 g). The solution was heated to 60°C with stirring. An aqueous solution (1mL) containing ZnCl<sub>2</sub> (0.5 mmol, 0.068g) was added to the stirring solution and allowed to stir further for one hour. The mixture was filtered while hot and the filtrate kept at room temperature. Colourless single crystals suitable for X- ray analysis were separated after one week.



Scheme 1. Synthetic procedure for compound I

### Crystallographic Data Collection/ Structure Determination

Suitable single crystals of the complex were carefully selected under polarized microscope and placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 K. Crystal structure determination by X-ray diffraction was performed on a Bruker SMART APEXII DUO CCD area-detector diffractometer equipped with

fine-focus sealed tube X-ray source [Mo K $\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ]. Reflection intensities were integrated using SAINT software. Absorption correction was done on multi-scan (SADABS; Bruker, 2009). Structure was solved on SHELXTL. For refinement, H atoms on C atoms were positioned geometrically, and held in the riding mode. O- and N- bound hydrogen atoms were located from the difference Fourier map and were refined freely. All non-hydrogen atoms were refined in the anisotropic approximation against F<sup>2</sup> of all reflections.

### Antimicrobial Activities

*In vitro* antifungal and antibacterial activities of the free ligands and the metal complex were tested against two bacteria (*Escherichia coli* and *Staphylococcus aureus*) and two fungi (*Candida albicans* and *Aspergillus niger*) by Agar well diffusion method. Both the antibacterial and antifungal activities were done at the concentration of 200mg/mL of DMSO. The culture media was prepared by the method of Fowale and Oso (2004). The test organisms (*Staphylococcus aureus*, and *Escherichia coli*) were sub-cultured into sterile Nutrient agar plates and labelled accordingly. *Candida albican* and *Aspergillus niger* were planted on sterile Sabouraud Dextrose agar plates and labelled accordingly.

Bacterial strains were incubated at 37°C for 24 hours and fungi at 28°C for 5 days. The medium was accurately weighed, dissolved in sterile water and autoclaved at 121°C for 10 minutes. About 25mL of the molten agar (at 45°C) was poured into petri dishes and left to set on the bench. The surface of the medium was dried at 60°C. 1mL each of diluted test organisms were used to seed the bored plates and the inoculums were spread on the surface of the media using hockey stick. The organisms were allowed to diffuse into the medium. The dissolved ligands and metal complex (200mg/mL) were used to fill the holes on the seeded plates. The plates were incubated at optimum temperature for 24 hours. Standard antibacterial and antifungal drugs were used for comparison under similar conditions. The diameter of inhibition zones were measured and recorded in mm.

## RESULTS AND DISCUSSION

### Physical Properties

Melting point determination indicates that the synthesised complex (**1**) is stable above 240°C (Table 1). The high melting point of the complex could be attributed to strong intermolecular and intramolecular hydrogen bonding interactions resulting in high lattice energy (Moghimi *et al.*, 2003; Khan *et al.*, 2011). The results of solubility test revealed that the complex is soluble in common organic solvents such as methanol and ethanol as well as in Dimethyl sulphoxide (DMSO). The poor solubility of the metal complex in acetonitrile and water (Table 2) could be attributed to low solvation energy of the solvent and strong non-covalent interaction existing in the complex.

Table 1: Physical properties of ligands and the complex

Compound	Physical states	Melting point (°C)	Colour
H <sub>2</sub> dipic	Crystalline	248	off-white
Hdatrz	powdery	205	colourless
Zn(dipic) <sub>2</sub> (C <sub>2</sub> H <sub>6</sub> N <sub>5</sub> ) <sub>2</sub> .4H <sub>2</sub> O( <b>1</b> )	Crystalline	>240	Colourless

Table 2: Solubility of ligands and metal complex in different solvents

Compound	Ethanol	Methanol	Acetonitrile	DMSO	Water
H <sub>2</sub> dipic	S	S	SS	S	S
Hdatrz	S	S	SS	S	S
Zn(dipic) <sub>2</sub> (C <sub>2</sub> H <sub>6</sub> N <sub>5</sub> ) <sub>2</sub> .4H <sub>2</sub> O( <b>6</b> )	S	S	SS	S	INS

SS = sparingly soluble, INS = insoluble, S = soluble

### Spectral Studies

#### (a) Infrared spectra

The compound (**1**) showed characteristic bands in two distinguishable regions. Selected IR bands for ligands and complex are presented in Table 3. In the high energy region, the absorption band at

3566 cm<sup>-1</sup> is assigned to the  $\nu(\text{OH})$  stretching of crystal water. Significant stretching vibrations of asymmetric and symmetric  $\nu(\text{NH}_2)$  absorption bands due to the amine groups of HdatrzH<sup>+</sup> appeared at 3373 and 3240 cm<sup>-1</sup> for  $\nu_{\text{as}}(\text{NH}_2)$  and  $\nu_{\text{s}}(\text{NH}_2)$ , respectively. A weak and broad absorption band at 2927 cm<sup>-1</sup> is assigned to the  $\nu(\text{CH})$  vibrations of the aromatic ring. In the low energy region strong absorption bands at 1699 - 1629 cm<sup>-1</sup> are associated with the asymmetric  $\nu_{\text{as}}(-\text{COO}^-)$  while the peaks at 1427 - 1377 cm<sup>-1</sup> are attributed to symmetric  $\nu_{\text{s}}(-\text{COO}^-)$  stretching modes of dipic<sup>2-</sup>. The value of  $\Delta(\nu_{\text{as}}(-\text{COO}^-) - \nu_{\text{s}}(-\text{COO}^-))$  is 272 cm<sup>-1</sup> for complex **1** indicating that the carboxylate group is in a monodentate binding mode (Nakamoto, 1997, Aghajani *et al.*, 2009), this is consistent with the X-ray crystal structure. The Zn-O and Zn-N stretching vibrations appeared at 586 and 451 cm<sup>-1</sup>, respectively.

Table 3: Selected IR vibration frequencies of the ligands and complex

Dipic	Hdatrz	1	Assignment
3445	3400	3566	$\nu(\text{OH})$
-	3313	3373	$\nu_{\text{as}}(\text{NH}_2)$
-	-	3240	$\nu_{\text{s}}(\text{NH}_2)$
3069	3318	3105	$\nu(\text{NH})$
2918	2923	2927	$\nu(\text{C-H})$
1696	-	-	$\nu(\text{C=O})$
-	1627	1629	$\nu_{\text{as}}(\text{COO})$
1461	1413	1427	$\nu_{\text{s}}(\text{COO}) + \delta(\text{NH})$
1330	-	1377	$\nu_{\text{s}}(\text{COO}) + \nu(\text{C-O})$
780	727	771	$\delta(\text{OCO}) + \gamma(\text{N-H})$
513	-	586	Zn-N
417	466	451	Zn-O

= stretching,  $\gamma$  = out of plane bending,  $\delta$  = ring deformation

### (b) Electronic Transition

The electronic spectrum of compound (**1**) in DMSO (Fig. 1) showed strong absorption bands at 230 and 269 nm. These are attributed to the  $\pi \rightarrow \pi^*$  intraligand charge transfer of the ligands and  $n \rightarrow \pi^*$  metal – ligand charge transfer, respectively. The Zn (II) complex has a d<sup>10</sup> configuration hence, no d-d transition.

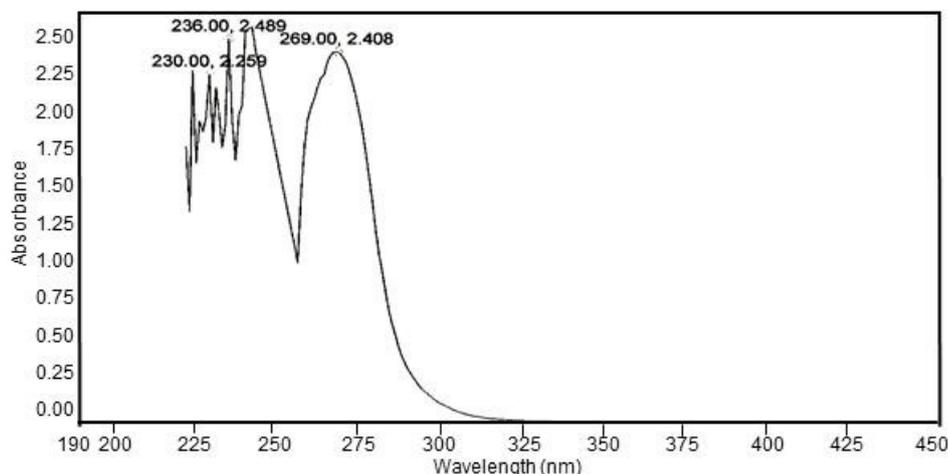


Figure 1. UV-Vis absorption bands of Zn(dipic)<sub>2</sub>(C<sub>2</sub>H<sub>6</sub>N<sub>5</sub>)<sub>2</sub>.4 H<sub>2</sub>O

### (c) <sup>1</sup>H-NMR of ligands and complex

Selected chemical shifts for the ligands and zinc (II) complex are presented in Table 4. The <sup>1</sup>H-NMR spectrum of compound **1** showed a sharp singlet at 8.25 ppm representing the aromatic protons of the pyridine ring. A broad singlet at 6.75 ppm is attributed to (NH<sub>2</sub>) protons of the triazolium ion. The disappearance of the broad singlet (br, 2H) of COOH at 13.28 ppm indicates

that the H<sub>2</sub>dipic ligand is deprotonated and coordinated to the Zn (II) ion. It further suggests that 3,5-diamino-1,2,4-triazole (Hdatrz) is protonated (Cai *et al.*,2011).The downfield shift in resonance of two NH<sub>2</sub> of Hdatrz from (4.76-5.50ppm) to 6.75 ppm indicates the formation of strong hydrogen bonding in the molecule.

Table 4: <sup>1</sup>H-NMR data of ligands and complex (ppm in DMSO-d<sub>6</sub>)

Compounds	H(Hdatrz) (δ,ppm)	H (dipic <sup>2-</sup> ) (δ,ppm)	H(-COOH) (δ,ppm)
H <sub>2</sub> dipic		8.24-8.13 (m,2H)	13.28 (br.s,2H)
Hdatrz	10.69 (s,1H,NH) 5.50-4.76 (br,4H,2NH <sub>2</sub> )		
(Zn(dipic) <sub>2</sub> (C <sub>2</sub> H <sub>6</sub> N <sub>5</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	6.75(s,1H)	8.25(m,1H)	

#### (d) Mass Spectrum of Compound 1

A comparison of the ESI-MS spectrum of compound **1** with those of the free ligands indicates the presence of both the carboxylate and the triazolium moieties in the complex (Fig.3). The [M+H]<sup>+</sup> peak at *m/z* =595 indicates the presence of [(C<sub>2</sub>H<sub>6</sub>N<sub>5</sub>)<sub>2</sub><sup>+</sup>(Zn(dipic)<sub>2</sub><sup>2-</sup>)], another peak at *m/z*= 496 indicates the loss of C<sub>2</sub>H<sub>5</sub>N<sub>5</sub> from [M+H]<sup>+</sup>, the peak at *m/z* = 396 is assigned to the loss of (C<sub>2</sub>H<sub>5</sub>N<sub>5</sub>)<sub>2</sub> from [M+H]<sup>+</sup>, the peak at *m/z* 168 is due to the presence of H<sub>2</sub>dipic and that at *m/z* =100 is assigned to C<sub>2</sub>H<sub>6</sub>N<sub>5</sub><sup>+</sup>. A daughter ion scan reveals that *m/z* 100, *m/z* 168, *m/z* and 396 are products *m/z* 496. There is no peak corresponding to the molecular ion (*m/z* = 667.88).The absence of molecular ion peak indicates that the four molecules of crystal water are not shown in the ESI-MS spectrum.

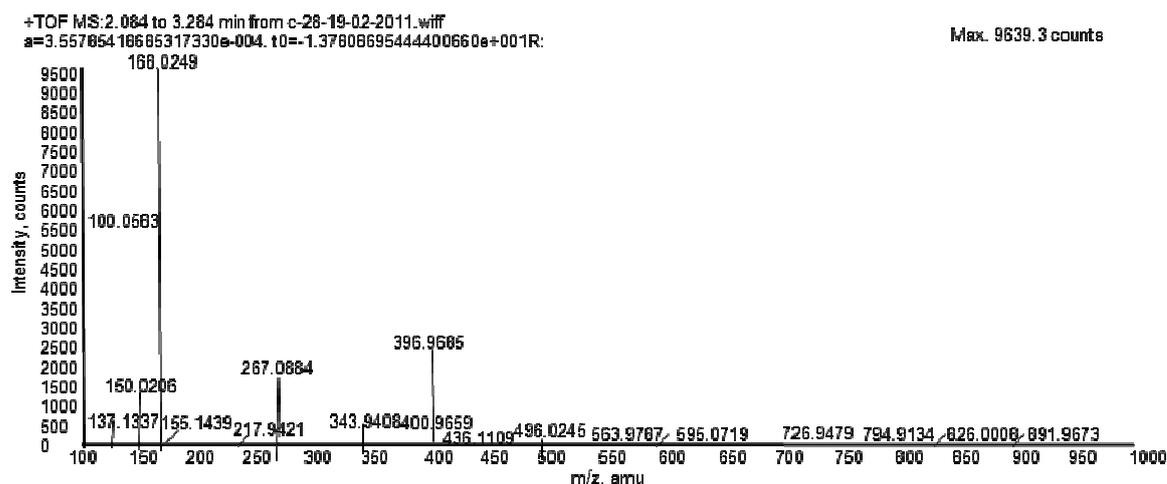


Figure 2. ESI-MS Spectrum of Zn(dipic)<sub>2</sub>(C<sub>2</sub>H<sub>6</sub>N<sub>5</sub>)<sub>2</sub>·4 H<sub>2</sub>O

The molecular structure of the title compound with the atom numbering scheme and the structure indicating hydrogen bonds are shown in Figs. 3 and 4, respectively. Selected bond lengths and angles for compound **1** are given in Table 6. In the unit cell, the molecular structure of the compound contains the [Zn(dipic)<sub>2</sub>]<sup>2-</sup> anion as the Zn(II) complex with (C<sub>2</sub>H<sub>6</sub>N<sub>5</sub>)<sub>2</sub><sup>+</sup> organic moiety, and water molecules in a 1: 2:4 molar ratio. The asymmetric unit of compound **1** contains two cations, one anion, and four water molecules. The coordination environment around the Zn (II) atom is distorted octahedral. The O1, O2, O3 and O4 atoms form the equatorial plane and the N1 and N2 atoms occupy the axial positions.

Due to torsion angles, O(2)#1-Zn(1)-O(2)-C(7) and O(1)#1-Zn(1)-N(1)-C(2) which are -88.70(8)° and 84.76(9)°, respectively, and regarding O(1)-Zn(1)-O(2) and O(1)#1-Zn(1)-O(2)#1 bond angles being 98.08(2)°, two (dipic)<sup>2-</sup> groups are perpendicular to each other. Intermolecular forces between the anionic and cationic units in this complex consist of hydrogen bonding and ion pairing. Four uncoordinated water molecules increase the number of hydrogen bonding in the

crystal lattice (Table 7). Hydrogen bonding therefore, plays an important role in the construction of the three dimensional framework. The bond distances and bond angles are consistent with literature values for related structures (Moghimi *et al.*, 2005, Aghabozorg *et al.*, 2008<sup>a</sup>).

### Crystal Structure Description of Compound 1

Details of crystal data, data collection and refinement are given in Table 5.

Table 5. Crystallographic data and data-collection parameters for the complex (I).

CCDC Number	1483561
Chemical formula	[(C <sub>2</sub> H <sub>6</sub> N <sub>5</sub> ) <sub>2</sub> <sup>+</sup> (Zn(dipic) <sub>2</sub> <sup>2-</sup> )].4H <sub>2</sub> O (1)
Empirical formula	ZnC <sub>18</sub> H <sub>26</sub> N <sub>12</sub> O <sub>12</sub>
Formula weight	667.88
Temperature	100 (2)
Wavelength	0.71073 Å
Crystal system/ space group	Monoclinic, C2/c
Unit cell dimensions (Å, °)	
<i>a</i> , alpha	16.7605(5) , 90
<i>b</i> , beta	10.6070(3), 110.9310(10)
<i>c</i> , gamma	15.2211(5), 90°
Volume (Å <sup>3</sup> )	2527.42(13)
Z	4
Calculated density (mg/m <sup>3</sup> )	1.755
Absorption coefficient (mm <sup>-1</sup> )	1.062
<i>F</i> (000)	1376
Crystal size (mm)	0.36 x 0.27 x 0.23
Theta range for data collection	2.96 - 32.49°
Limiting indices	-25 ≤ <i>h</i> ≤ 25, -12 ≤ <i>k</i> ≤ 16 -19 ≤ <i>l</i> ≤ 22
Reflections collected/unique	13992 / 4511
[ <i>R</i> (int) =	0.0195]
Max and min. Transmission	0.7954 and 0.7037
Refinement	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data / restraints / parameters	4511 / 0 / 235
Goodness of fit on <i>F</i> <sup>2</sup>	1.245
Final R indices [ <i>I</i> ≥ 2 ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0257, <i>wR</i> <sub>2</sub> = 0.0810
R indices (all data)	<i>R</i> <sub>1</sub> = 0.0302, <i>wR</i> <sub>2</sub> = 0.1045
Largest diff. Peak and hole e.Å <sup>-3</sup>	0.720 and -0.534

### Magnetic Susceptibility

The room temperature magnetic susceptibility measurement gave a magnetic moment less than zero (< 0) B.M. which further confirmed its diamagnetic nature.

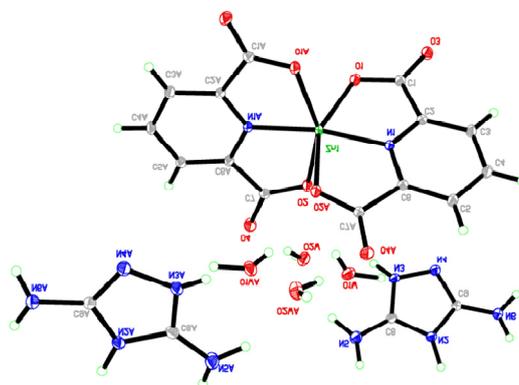


Figure 3. Ortep diagram of (1) with atom labelling Displacement ellipsoids are drawn at 50% probability level and H atoms are shown as small spheres.

Table 6. Selected bond lengths (Å) and angles (°) [(C<sub>2</sub>H<sub>6</sub>N<sub>5</sub>)<sub>2</sub> (Zn(dipic)<sub>2</sub>)].4H<sub>2</sub>O

(Å)			
Zn(1)-N(1)	1.9971(6)	N(1)-C(2)	1.3348(9)
Zn(1)-N(1)#1	1.9971(6)	N(1)-C(6)	1.3357(9)
Zn(1)-O(1)	2.1968(6)	N(1)-C(2)	1.3348(9)
Zn(1)-O(2)	2.1968(9)	N(5)-H(1N5)	0.857(16)
O(1)-C(1)	1.2735(9)	C(1)-C(2)	1.5149(10)
O(2)-C(7)	1.2740(9)	C(2)-C(3)	1.3881(10)
O(4)-C(7)	1.2406(9)	O(1W)-H(2W1)	1.02(3)
(°)			
N(1)-Zn(1)-N(1)#1	170.25(4)	N(1)-Zn(1)-O(1)-C(1)	4.95(8)
N(1)-Zn(1)-O(1)#1	110.03(2)	N(1)#1-Zn(1)-O(1)-C(1)	178.03(8)
N(1)#1-Zn(1)-O(1)#1	77.12(2)	O(2)#1-Zn(1)-O(1)-C(1)	3.74(13)
N(1)-Zn(1)-O(2)	98.08(2)	N(1)#1-Zn(1)-O(2)-C(7)	8.34(8)
N(1)#1-Zn(1)-O(2)	76.98(2)	O(1)#1-Zn(1)-O(2)-C(7)	9.55(13)
O(1)#1-Zn(1)-O(2)	154.12(3)	O(1)-Zn(1)-O(2)-C(7)	117.17(8)

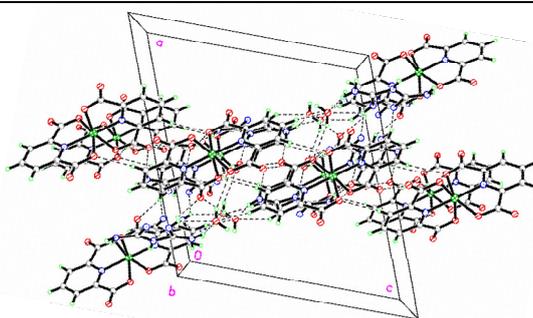


Figure 4. The crystal packing of the compound, showing a three-dimensional molecular network.

Table 7. Hydrogen bond of Compound 1

D-H...A	d(D-H) (Å)	d(H...A) (Å)	d(D...A) (Å)	Angle (D-H...A) (°)
N2—H1N2...O1W <sup>i</sup>	0.86 (2)	1.91 (2)	2.7360 (14)	160.7 (17)
N3—H1N3...O2W	0.88 (2)	2.26 (2)	2.9218 (10)	131.9 (14)
N3—H1N3...N4 <sup>ii</sup>	0.81 (2)	2.29 (2)	2.8984 (13)	132 (2)
N5—H1N5...O2W	0.93 (2)	2.05 (2)	2.9190 (14)	154 (2)
N5—H2N5...O3 <sup>iii</sup>	0.93 (2)	1.94 (2)	2.8513 (14)	166 (2)
N6—H1N6...O1W <sup>iv</sup>	0.83 (2)	2.38 (2)	3.1970 (13)	170.2 (18)
N6—H2N6...O1 <sup>v</sup>	0.836 (19)	2.130 (19)	2.9495 (12)	166.5 (19)
O1W—H1W1...O2	0.66 (3)	2.15 (3)	2.7875 (11)	164 (3)
O1W—H2W1...O3 <sup>vi</sup>	1.02 (3)	1.82 (3)	2.7887 (12)	158 (3)
O2W—H1W2...O1 <sup>vii</sup>	0.77 (3)	2.44 (3)	3.1718 (13)	162 (3)
O2W—H2W2...O4	0.86 (3)	1.93 (2)	2.7956 (13)	174 (2)
C3—H3A...O2 <sup>vi</sup>	0.95	2.53	3.2586 (13)	134
C4—H4A...O2W <sup>viii</sup>	0.95	2.56	3.4179 (13)	151
C5—H5A...O4 <sup>viii</sup>	0.95	2.30	3.1149 (14)	144

Symmetry codes:

- |       |                          |        |                          |
|-------|--------------------------|--------|--------------------------|
| (i)   | $x+1/2, y+1/2, z;$       | (ii)   | $-x+1/2, -y+1/2, -z;$    |
| (iii) | $x, y-1, z;$             | (iv)   | $-x+1/2, y+1/2, -z-1/2;$ |
| (v)   | $-x+1/2, y+3/2, -z-1/2;$ | (vi)   | $x+1/2, y+3/2, z;$       |
| (vii) | $x, -y-1, z-1/2;$        | (viii) | $x-1/2, -y+1/2, z-3/2.$  |

### Thermal Analysis of Compound 1

Thermal decomposition of complex (1) proceeds in three stages as shown in Fig. 5. The first decomposition process takes place in the temperature range of 135-198.15°C (DSC<sub>max</sub> =180°C). This is related to the removal of two water molecules (found 5.630%, calcd 5.390%). The second stage is related to the loss of two water molecules, one protonated triazole (HdatrzH)<sup>+</sup> and one

dipic<sup>2-</sup> molecule in the range 198.58 -358.58°C (found 46.11%, calcd 45.06%). The third decomposition stage in the range 358.58-1195.59°C corresponds to the loss of the remaining (HdatrzH)<sup>+</sup>, dipic<sup>2-</sup> with the release of CO ( found 43.07%, calcd 43.87%).

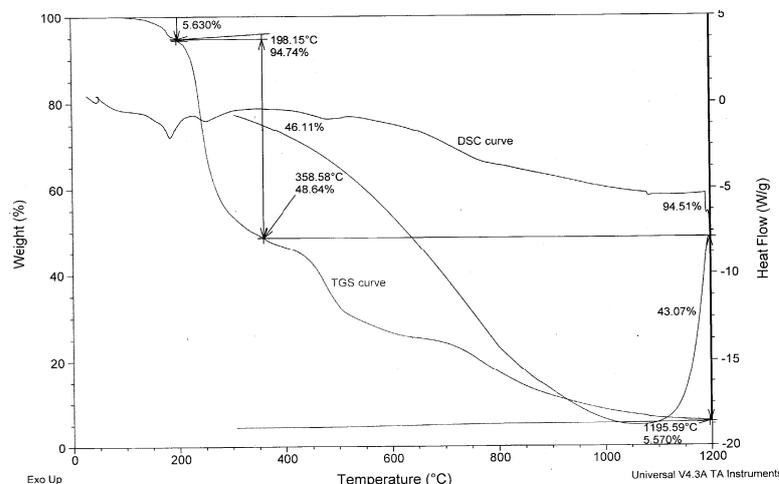


Figure 5 Thermal analysis curves for (1) [Zn(dipic)<sub>2</sub>(C<sub>2</sub>H<sub>6</sub>N<sub>5</sub>)<sub>2</sub>].4 H<sub>2</sub>O

The total weight loss (found 94.81%, calcd 94.32%) represents the weight of four molecules of water, two triazolium ions and two dipicolinate ions.

### Antimicrobial Activities

The antimicrobial activity of metal complexes generally depends on factors such as the chelation ability of the ligand, the nature of nitrogen donor ligands, the total charge of the complex, the nuclearity of the metal centre in the complex and the concentration of metal complex. Although metal complexes containing dipicolinate moiety have been reported to show antimicrobial activity (Cai *et al.*, 2011, Çolaka *et al.*, 2010, Çolaka *et al.*, 2009, Khan *et al.*, 2009), the ligands and metal complex evaluated in this study showed no activity when 200µg/mL and 1mg/mL were used respectively, for antifungal and antibacterial analyses. However, at a much higher concentration of 200mg/mL, both the ligands and the metal complex evaluated showed significant activities against two bacteria (*E. coli* and *S. aureus*) and two fungi (*C. albicans* and *A. niger*). The results of the antimicrobial studies are presented in Table 8. In order to clarify any participating role of the solvent (DMSO) in the antimicrobial test, studies were also carried out for the solvent without the ligands or metal complex and the results revealed that DMSO has no inhibitory effect against the tested microorganisms.

Table 8. Antimicrobial activities of ligands and metal complex

Compounds	Diameter of growth inhibition in (mm)				
	Conc.(mg/ml)	<i>E.coli</i>	<i>S.aureu</i>	<i>C.albicans</i>	<i>A.niger</i>
DMSO	200	-	-	-	-
H <sub>2</sub> dipic	200	3	-	-	30
Hdatrz	200	35	30	-	-
[Zn(dipic) <sub>2</sub> (C <sub>2</sub> H <sub>6</sub> N <sub>5</sub> ) <sub>2</sub> ].4 H <sub>2</sub> O (1)	200	28	30	-	20

In Table 8, the ligand, 3,5-diamino-1,2,4-triazole (Hdatrz) showed good inhibitory effect against the two bacteria with inhibition zones of 35 and 30 mm for *E.coli* and *S.aureus*, respectively, but no activity against the two fungi. Pyridine 1-2,6-dicarboxylic acid showed good inhibitory effect against *A. niger* but weak or no antimicrobial activity against *E.coli*, *S. aureus* and *C. albicans*. Similar result was reported by Çolaka *et al.* (2009<sup>b</sup>). The zinc complex, (C<sub>2</sub>H<sub>6</sub>N<sub>5</sub>)<sub>2</sub>[Zn(dipic)<sub>2</sub>].4H<sub>2</sub>O (1) exhibited good inhibitory effect against the two bacteria, with inhibition zones of 28 and 30mm for *E. Coli* and *S.aureus*, respectively, a moderate effect against *A.niger* but non against *C. albicans*. The lack of activities in these ligands and metal complex at

low concentration may be attributed to the inability of the ligands and complex to form bonds with the cell constituents of the microorganism (John *et al.*, 2004). It could also be due to low antimicrobial activity of the ligands or the metal ion (Cai *et al.*, 2011). The work of Çolaka *et al.* (2009<sup>b</sup>) revealed that the activity of complexes increases as the concentration increases. This is consistent with the results of this investigation.

### CONCLUSION

A new compound ( $[(\text{HdatzH}^+)_2 (\text{Zn}(\text{dipic})_2^{2-})].4\text{H}_2\text{O}$  ( HdatzH = 3,5-diamino-1,2,4-triazolium ion, dipic = dipicolinate ion) has been prepared and characterised by elemental analyses, spectral (IR, UV-Vis, ESI-MS and <sup>1</sup>H-NMR) analyses, thermal analysis, magnetic susceptibility measurement and single-crystal X-ray diffraction technique. Compound **1** crystallised in the monoclinic crystal system space group C2/c. The common bond distances and angles of (**1**) are in agreement with the corresponding values in the literature. The Zn (II) complex has a distorted octahedral geometry with two tridentate dipicolinate ions. Strong hydrogen bonds between uncoordinated water, (HdatzH<sup>+</sup>)<sub>2</sub> and carboxylate play important roles in the construction of the supramolecular network. The strong antibacterial activity is attributed to the ability of the complex to permeate the lipid membrane of the microorganisms.

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