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Synthesis, Spectroscopic, Thermal, Crystal Characterization and Biological Activity of $\{[Ni(phen)_3][Ni(dipic)_2]\}_2.17H_2O$ (H_2dipic:Pyridine-2,6-dicarboxylic Acid, Phen: 1,10-Phenanthroline)

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The new $\{[Ni(phen)_3][Ni(dipic)_2]\}_2.17H_2O$ (**1**) (phen = 1,10-phenanthroline, dipic = dipicolinate)) has been prepared and characterized by elemental analysis, IR, UV-Vis, magnetic measurement and single crystal X-ray diffraction. The complex consists of two tris(1,10-phenanthroline)nickel(II) cations, two bis(dipicolinato)nickelate(II) anions and seventeen uncoordinated water molecules. The Ni(II) complex crystallizes in the triclinic space group *P*-1. The complex consisting of cation has distorted octahedral coordination by three bidentate phen ligands. In the complex anion, each dipic ligand simultaneously exhibits tridentate coordination modes through N atom of pyridine ring and oxygen atoms of the carboxylate groups. The crystal packing of **1** is a composite of intermolecular hydrogen bonding, π-π and C-H···π interactions. The complex has also been investigated in terms of biological activity and it showed high activity against *S. aureus* from Gram positive bacteria and *C. albicans* from yeast tested.

Keywords: Dipicolinato complex, 1,10-Phenanthroline complex, Nickel(II) complex, Antimicrobial activity

INTRODUCTION

Pyridine-2,6-dicarboxylic acid (Dipicolinic acid) was first discovered in a biological system in 1936 and is now known to be a major component of bacterial spores [1]. H_2dipic is used in a variety of processes as an enzyme inhibitor, plant preservative, food sanitizer [2]. Recent investigations of the H_2dipic exhibit that this acid prevents the oxidation of low density lipoprotein [3]. 2,6-Pyridinedicarboxylic acid (H_2dipic) and its anions ($Hdipic^-$, $dipic^{2-}$) have proved to be well suited for the construction of multidimensional frameworks, due to the presence of two adjacent O atoms of carboxylate groups as substituents on the *N*-heterocyclic pyridine ring (N donor atoms) [2]. The dipic ligand exhibits eleven different coordination modes so far crystallographically characterized [4]. Among the diversity of pyridine-2,6-dicarboxylic acid complexes known potential applications in fields of aqueous chemistry, catalysis, biochemistry, water-soluble drugs, antitumor activity, magnetic materials, bleaching, bactericidal compositions, development of more effective anti-HIV agents and design of insulin-mimetic agents [2,4-7]. Although the literature lists many reports on the coordinating presences of dipic moiety in transition metal complexes, from the X-ray crystal structure point of view only a limited number of structures including both cations and anions' nickel complexes with dipic have been obtained until

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now, $[Ni(cyclam)(H_2O)_2][Ni(dipic)_2].2.5H_2O$ [4] (cyclam = 1,4,8,11-tetraazacyclotetradecane), $[Ni(H_2O)_6][Ni(dipic)_2].3H_2O$ [8], $[Ni(H_2O)_5Ni(dipic)_2].2H_2O$ [9] and $[Ni(data)_2(H_2O)_2][Ni(dipic)_2].5H_2O$ [10] (data = 2,2′-diamino-4,4′-bi-1, 3-thiazole). In previous studies, a few of nickel-dipic complexes were synthesized with aqua, bta (bta = benzotriazole), and phen ligands; $[Ni(dipic)(H_2O)_2]$ [11], $[Ni(dipic)(bta)_3]$ [12], $[Ni(H_2O)_5Ni(dipic)_2].2H_2O$ [9], $[Ni(dipic)(phen)(H_2O)].H_2O$ [13].

The increasing prevalence of multidrug resistant strains of bacteria and the recent appearance of strains with reduced susceptibility to antibiotics raises the specter of untreatable bacterial infections and adds urgency to the search for new infection-fighting strategies [14]. Discovery of novel, safe and effective antifungal drugs with novel modes of action is needed since extensive use of antifungal drugs has caused the emergence of resistant pathogens such as *Candida*. In addition, antifungal drugs can cause toxic or adverse drug reactions. For example, the polyene antifungal, amphotericin B, has a broad range of activity but is limited in its use due to numerous adverse effects [15].

In this study, we describe the preparation, spectral, thermal, structural characterization and antimicrobial activity of dipic complex of nickel(II) with 1,10-phenanthroline, $\{[Ni(phen)_3][Ni(dipic)_2]\}_2.17H_2O$ (**1**).

EXPERIMENTAL

Materials and Measurements

All chemicals used were analytical reagent. Elemental analysis for C, H and N were carried out by Elementar Elemental Analyzer. Magnetic susceptibility measurements were performed at room temperature using a Sherwood Scientific MK1 model Gouy magnetic balance. UV-Vis spectrum was obtained in the methanol solutions (10^{-3} M) of the complex with a Shimadzu Pharmaspec UV-1700 spectrometer in the range of 1000-190 nm. FT-IR spectra were recorded in the 4000-400 cm^{-1} region with a Bruker Optics, Vertex 70 FT-IR spectrometer using KBr pellets. Diamond TG/DTA thermal analyzer was used to record simultaneous TG, DTG and DTA curves in the static air atmosphere at a heating rate of 10 °C min^{-1} in the temperature range 20-600 °C using platinum crucibles.

Crystallographic Analysis

For the crystal structure determination, the single-crystal of the compound $\{[Ni(phen)_3][Ni(dipic)_2]\}_2.17H_2O$ 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 Mo-Kα radiation (λ = 0.71073 Å) and oscillation scans technique with $\Delta\omega = 5°$ for one image were used for data collection. Image for **1** was taken successfully by varying ω with three sets of different χ and φ values. 108 images for six different runs covering about 99.7% of the Ewald spheres were taken for each compound. The lattice parameters were determined by the least-squares method 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 were performed using Crystal Clear software [18]. The structures were solved by direct methods (SHELXS-97) [16] and non-H atoms were refined by full-matrix least-squares method with anisotropic temperature factors (SHELXL-97) [16]. Molecular drawings were obtained using ORTEP-III [17]. The H atoms of water molecules could not be located from a Fourier map. It is possible to see that water molecules are involved in hydrogen bonds on the basis of interatomic distances.

In vitro Antimicrobial Activity of the Compound

Antimicrobial activity of test compound was carried out according to modified agar well diffusion assay [19]. The following test conditions were applied; compound was dissolved in Dimethylsulfoxide (DMSO, Merck). Fifteen milliliters of the specified molten agar (45 °C) were poured into sterile Petri dishes (Ø 90 mm). The cell suspensions containing 10^8 CFU/ml cells for bacteria, 10^7 CFU/ml cells for yeasts, and 10^5 spore/ml of fungi were prepared and evenly spread onto the surface of the agar plates of Nutrient Agar (Fluka) for bacteria and yeast and Potato Dextrose Agar (Merck) medium for fungi using sterile swab sticks. The plates were dried aseptically at 35 °C for about 40 min in an incubator. At the same time, 10 mm wells were bored using a sterile cork borer and impregnated with known concentrations determined previously by MIC tests (500-0.2 µg ml^{-1} for each well). 2 µg ml^{-1} for each well $[Ni(H_2O)_6][Ni(dipic)_2]$, 1,10-phenanthroline and $\{[Ni(phen)_3][Ni(dipic)_2]\}_2.17H_2O$, (100 µl) were placed into the wells. The plates were preincubated

for 2 h at room temperature, then the plates were incubated at 37 °C for 24 h for bacterial strains, 48 h for yeasts and 72 h for fungi at room temperature. Tetracycline (30 µg ml^{-1}) for bacteria and Amphotericin B (10 µg ml^{-1}) for yeasts and fungi were used as positive controls. DMSO was used as negative control. Antimicrobial activity was evaluated as zones of inhibition of growth around wells.

Microbial Strains

A total of 7 microbial species including 4 bacteria, 2 molds and 1 yeast were used as test organisms in this study. *Staphylococcus aureus* ATCC 25923, *Escherichia coli* ATCC 25922, *Salmonella typhimurium* ATCC 14028, *Aspergillus niger* ATCC 10949 were obtained from American Type Culture Collection; *Bacillus subtilis* NRRL -B-209, *Candida albicans* NRRL Y-12983 from USDA, Agriculture Research Service, Peria, USA; *Fusarium solani* (wild type), from Eskişehir Osmangazi University Faculty of Science and Arts, Eskişehir-Turkey. Bacterial and fungal cultures of test organisms were maintained on Nutrient Agar and Potato Dextrose Agar slants at 4 °C, respectively, and were subcultured in petri dishes prior to use.

Synthesis of $\{[Ni(phen)_3][Ni(dipic)_2]\}_2 \cdot 17H_2O$ (1)

The synthesis of $[Ni(H_2O)_6][Ni(dipic)_2]$ was achieved employing literature methods [8]. A solution of $[Ni(H_2O)_6][Ni(dipic)_2]$ (1 mmol, 0.65 g) in ethanole-water (1:1; 20 ml) was added drop wise by stirring at room temperature into a solution of 1,10-phenanthroline (3 mmol, 0.60 g) in ethanol (40 ml). The mixture was stirred for 30 min at room temperature. The crystals formed were filtered and washed with 10 ml of cold ethanol and dried on air. Analytical data: $C_{100}H_{94}N_{16}O_{33}Ni_4$ (2282.69 g mol^{-1}); C 53.31 (calcd. 52.62); H 3.89 (4.15); N 9.71 (9.82)%.

RESULTS AND DISCUSSION

Infrared Spectrum

The most significant frequencies in the IR spectrum of **1** are given in Table 1. The strong and broad absorption bands at 3417 cm^{-1} is attributed to the ν(OH) vibrations of crystal water molecules. The relatively weak band at 3063 cm^{-1} is due to the ν(CH) vibrations. The carboxylate groups exhibited strong bonds in the region 1682-1582 cm^{-1}. These strong bands were shifted and broadened with respect to free dipicolinic acid. The presence of carboxylate COO^- is reflected by IR spectrum in absorption bands of the asymmetric (ν_{as}) and symmetric (ν_s) stretch vibrations at 1625 and 1459 cm^{-1}, respectively, and moreover the differences between the asymmetric and symmetric stretches of the carboxylate groups of 1, Δ = 166 cm^{-1} suggest a monodentate binding of the carboxylate group to the metal ion [20]. The absorption band at 1582 cm^{-1} is due to ν(C=C)+ν(C=N) vibration of dipic and phen ligands. Similar spectral results were obtained for the compounds $[Ni(cyclam)(H_2O)_2][Ni(dipic)_2].2.5H_2O$ [4] and $[Ni(H_2dipic)(H_2O)_3][Ce(dipic)_3].3H_2O$ [21]. The weak bands in the 644 and 444 cm^{-1} region are due to Ni-O and Ni-N stretching vibrations, respectively.

Thermal Analysis

The TG-DTG and DTA curves of the complexes are shown in Fig. 1. The endothermic peak of **1** (DTG_{max} = 103 ºC) between 28 and 125 ºC corresponds to the loss of the 17 moles crystal water molecules (found 12.96, calcd. 13.40%).

Table 1. IR Spectral Data of 1[a] (cm^{-1})

Assignment	**1**	$[Ni(H_2O)_6][Ni(dipic)_2]$ [8]
νOH_{water}	3417 m	3481 s, 3220 s, b
νCH	3063 w	-
$\delta H_2O+\nu_{as}(COO)$	1625 vs	1652 m, 1612 s, 1577 s, b
ν(C=C)+ν(C=N)	1582 s	-
$\nu_s(COO)$	1459 m	1433 m, 1385 s
M-O, M-N	644 w, 444 w	-

[a]Abbreviations: w = weak; m = medium; s = strong; vs = very strong, b = broad.

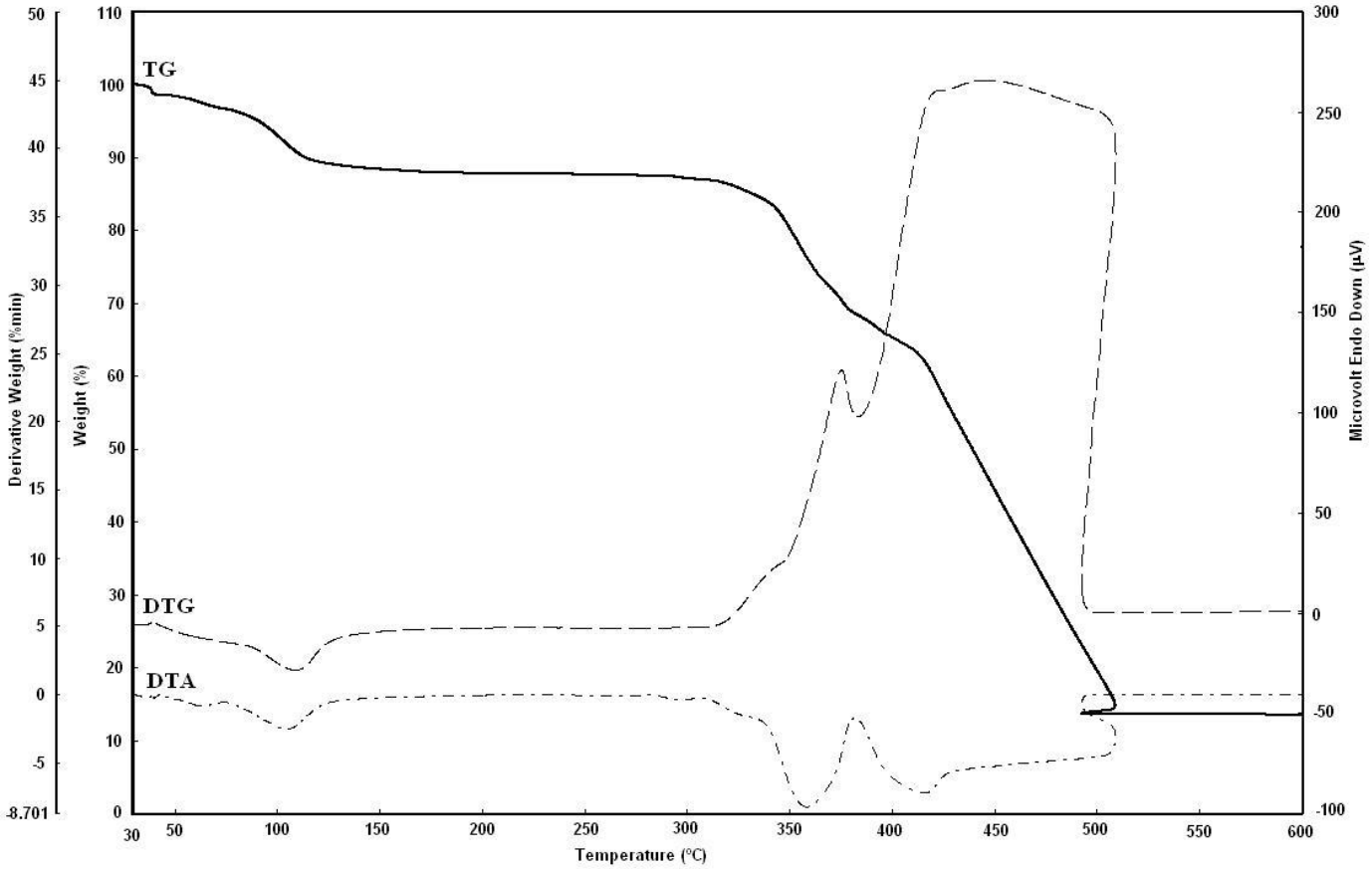

Fig. 1. TG, DTG and DTA curves of **1**.

The anhydrous complex is thermally stable up to about 300 ºC. The second endothermic stage in the temperature range of 300-383 ºC (DTG_{max} = 374 ºC) is related to the release of phen ligands and decarboxylation of dipic ligands. In the last stage between 383 and 516 ºC, the strong exothermic mass loss process occurs in a single step. During this stage, the remaining organic part is abruptly burnt (DTG_{max} = 418 ºC). The final decomposition product, NiO, was identified by IR spectroscopy (found 13.60%, calcd. 13.08%).

UV-Vis Spectrum and Magnetic Susceptibility

The electronic spectrum of **1** in H_2O exhibit three absorption bands at 353, 761 and 914 nm and the corresponding ε values are 50, 5 and 4 M^{-1} cm^{-1}, respectively. These values were assigned to the following d-d transitions; $^3A_{2g} \rightarrow {}^3T_{1g}(P)$, $^3A_{2g} \rightarrow {}^3T_{1g}$ and $^3A_{2g} \rightarrow {}^3T_{2g}$, respectively.

The Δ_o values for **1** was calculated as 10941 cm^{-1} since $\Delta_o = \nu_1$ for d^8 complexes. The **1** exhibits magnetic moment value of 5.23 BM. However, this magnetic moment value is lower than the spin only value for two unpaired electrons in four Ni(II) complex, indicating to antiferromagnetic effect.

Crystal Structure of 1

Details of crystal structure are given in Table 2. The molecular structure of $\{[Ni(phen)_3][Ni(dipic)_2]\}_2.17H_2O$ is shown in Fig. 2. The selected geometric parameters of **1** are presented in Table 3. The asymmetric unit of **1** is composed of two crystallographic independent $[Ni(phen)_3][Ni(dipic)_2]$ and seventeen lattice water molecules (Fig. 2). The absolute configuration of the Ni(II) center is Λ and Δ, which is the highest energy conformation [22]. The Ni(II) ion in the $[Ni(phen)_3]^{2+}$ cation is six-coordinated by the six N atoms of

Table 2. Crystal Data and Structure Refinement Parameters for the Complexes

	1
Empirical formula	$C_{100}H_{60}N_{16}O_{33}Ni_4$
Formula weight	2248.48
Temperature (K)	293 (2)
Wavelength (Å)	0.71073 Mo-Kα
Crystal system	Triclinic
Space group	P-1
a (Å)	14.591 (5)
b (Å)	15.997 (5)
c (Å)	23.494 (6)
α, β, δ (º)	89.820 (5); 79.002 (5); 66.755 (5)
V (Å^3)	4930 (3)
Z	2
Absorption coefficient (mm^{-1})	0.85
D_{calc} (Mg m^{-3})	1.515
Theta range for data collection (˚)	2.10-30.55
Measured reflections	101642
Independent reflections	20381
Absorption correction	Rigaku R-AXIS RAPID-S/*w*
Refinement method	Full-matrix least-squares on F^2
Final R indices [I > 2σ(I)]	R_{int} = 0.126
Final R indices (all data)	R_1 = 0.087; wR_2 = 0.258
Goodness-of-fit on F^2	1.01
$\Delta\rho_{max}$ (eÅ^{-3})	0.64
$\Delta\rho_{min}$ (eÅ^{-3})	-0.54

three phen ligands, forming a distorted octahedral geometry. Nitrogen atoms of phen are bonded to Ni(II) to form a five-member chelate ring. The Ni-N distances lie in the range of 1.959(5)-1.970(5) and 1.957(7)-2.017(10) Å in Ni(1) and Ni(3), respectively. These bond distances are shorter than the corresponding values found in $[Zn(H_2O)_6][Ni(dipic)_2]\cdot 3H_2O$ [2.115(2) Å], [8] and $[Ni(H_2O)_6][Ni(dipic)_2].5H_2O$ [2.147(2) Å] [8]. The Ni-O bond distance of average 2.239 Å is longer than the corresponding bond in $[Ni(cyclam)(H_2O)_2][Ni(dipic)_2].2.5H_2O$ [2.132(2) and 2.146(2) Å] [4]. Comparison of values of the Ni-O, Ni-N distances, of the O-Ni-N angle for similar Ni(II)-dipicolinate complexes are given in Table 4.

The C-N and C-C distances in the phen ligands are normal. All the N-Ni-N bond angles deviate significantly from 90 or 180º, which is presumably a result of the steric constraints arising from the shape of the ligands [N5-Ni2-N6 = 79.7(2)

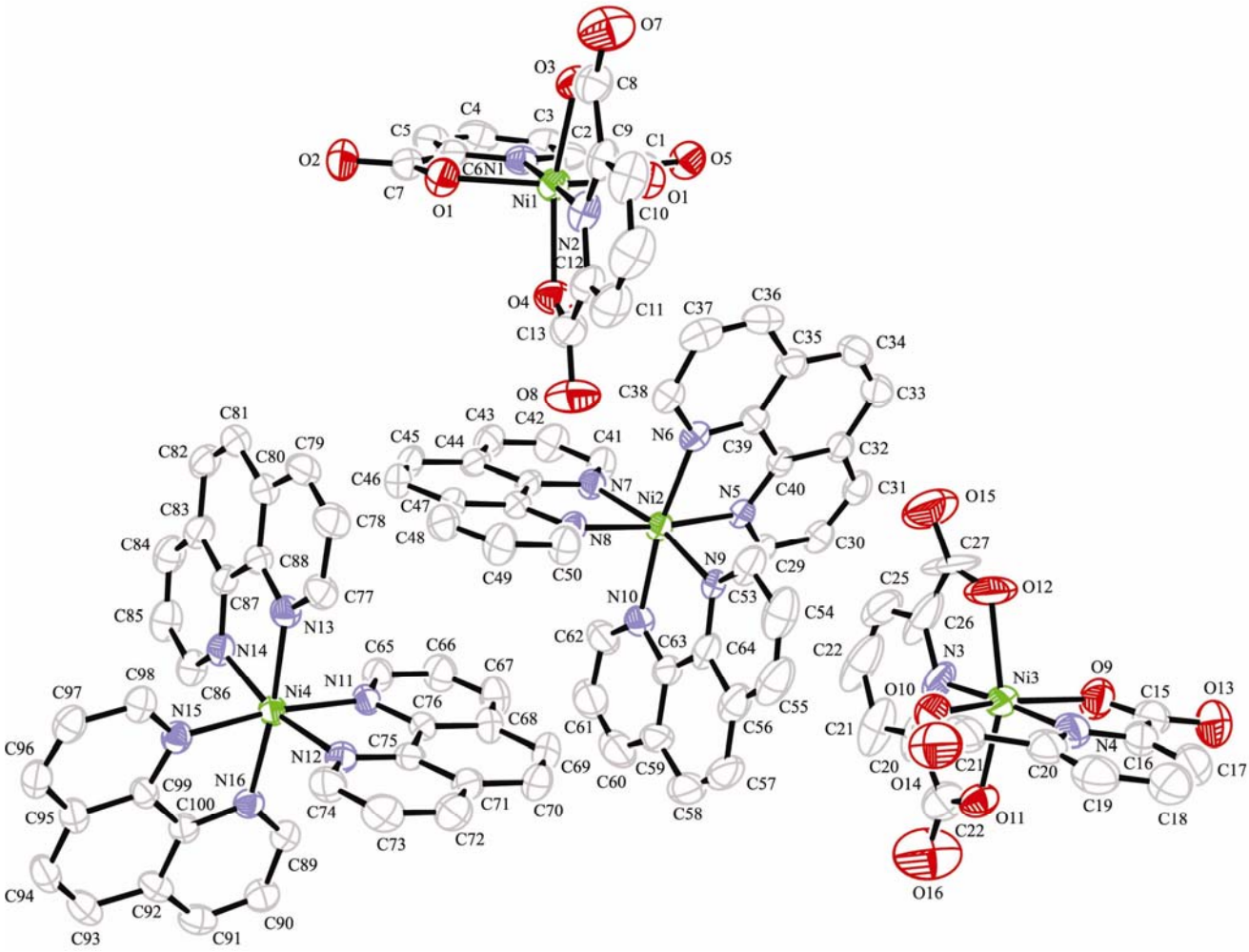

Fig. 2. The molecular structure of **1**.

and N7-Ni2-N9 = 168.2(2)º]. In the anionic $[Ni(dipic)_2]^{2-}$ complex, the Ni(II) ion lies in a distorted octahedral environment with four oxygen atoms of carboxylate groups and two pyridine nitrogen atoms of dipic anions. The intermolecular interactions between the cationic and anionic units in this complex consist of hydrogen bonding, C-H···π and π···π stacking. Seventeen crystal water molecules increase the number of hydrogen bonds in the structure.

The dipic ligands in **1** is essentially planar, with a slight deviation from planarity arising from the non-zero torsion angle between the carboxylate group and the ring [N(1)-C(1)-C(2)-O(5) = 176.9(6)º, N(1)-C(1)-C(2)-O(1) = -2.8(9)º and N(2)-C(13)-C(14)-O(4) = -0.6(11)º and N(2)-C(13)-C(14)-O(8) = -177.8(8) º]. This torsion angle indicates that distortion of the dipic ligand is caused by coordination to the Ni(II) ion while this torsion angle of Ni(3) anion is wider than the value for Ni(4) complex anion. It was not possible to locate the H atoms of all water molecules from difference Fourier.

Antimicrobial Activity

In the present study, *in vitro* potential antimicrobial activity of $[Ni(H_2O)_6][Ni(dipic)_2]$, 1,10-phenanthroline and $\{[Ni(phen)_3][Ni(dipic)_2]\}_2.17H_2O$ were tested according to agar well diffusion method. Table 5 shows the effects of 12 different concentrations against the growth of gram positive, gram negative bacterial strains, yeast strain and fungal strains.

Table 3. Selected Geometric Parameters (Å, ˚) for **1**

N1-Ni1		1.970 (5)		N4-Ni3		1.957 (7)	
N2-Ni1		1.959 (5)		N3-Ni3		2.017 (10)	
O4-Ni1		2.136 (5)		O9-Ni3		2.106 (5)	
O2-Ni1		2.104 (5)		O10-Ni3		2.110 (6)	
O3-Ni1		2.130 (4)		O11-Ni3		2.087 (5)	
O1-Ni1		2.114 (4)		O12-Ni3		2.126 (8)	
N7-Ni2		2.077 (5)		N16-Ni4		2.098 (5)	
N5-Ni2		2.082 (5)		N14-Ni4		2.089 (5)	
N8-Ni2		2.097 (5)		N15-Ni4		2.080 (5)	
N6-Ni2		2.072 (5)		N13-Ni4		2.106 (5)	
N10-Ni2		2.091 (6)		N11-Ni4		2.079 (5)	
				N12-Ni4		2.073 (5)	
N2-Ni1-N1	178.1(2)	N6-Ni2-N7	94.8(2)	N4-Ni3-N3	173.0(3)	N12-Ni4-N11	79.8(2)
N2-Ni1-O2	100.1(2)	N6-Ni2-N9	94.2(2)	N4-Ni3-O11	97.4(2)	N12-Ni4-N15	98.0(2)
N1-Ni1-O2	78.1(2)	N7-Ni2-N9	168.2(2)	N3-Ni3-O11	77.6(3)	N11-Ni4-N15	172.0(2)
N2-Ni1-O1	103.5(2)	N6-Ni2-N5	79.7(2)	N4-Ni3-O9	78.2(3)	N12-Ni4-N14	168.1(2)
N1-Ni1-O1	78.2(2)	N7-Ni2-N5	96.7(2)	N3-Ni3-O9	97.0(3)	N11-Ni4-N14	92.5(2)
O2-Ni1-O1	156.4(2)	N9-Ni2-N5	92.4(2)	O11-Ni3-O9	91.6(2)	N15-Ni4-N14	90.8(2)
N2-Ni1-O3	77.8(2)	N6-Ni2-N10	170.9(2)	N4-Ni3-O10	79.1(3)	N12-Ni4-N16	94.9(2)
N1-Ni1-O3	102.9(2)	N7-Ni2-N10	92.5(2)	N3-Ni3-O10	105.8(3)	N11-Ni4-N16	93.0(2)
O2-Ni1-O3	94.5(2)	N9-Ni2-N10	79.2(2)	O11-Ni3-O10	92.9(2)	N15-Ni4-N16	79.5(2)
O1-Ni1-O3	90.61(2)	N5-Ni2-N10	94.2(2)	O9-Ni3-O10	157.2(3)	N14-Ni4-N16	94.5(2)
N2-Ni1-O4	78.4 (2)	N6-Ni2-N8	94.6(2)	N4-Ni3-O12	109.4(5)	N12-Ni4-N13	91.2(2)
N1-Ni1-O4	101.0(2)	N7-Ni2-N8	79.7(2)	N3-Ni3-O12	75.8(5)	N11-Ni4-N13	90.8(2)
O2-Ni1-O4	94.1(2)	N9-Ni2-N8	92.0(2)	O11-Ni3-O12	153.3(5)	N15-Ni4-N13	97.0(2)
O1-Ni1-O4	90.5(2)	N5-Ni2-N8	173.0(2)	O9-Ni3-O12	93.8(3)	N14-Ni4-N13	79.7(2)
O3-Ni1-O4	155.8(2)			O10-Ni3-O12	92.2(3)	N16-Ni4-N13	173.3(2)

Table 4. Comparison of the Bond Distances (Å) and Angles (º) of the Ni-dipicolinic Acid Complexes

Complexes	Ni3-O1	Ni3-O	Ni3-N	O1-Ni3-N	O1-Ni3-O4
$[Ni(cyclam)(H_2O)_2][Ni(dipic)_2].2.5H_2O$ [4]	2.132(2)	2.146(2)	1.931(3)	78.35(5), 78.29(5)	156.70(10)
$[Zn(H_2O)_6][Ni(dipic)_2].3H_2O$ [8]	2.115(2)	2.115(2)	1.960(3)	78.09(6)	156.17(8)
$[Ni(H_2O)_6][Ni(dipic)_2].3H_2O$ [8]	2.147(2)	2.126(2)	1.964(3)	77.53(10)	155.68(9)
$[Ni(H_2O)_5Ni(dipic)_2].2H_2O$ [9]	2.164 (3)	2.179 (3)	1.974 (3)	76.97 (12), 77.64 (12)	154.38 (11)
$[Ni(dipic)(H_2O)_2]$ [11]	2.005	2.006	1.903	80.20, 80.41	160.15
$[Ni(dipic)(bta)_3]$ [12]	2.586	2.112	1.992	78.39, 76.44	154.82
$[Ni(dipic)(phen)(H_2O)].H_2O$ [13]	2.107 (2)	2.132 (2)	1.986 (2)	78.17, 77.34	155.31 (6)
$[Ni(dipicH_2)(H_2O)_3][Ce(dipic)_3].3H_2O$ [21]	2.178(3)	2.172(3)	1.994(3)	76.35(12), 77.11(12)	153.40(11)
$\{[Ni(phen)_3][Ni(dipic)_2]\}_2.17H_2O$, This work	2.087 (5), 2.110 (6)	2.106(5) 2.126 (8)	1.957 (7) 2.017 (10)	75.8(5), 77.6(3)	157.2 (3), 153.3 (5)

bta = benzotriazole, cyclam = 1,4,8,11-tetraazacyclotetradecane.

The $[Ni(H_2O)_6][Ni(dipic)_2]$ exhibited high antimicrobial activity against *E. coli* (19 mm) with moderate activity against *B. subtilis* (15 mm) at 500 µg/well. The most significant results were inhibition of fungus isolates *F. solani, A. niger* by $[Ni(H_2O)_6][Ni(dipic)_2]$, and longer diameter of the inhibition zone than standard antibiotic Amphoterice B. 1,10-phenanthroline exhibited weak inhibition effects against *A. niger* and *F. solani* the tested fungal strains. *S. aureus* and *S. typhimirium* were the most sensitive strains to the antibacterial effect of 1,10-phenanthroline followed by *E. coli* whereas *B. subtilis* was the least sensitive organism. 1,10-Phenanthroline had more activity against bacteria than the tested fungus strain. However, $[Ni(H_2O)_6][Ni(dipic)_2]$ showed more activity in terms of fungus strains than bacteria strains. In classifying the antibacterial activity as Gram-positive or Gram-negative, it would generally be expected that a much greater number would be active against Gram-positive than Gram-negative bacteria [23]. However, in this study, the compounds were active against both Gram positive and Gram negative bacteria.

$[Ni(H_2O)_6][Ni(dipic)_2]$ had more activity against *A. niger* and *F. Solani* with an inhibition zone of 25 mm i.d. at 500 µg/well concentration. Although $\{[Ni(phen)_3][Ni(dipic)_2]\}_2.17H_2O$ had least antifungal activity with inhibition zone of 13 mm. 1,10-Phenanthroline and $\{[Ni(phen)_3][Ni(dipic)_2]\}_2.17H_2O$ showed the same as effective fungus strains. However, $\{[Ni(phen)_3][Ni(dipic)_2]\}_2.17H_2O$ showed weaker activity against gram negative bacteria than 1,10-phenanthroline.

Supplementary Material

Crystallographic data for the structure reported here have been deposited at the CCDC as supplementary data, CCDC No. 650252. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. E-mail: deposit@ccdc.-cam.ac.uk.

CONCLUSIONS

In this study, the $\{[Ni(phen)_3][Ni(dipic)_2]\}_2.17H_2O$ has

Table 5. Antibacterial and Antifungal Activity $[Ni(H_2O)_6][Ni(dipic)_2]$, 1,10-Phenanthroline and $\{[Ni(phen)_3][Ni(dipic)_2]\}_2.17H_2O$ as Inhibition Zones (mm) (well Ø 10 mm)

Compound	Strains	Concentrations (µg/well)											
		500	250	125	62.5	31.2	15.6	7.8	3.9	1.9	0.9	0.4	0.2
$[Ni(H_2O)_6][Ni(dipic)_2]$ [8]	*B. subtilis*	15±0.2	13±0.1	12±0.2	11±0.1	-	-						
	S. aureus	18±0.1	16±0.4	14±0.1	12±0.1	11±0.4	-	-	-	-	-	-	-
	E. coli	19±1.1	16±0.1	12±0.2	-	-	-	-	-	-	-	-	-
	S. typhimirium	18±0.1	16±0.6	14±0.1	12±0.1	11±0.1	-	-	-		-	-	-
	C. albicans	14±0.1	12±0.1	11±0.5	11±0.1								
	A. niger	24±0.2	22±0.1	18±0.1	14±0.4	11±0.1							
	F. solani	25±0.1	16±0.1	14±0.1	11±0.1								
1,10-phenanthroline	*B. subtilis*	17±0.1	14±0.1	12±0.1	11±0.1	-	-	-	-	-	-	-	-
	S. aureus	25±0.1	22±0.1	16±0.1	14±0.1	11±0.1	-	-	-	-	-	-	-
	E. coli	25±0.1	22±0.7	20±1,2	18±0.1	14±0.2	12±0.1	11±0.1	-	-	-	-	-
	S. typhimirium	25±0.1	22±1.3	18±0.1	16±0.1	14±1.5	12±0.1	11±0.1	-	-	-	-	-
	C. albicans	18±0.1	16±1.1	11±0.1									
	A. niger	12±1.1	11±0.1										
	F. solani	13±0.1	11±1.5										
1	*B. subtilis*	20±0.1	18±0.1	16±0.1	14±0.1	12±0.5	11±0.1	-	-	-	-	-	-
	S. aureus	25±0.1	24±0.4	18±0.1	15±0.1	14±1.2	12±0.9	12±0.1	11±0.1	-	-	-	-
	E. coli	13±1.2	12±0.1	11±1.2	-	-	-	-	-	-	-	-	-
	S. typhimirium	15±0.1	14±0.1	12±0.1	11±0.1	-	-	-	-	-	-	-	-
	C. albicans	22±1.0	17±0.1	14±0.1	11±0.1								
	A. niger	13±0.1	12±0.1	11±0.1									
	F. solani	12±0.1	11±0.1										
	Standard antibiotics (disc Ø 6mm),												
		1	**2**										
	B. subtilis	36±0.1	-										
	S. aureus	29±0.2	-										
	E. coli	30±0.1	-										
	S. typhimirium	14±0.7	-										
	C. albicans	-	13±0.4										
	A. niger	-	9±0.1										
	F. solani	-	9±0.2										

-; No inhibition of zone 1; Tetracycline 30 µg $disc^{-1}$ 2; Amphotericin B 10 µg $disc^{-1}$, All the microorganisms were resistant to the control DMSO.

been prepared and characterized. The Ni(II) ions have distorted octahedral coordination by three bidentate phen and two tridentate dipic ligands. The complex has created a supramolecular structure by hydrogen bonds, π-π and C-H···π interactions. Ni-dipic, the first complex on which biological activity test was performed, has shown higher activity against gram positive than gram negative bacteria. Besides, it is quite effective against *C. Albicans* being used as test microorganism.

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