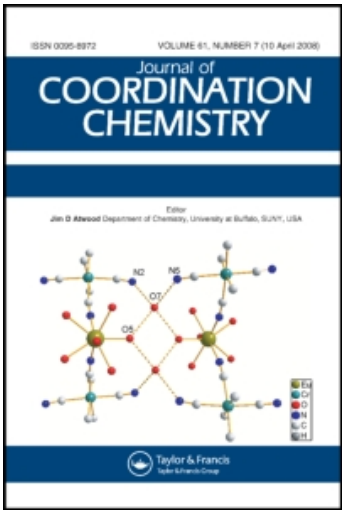

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, characterization, crystal structure and biological activities of supramolecular compounds of Mn(II) and Zn(II) with dipicolinic acid and 8-hydroxyquinoline

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To cite this Article Çolak, Alper Tolga , Çolak, Ferdağ , Yeşilel, Okan Zafer and Büyükgüngör, Orhan(2009) 'Synthesis, characterization, crystal structure and biological activities of supramolecular compounds of Mn(II) and Zn(II) with dipicolinic acid and 8-hydroxyquinoline', Journal of Coordination Chemistry, 62: 10, 1650 — 1660
To link to this Article: DOI: 10.1080/00958970802676656
URL: http://dx.doi.org/10.1080/00958970802676656

Journal of Coordination Chemistry
Vol. 62, No. 10, 20 May 2009, 1650–1660

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Synthesis, characterization, crystal structure and biological activities of supramolecular compounds of Mn(II) and Zn(II) with dipicolinic acid and 8-hydroxyquinoline

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(*Received 29 May 2008; in final form 18 August 2008*)

Two compounds, $(8\text{-}H_2Q)_2[Mn(dipic)_2]\cdot 6H_2O$ (**1**) and $(8\text{-}H_2Q)_2[Zn(dipic)_2]\cdot 6H_2O$ (**2**) (8-HQ = 8-hydroxyquinoline (oxine), H_2dipic = dipicolinic acid), have been prepared and characterized by elemental, spectroscopic (IR and UV–Vis), and thermal analyses, magnetic measurements and single crystal X-ray diffraction techniques. Compounds **1** and **2** consist of two 8-hydroxyquinolinium cations, one bis(dipicolinato)M(II) anion (M = Mn(II) and Zn(II)) and six uncoordinated water molecules. Both **1** and **2** crystallize in the monoclinic space group $C2/c$. In the complex anion, each dipic ligand is tridentate through *N* of pyridine and oxygens of the carboxylate groups. Crystal packing of **1** and **2** is a composite of intermolecular hydrogen bonding interactions. The *in vitro* antibacterial and antifungal activities of **1** and **2** were evaluated by the agar well diffusion method by MIC (Minimal Inhibition Concentration), looking for compounds which display high-inhibitory effect against gram positive bacteria and fungi. No growth inhibition was observed against tested gram negative bacteria.

Keywords: Dipicolinic acid; 8-Hydroxyquinoline; Antimicrobial activity

1. Introduction

Dipicolinic acid, first discovered in a biological system in 1936, is now known to be a major component of bacterial spores [1]. Investigation on dipicolinic acid shows that it prevents oxidation of low-density lipoprotein, which is involved in the pathogenesis of arteriosclerosis [2]. Dipicolinic acid is a known enzyme inhibitor, plant preservative, and food sanitizer [3]. 8-Hydroxyquinoline and its derivatives are well known for their antifungal, antibacterial, and antiamoebic activities [4]. ''Antimicrobial agents'' have

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970802676656

been introduced for decades to treat and prevent infectious diseases and infections. Decreased efficacy and resistance of pathogens to antibiotics has necessitated development of new alternatives. The problem has escalated as the prevalence of antibiotic-resistant bacteria has increased and multi-drug-resistant strains have emerged in many species. Such multi-drug resistance, arising mainly through antibiotic misuse, is a global problem.

Dipicolinic acid (H_2dipic) and its anions (Hdipic, dipic^{2-}) are well suited for construction of multidimensional frameworks because of the presence of two adjacent O atoms of carboxylates as substituents on the *N*-heterocyclic pyridine [3].

Dipicolinate complexes have applications in aqueous chemistry, catalysis, biochemistry, as water-soluble drugs, magnetic materials, in bleaching, bactericidal compositions [3], and antitumor activities [5, 6].

Single-crystal X-ray structure determinations of other Zn(II)–dipic and Mn(II)-dipic proton transfer compounds are (creatH)[Zn(pydc)(pydcH)] · $4H_2O$ [7], [pyda · H][Zn(pydc)(pydc · H)] · $3H_2O$ [8], (pipzH_2)[Zn(pydc)$_2$] · $4H_2O$, (EDGnH_2)[Zn(pydc)$_2$] · $3H_2O$, and (pdaH_2)[Zn(pydc)$_2$] · $4H_2O$ [9], (tata$H$)$_2$[Zn(pydc)$_2$] · $10H_2O$ [10], (im$H$)$_2$[Zn(pydc)] · $2H_2O$ [11], (2im$H$)$_2$[Zn(pydc)] [12], (im$H$)$_2$[Mn(pydc)] · $2H_2O$ [11], (2im$H$)$_2$[M(pydc)] [12] (M = 7 : 3 Mn/Cu); (creat = creatinine, pydc = dipicolinic acid, pyda = 2,6-pyridinediamine, pipz = piperazine, EDGn = ethylenediguanidine, pda = propane-1,3-diamine, tata = melamine, im = imidazole, 2im = 2-methylimidazole).

In this study we report the synthesis, spectroscopic, thermal analyses, crystal structure, and biologic activities of two isomorphous compounds (8-H_2Q)$_2$[Mn(dipic)$_2$] · $6H_2O$ (**1**) and (8-H_2Q)$_2$[Zn(dipic)$_2$] · $6H_2O$ (**2**). Compound **1** exhibited high-antifungal activity against *Candida albicans* (55 mm); **2** showed weak antimicrobial activity at 500 μg concentrations against the yeast *C. albicans* (25 mm). Compounds **1** and **2** showed the same activity against *Aspergillus niger*.

2. Experimental

2.1. *Materials and instrumentation*

All chemicals and solvents used for the synthesis were of reagent grade. Dipicolinic acid, 8-hydroxyquinoline, and C_2H_5OH (Aldrich) were used as received. Elemental analyses (C, H, and N) were performed using a Vario EL III CHNS elemental analyzer. Magnetic susceptibility measurements at room temperature were performed using a Sherwood Scientific MK1 model Gouy magnetic balance. UV-vis spectra were obtained in water solutions (10^{-3} mol L^{-1}) of the complex with a Shimadzu Pharmaspec UV-1700 spectrometer from 1000 to 190 nm. FT–IR spectra were recorded from 4000 to 400 cm^{-1} with a Bruker Optics, Vertex 70 FT–IR spectrometer using KBr pellets. A Diamond TG/DTA thermal analyzer was used to record simultaneous TG, DTG, and DTA curves in static air at a heating rate of 10°C min^{-1} from 20 to 1000°C using platinum crucibles.

2.2. *Crystallographic analyses*

Data collections (**1** and **2**) were performed on a STOE IPDS II image plate detector using MoKα radiation ($\lambda = 0.71019$ Å). Intensity data were collected in the θ range

2–25.5° at 293(2) K. Data collections: Stoe X–AREA [13]. Cell refinement: Stoe X–AREA [13]. Data reduction: Stoe X–RED [13]. The structure was solved by direct methods and anisotropic displacement parameters were applied to nonhydrogen atoms in a full-matrix least-squares refinement based on F^2 using SHELXL–97 [14]. Molecular drawings were obtained using ORTEP–III [15].

2.3. *Biological activity of compounds*

A total of six microbial species including four bacteria, a mould, and a yeast were used as test organisms in this study. *Staphylococcus aureus* ATCC 25923, *Escherichia coli* ATCC 25922, *Salmonella typhimurium* ATCC 14028, *A. niger* ATCC 10949, *C. albicans* (ATCC 10231) were obtained from American-Type Culture Collection; *Bacillus subtilis* NRRL –B-209 from USDA, Agriculture Research Service, Peria, USA. Bacterial and fungal cultures of test organisms were maintained on nutrient agar and malt extract agar slants at 4°C, respectively, and were subcultured in Petri dishes prior to use.

Antimicrobial activity of test compounds was carried out according to modified agar well diffusion assay [16, 17]. Compound was dissolved in dimethylsulfoxide (DMSO, Merck). Fifteen millilitres of the specified molten agar (45°C) were poured into sterile Petri dishes (Ø 90 mm). The cell suspensions containing 10^8 CFU mL^{-1} cells for bacteria, 10^7 CFU mL^{-1} cells for yeasts, and 10^5 spore mL^{-1} 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. The agar well method for the estimation of MIC values (the lowest concentration of compounds required to inhibit the growth of the tested microorganisms) was applied to evaluate the antimicrobial activity. At the same time, 10 mm wells were bored using a sterile cork borer and impregnated with known concentrations, determined previously by MIC tests (500–0.4 $\mu g\,mL^{-1}$ for each well) from each compound (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 [inhibiting the protein synthesis (30 $\mu g\,mL^{-1}$)] for bacteria and Nystain [binding to sterols in the fungal cellular membrane, altering the permability and allowing leakage of the cellular contents (100 U)] for fungi were used as positive control. DMSO was used as a negative control. Antimicrobial activity was evaluated as zones of inhibition around wells. All samples were tested in triplicate.

2.4. *Synthesis of (8-H_2Q)$_2$[Mn(dipic)$_2$]·6H_2O (1) and (8-H_2Q)$_2$[Zn(dipic)$_2$]·6H_2O (2)*

A solution of dipicolinic acid (1 mmol, 0.167 g) in ethanol–water (1 : 1; 20 mL) was added dropwise with stirring at room temperature to a solution in water of 20 mL $MnSO_4 \cdot H_2O$ (0.5 mmol, 0.085 g) or $ZnSO_4 \cdot H_2O$ (0.5 mmol, 0.090 g). To this solution a solution in ethanol (20 mL) of 8-hydroxyquinoline (2 mmol, 0.290 g) was added. After 1 day stirring at room temperature, yellow, **1**, and clear yellow, **2**, solutions were observed. After 1 month, crystals formed, were filtered and washed with 10 mL of cold ethanol and dried in air. Anal. Calcd for **1** $C_{32}H_{34}N_4O_{16}Mn$: C, 48.93; H, 4.36; N, 7.13.

Found: C, 48.89; H, 4.15; N, 7.21%. Anal. Calcd for **2** $C_{32}H_{34}N_4O_{16}Zn$: C, 48.28; H, 4.31; N, 7.04. Found: C, 48.20; H, 4.16; N, 7.10%.

3. Results and discussion

3.1. *IR spectra*

Strong and broad absorption bands at 3368 and 3366 cm^{-1} are attributed to ν(OH) of water in **1** and **2**, respectively. Absorption bands at 3206 and 3189 cm^{-1} are attributed to $\nu(NH) + \nu(OH)$ vibrations of $(8\text{-}H_2Q)^+$. Relatively weak bands at 3086 and 3070 cm^{-1} are due to ν(CH) vibrations. The most distinct feature in the IR spectrum is the presence of strong asymmetrical and symmetrical carboxylate stretching frequencies at 1550–1610 and 1300–1420 cm^{-1}, respectively [18]. The difference between the asymmetric and symmetric carboxylate stretches [19] is ~170 cm^{-1} for ionic carboxylate [19]. The values of Δ_{OCO} ($\upsilon_{OCOasym}$–υ_{OCOsym}) calculated for the complexes (185 and 182 cm^{-1}) can be due to presence of strong hydrogen bonds, formed by both carboxylate oxygens as well as the electron effect of pyridine ring to carboxylate [19]. The absorption band at 1580 and 1591 cm^{-1} is due to $\nu(C{=}C) + \nu(C{=}N)$ of dipic and $(8\text{-}H_2Q)^+$ (**1** and **2**) or dipic ligands. The strong IR bands at 1376 and 1393 cm^{-1} are $\nu(CH)_{py}$. Bands at 1327, 1281, 1076, 742 cm^{-1} and 1328, 1284, 1082, 743 cm^{-1} are due to ν(C–O) and δ(O–C–O) vibrations of dipic ligand [19, 20]. Absorption bands at 620, 426 cm^{-1} and 620, 433 cm^{-1} are attributed to M–O and M–N vibrations of **1** and **2**, respectively. Similar spectroscopic results were obtained for $[Zn(dipicolH)_2] \cdot 3H_2O$ [19], $[Cu(H_2O)_5Zn(dipic)_2] \cdot 3H_2O$ [20], $[Mn_3(pdc)_3(bpy)_3(H_2O)_2] \cdot 9H_2O$ [21], $[Mn(pdc)(bpy)(Him_2)] \cdot H_2O$ [21], $[Mn(dipic)] \cdot 1.5H_2O$ [22], $[Mn(dipic)(bipy)_2] \cdot 4.5H_2O$ [22], $[Mn(dipic)(bipy)_2] \cdot 2H_2O$ [22], $[Mn(dipic)(phen)_2] \cdot 2H_2O$ [22], and $[Zn(pydc)_2][Zn(phen)_2(H_2O)_2] \cdot 7H_2O$ [23] (bpy or bipy = 2,2′-bipyridine, pdc, dipic, dipicol, or pydc = dipicolinato, phen = 1,10-phenanthroline, im = imidazole).

3.2. *UV–Vis spectra and magnetic susceptibilities*

Electronic spectra of the complexes were recorded in water from 250 to 550 nm. Electronic spectra of **1** show an absorption *ca* 307 nm ($\varepsilon = 3981\ M^{-1}\ cm^{-1}$), assigned to intra-ligand charge transfer (n–π^* or π–π^*). Manganese(II) complexes have extremely weak bands in the electronic spectrum in an octahedral environment [24]. Electronic spectra of **2** show absorptions in the UV region at *ca* 355 nm and *ca* 319 nm ($\varepsilon = 2723$ and $3414\ M^{-1}\ cm^{-1}$), assigned to intra-ligand charge transfer (n–π^* and π–π^*). The imine group in $(8\text{-}H_2Q)^+$ caused yellow color at **1** and **2**.

The room temperature magnetic moment of powdered sample for **1** of 5.35 BM corresponds to five unpaired electrons in an octahedral geometry [24].

3.3. *Thermal analysis*

The TG–DTG and DTA curves are shown in Supplementary Material. The endothermic peaks of **1** ($DTG_{max} = 61.55°C$) between 30 and 176°C correspond to

loss of six crystal water molecules (found 12.23, Calcd 13.75%). Similar results are found for **2** ($DTG_{max} = 100°C$; found 11.65, Calcd 13.56). Anhydrous **1** is thermally stable to 226°C. Two $(dipic)^{2-}$ and two $(8\text{-}H_2Q)^+$ groups are lost in two steps at 254.09°C and 438.23°C for **1**, but in compound **2**, these ions decomposed in four steps at 181.05°C, 212.91°C, 248.31°C, and 481.96°C.

3.4. *Crystal structure of $(8\text{-}H_2Q)_2[Mn(dipic)_2]\cdot 6H_2O$ (1)*

Details of the crystal structure are given in table 1, the molecular structure is shown in figure 1 and selected bond lengths and angles are given in table 2. The asymmetric unit of **1** includes one bis(dipicolinato)manganate(II) dianionic complex and two units of 8-hydroxyquinolinium ($8\text{-}H_2Q^+$) as cations. Proton transfer occurs between the starting acid and the amine leaving dipicolinate as an ionic ligand and 8-hydroxyquinolinium as a counter ion. The coordination geometry around Mn(II) is distorted octahedral with dipic tridentate through two O atoms of carboxylate and one N atom of pyridine; two 8-hydroxyquinolinium cations, $(8\text{-}H_2Q)^+$, are counter ions. Oxygens (O1, $O1^i$, O3, and $O3^i$) of carboxylate occupy the equatorial positions and two nitrogens (N1, $N1^i$) of pyridine [$(N1\text{–}Mn\text{–}N1^i) = 168.74(7)°$] comprise the axial positions. The Mn1–O1 and Mn1–O3 bond distances are 2.229(1) and 2.222(1) Å, and Mn1–N1 is 2.141(1) Å. These bond distances are comparable to those reported for $[Mn(dipic)(H_2O)(phen)]\cdot H_2O$ [2.237(2), 2.266(2), and 2.179(3) Å] [25], but different from the values observed in $[Mn(pdc)(bpy)(Him)_2]$ [21] (2.372(4), 2.349(4), 2.324(5) Å).

Table 1. Crystal data and structure refinement parameters.

	1	**2**
Empirical formula	$C_{32}H_{34}N_4O_{16}Mn$	$C_{32}H_{34}N_4O_{16}Zn$
Formula weight	785.57	796.00
Temperature (K)	293(2)	
Wavelength (Å)	0.71073 Mo–Kα	
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*
Unit cells and dimension (Å, °)		
a	18.4205(7)	18.4087(7)
b	10.3093(4)	10.3462(3)
c	19.2854(8)	19.1446(7)
β	109.606(3)	110.404(3)
V (Å^3)	3450.0(2)	3417.5(2)
Z	4	4
Absorption coefficient (mm^{-1})	0.47	0.80
D_{Calcd} (Mg m^{-3})	1.512	1.547
Crystal size (mm)	0.64 × 0.50 × 0.38	0.65 × 0.54 × 0.34
θ range for data collection (°)	2.24, 27.29	2.23, 27.29
Measured reflections	25296	12654
Independent reflections	3382	3544
Absorption correction	Integration	Integration
Refinement method	Full-matrix least squares on F^2	
Final *R* indices [$I > 2\sigma(I)$]	0.044	0.033
$R[F^2 > 2\sigma(F^2)]$	0.034	0.031
$wR(F^2)$	0.091	0.083
Goodness-of-fit on F^2	1.03	1.03
Largest difference peak and hole (Å^{-3})	0.26; −0.30	0.19; −0.42

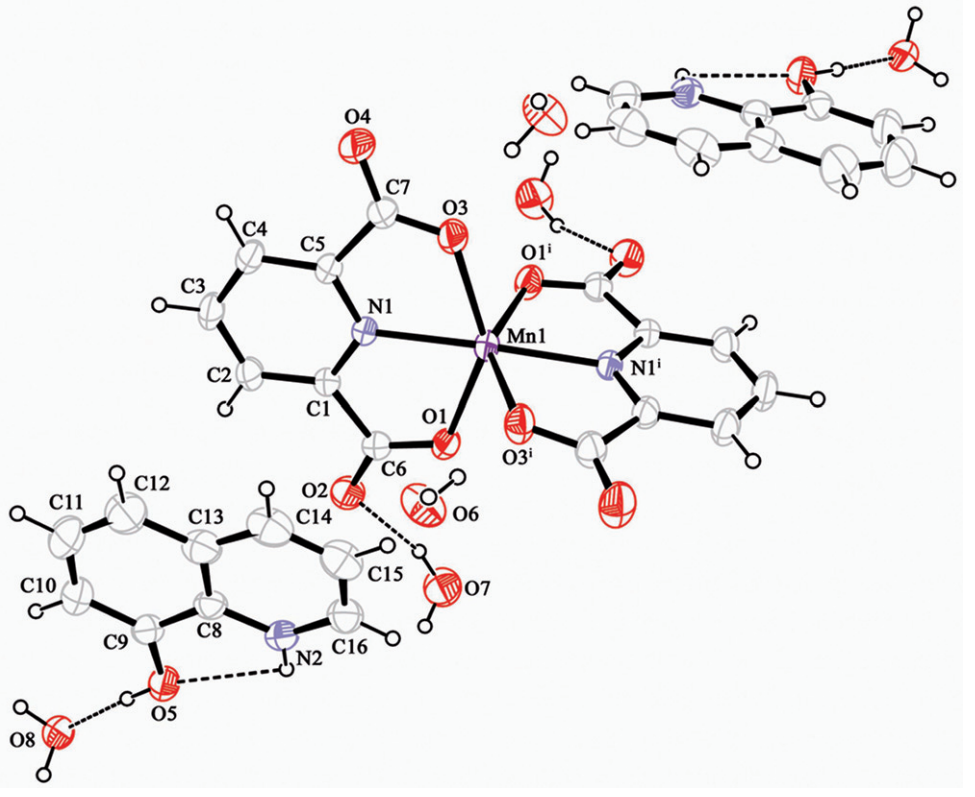

Figure 1. Molecular structure of $(8\text{-}H_2Q)_2[Mn(dipic)_2]\cdot 6H_2O$ (**1**) with 30% probability level, hydrogen bonds are shown with dashed lines.

Table 2. Comparison of the bond distances and angles (Å, °).

$(8\text{-}H_2Q)_2[Mn(dipic)_2]\cdot 6H_2O$ (**1**)			
Selected atoms			
N1–Mn1	2.1414(13)	O3–Mn1	2.2216(12)
O1–Mn1	2.2292(12)		
$N1^i$–Mn1–N1	168.74(7)	$O3–Mn1–O1^i$	93.24(5)
N1–Mn1–O3	73.32(5)	N1–Mn1–O1	72.57(5)
$N1–Mn1–O3^i$	114.43(5)	O3–Mn1–O1	145.87(4)
$O3–Mn1–O3^i$	99.71(8)	$O1_i$–Mn1–O1	93.40(7)
$N1–Mn1–O1^i$	99.49(5)		
$(8\text{-}H_2Q)_2[Zn(dipic)_2]\cdot 6H_2O$ (**2**)			
N1–Zn1	2.0052(12)	O3–Zn1	2.1865(12)
O1–Zn1	2.2020(12)		
$N1^i$–Zn1–N1	172.19(8)	$O3–Zn1–O1^i$	92.31(5)
$N1–Zn1–O3^i$	108.58(5)	N1–Zn1–O1	75.95(5)
N1–Zn1–O3	76.88(5)	O3–Zn1–O1	152.82(4)
$O3^i$–Zn1–O3	95.51(8)	$O1^i$–Zn1–O1	92.49(7)
$N1–Zn1–O1^i$	98.54(5)		

Note: Symmetry codes: (i) $-x\pm1, y, -z\pm3/2$.

Intra- and inter-molecular N–H···O and O–H···O hydrogen bonds are given in table 3.

3.5. *Crystal structure of (8-H_2Q)$_2$[Zn(dipic)$_2$]·6H_2O (2)*

Details of the crystal structure are given in table 1. Selected bond lengths and angles together with the hydrogen bonding geometry are given in tables 2 and 3. Each dipicolinic acid donates two protons to the 8-hydroxyquinoline molecules, forming the bis(8-hydroxyquinolinium) bis(dipicolinato)zincate(II) hexahydrate, with two 8-hydroxyquinolinium cations, $(8\text{-}H_2Q)^+$, $[Zn(dipic)_2]^{2-}$ and six water molecules (figure 2). The Zn(II) is hexacoordinate by two tridentate dipic ligands through two nitrogens and four oxygens. Oxygens (O1, O1^i, O3, and O3^i) of carboxylate occupy the equatorial positions and two nitrogen atoms (N1, N1^i) of pyridine (N1–Zn–N1^i = 172.19 (8)°) comprise the axial positions. Dipic is essentially planar with slight deviation from planarity arising from nonzero torsion angles between the carboxylate and ring [N1–C1–C6–O1 = 1.7(2)°, 1.1(2) and N1–C5–C7–O3 = −7.1(3)°, −6.5(2) for Mn(II) and Zn(II) compounds, respectively]. These torsion angles indicate that distortion of the dipicolinate ligand is caused by coordination to manganese(II). The dihedral angle between pyridine and carboxyl group is 7.82°. The Zn(II)–O1/O3 [2.202(1) and 2.187(1) Å] and Zn(II)–N [2.005(1) Å] bond distances of the compound are consistent with those found in (pydaH)[Zn(pydc)(pydcH)]·3H_2O [2.155(2), 2.217(2) and 2.015(2) Å] [8], (tataH)$_2$[Zn(pydc)$_2$]·10H_2O [2.123(2), 2.238(2), 2.032(2) Å] [10], (creatH)[Zn(pydc)(pydcH)]·4H_2O [2.226(2), 2.141(2) and 2.029(3) Å] [7].

The details of hydrogen bonding geometry are given in table 3. Anions and $(8\text{-}H_2Q)^+$ are connected via intramolecular (O5−H5···O8) and intermolecular (N2−H2A···O4^{ii},

Table 3. Hydrogen bonding interactions in the complexes.

D−H···A	d(D–H), Å	d(H···A), Å	d(D···A), Å	<(DHA), °
(8-H_2Q)$_2$[Mn(dipic)$_2$]·6H_2O (**1**)				
N2–H2A···O4^{ii}	0.86	1.92	2.656(2)	142
O5–H5···O8	0.850(16)	1.712(16)	2.560(2)	176(2)
O6–H6A···O3^i	0.832(15)	2.106(15)	2.906(2)	161(2)
O6–H6B···O7^{iii}	0.819(15)	1.975(15)	2.775(3)	165(2)
O7–H7A···O2	0.835(15)	1.962(17)	2.762(2)	160(2)
O7–H7B···O4^{ii}	0.824(15)	2.289(16)	3.096(3)	167(2)
O8–H8A···O1^{iv}	0.836(15)	1.933(15)	2.7544(18)	167(2)
O8–H8B···O6^v	0.815(15)	2.026(16)	2.815(2)	163(2)
(8-H_2Q)$_2$[Zn(dipic)$_2$]·6H_2O (**2**)				
N2–H2A···O4^{ii}	0.86	1.94	2.668(2)	142
O5–H5···O8	0.82	1.75	2.5504(19)	167
O6–H6A···O7^{iii}	0.83(3)	1.95(3)	2.770(3)	166(3)
O6–H6B···O3	0.82(3)	2.16(3)	2.929(2)	156(3)
O7–H7A···O2	0.86(3)	1.90(3)	2.738(2)	163(3)
O7–H7B···O4^{ii}	0.78(3)	2.28(3)	3.053(3)	173(3)
O8–H8A···O1^{iv}	0.84(3)	1.91(3)	2.7344(18)	166(3)
O8–H8B···O6^v	0.75(3)	2.07(3)	2.803(2)	164(3)

Notes: Symmetry codes: (i) $-x+1$, y, $-z+3/2$; (ii) $x+1/2$, $y+1/2$, z; (iii) x, $y-1$, z; (iv) x, $-y+2$, $z-1/2$; (v) $-x+3/2$, $-y+3/2$, $-z+1$ for **1** and (ii) $x-1/2$, $y\pm1/2$, z; (iii) $-x\pm1$, $y-1$, $-z\pm3/2$; (iv) x, $-y\pm1$, $z\pm1/2$; (v) $x-1/2$, $-y\pm1/2$, $z\pm1/2$ for **2**.

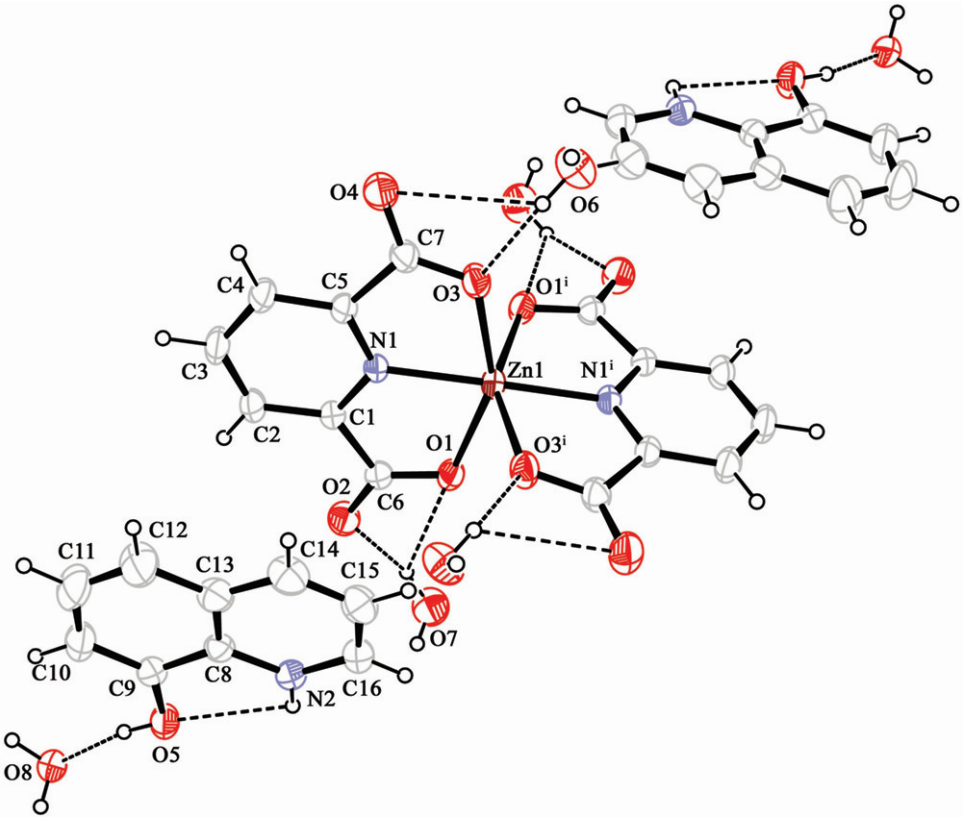

Figure 2. Molecular structure of $(8\text{-}H_2Q)_2[Zn(dipic)_2]\cdot 6H_2O$ (**2**) with 30% probability level, hydrogen bonds are shown with dashed lines.

(ii) $= x-1/2, y+1/2, z$) hydrogen bonds. There is also an intramolecular hydrogen bond between N2 and O5.

3.6. *Antimicrobial activity*

In vitro antimicrobial activity of **1** and **2** were tested according to the agar well diffusion method for estimation of MIC values (the lowest concentration of compounds required to inhibit the growth of the tested microorganisms) was applied to evaluate the antimicrobial activity. Table 4 shows the effect of 11 different concentrations against growth of gram positive, gram negative bacterial strains, yeast strain, and fungal strain.

Compounds **1** and **2** display no inhibition against *E. coli* and *S. thyhimirium* (table 4). Compound **1** has good activity against gram positive bacteria (*S. aureus* and *B. subtilis*) and higher activity against *S. aureus* (75 mm) than the reference antibiotic (at concentration of 30 µg mL^{-1}). Compound **1** has stronger activity against gram positive bacteria and fungi than **2**. Shivankar *et al.* [26] found metal complexes with 8-hydroxyquinoline or amino acids possess biological activities; 8-hydroxyquinoline showed activity against gram positive and gram negative bacteria at 200 ppm [24]. While **1** exhibited high-antifungal activity against *C. albicans* (55 mm), **2** showed weak

Table 4. Antibacterial and antifungal activity, $(8\text{-}H_2Q)_2[Mn(dipic)_2]\cdot 6H_2O$ (**1**), $(8\text{-}H_2Q)_2[Zn(dipic)_2]\cdot 6H_2O$ (**2**) as inhibition zones (mm) (well Ø 10 mm).

		Concentration (μg per well)										
Compounds	Strains	500	250	125	62.5	31.2	15.6	7.8	3.9	1.9	0.9	0.4
$(8\text{-}H_2Q)_2[Mn(dipic)_2]\cdot 6H_2O$ (**1**)	*B. subtilis*	68	55	48	31	27	23	18	–	–	–	–
	S. aureus	75	62	54	50	35	30	26	12	–	–	–
	E. coli	–	–	–	–	–	–	–	–	–	–	–
	S. typhimirium	–	–	–	–	–	–	–	–	–	–	–
	C. albicans	55	45	30	15	–	–	–	–	–	–	–
	A. niger	32	25	15	–	–	–	–	–	–	–	–
$(8\text{-}H_2Q)_2[Zn(dipic)_2]\cdot 6H_2O$ (**2**)	*B. subtilis*	48	34	30	22	18	14	–	–	–	–	–
	S. aureus	70	50	38	30	24	12	–	–	–	–	–
	E. coli	–	–	–	–	–	–	–	–	–	–	–
	S. typhimirium	–	–	–	–	–	–	–	–	–	–	–
	C. albicans	25	14	–	–	–	–	–	–	–	–	–
	A. niger	30	13	–	–	–	–	–	–	–	–	–
		Standard antibiotic (disc Ø 6 mm)										
		1	**2**									
	B. subtilis	35	–									
	S. aureus	30	–									
	E. coli	28	–									
	S. typhimirium	20	–									
	C. albicans	–	22									
	A. niger	–	20									

Notes: (–): No inhibition of zone 1: Tetracycline 30 μg per disc 2: Nystatin 100 U. All microorganismis were resistant to the control DMSO.

antimicrobial activity at 500 μg (25 mm). Compounds **1** and **2** showed the same activity against *A. niger*.

4. Conclusions

Two compounds, $(8\text{-}H_2Q)_2[Mn(dipic)_2]\cdot 6H_2O$ and $(8\text{-}H_2Q)_2[Zn(dipic)_2]\cdot 6H_2O$, were prepared and characterized by elemental, spectroscopic (IR and UV-vis) and thermal analyses, magnetic measurements, and single crystal X-ray diffraction. Dipic is tridentate through two O atoms of carboxylate and one N of pyridine ring; two 8-hydroxyquinolinium cations, $(8\text{-}H_2Q)^+$, are counter ions. Two protons transfer from each dipicolinic acid to two 8-hydroxyquinoline. Strong hydrogen bonds between uncoordinated water, $(8\text{-}H_2Q)^+$ and carboxylate play important roles in the construction of the 3-D supramolecular networks. Compound **1** exhibited high-antimicrobial activity against gram positive bacteria and yeast.

Supplementary Material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as the supplementary publication No. CCDC 686508 and 686509 for **1** and **2**, respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033 or Email: deposit@ccdc.cam.ac.uk).

Acknowledgment

The authors are indebted to the Dumlupinar University Research Found for support (Grant No: 2007/14).

References

[1] J.R.H. Xie, V.H. Smitth Jr., R.E. Allen. *Chem. Phys*, **322**, 254 (2006).
[2] Z. Vargova, V. Zeleoak, I. Cisaova, K. Györyova. *Thermochim. Acta*, **423**, 149 (2004).
[3] M.V. Kirillova, M.F.C.G. Da Silva, A.M. Kirillov, J.J.R.F. Da Silva, A.J.L. Pombeiro. *Inorg. Chim. Acta*, **360**, 506 (2007).
[4] K. Arıcı, M. Yurdakul, S. Yurdakul. *Spectrochim. Acta, Part A*, **61**, 37 (2005).
[5] A. Szorcsik, L. Nagy, A. Deak, M. Scopelliti, Z.A. Fekete, A. Csaszar, C. Pellerito, L. Pellerito. *J. Organomet. Chem*, **689**, 2762 (2004).
[6] İ. Uçar, B. Karabulut, A. Bulut, O. Büyükgüngör. *J. Mol. Struct*, **834–836**, 336 (2007).
[7] A. Moghimi, M.A. Sharif, A. Shokrollahi, M. Shamsipur, H. Aghabozorg. *Z. Anorg. Allg. Chem*, **631**, 902 (2005).
[8] M. Ranjbar, A. Moghimi, H. Aghabozorg, G.P.A. Yap. *Anal. Sci*, **18**, 219 (2002).
[9] H. Aghabozorg, M. Ghadermazi, F. Zabihi, B. Nakhjavan, J. Soleimannejad, E. Sadr-khanlou, A. Moghimi. *J. Chem. Cyrstallogr.*, **38**, 645 (2008).

[10] Z. Aghajani, M.A. Sharif, H. Aghabozorg, A. Naderpour. *Acta Crystallogr*, **E62**, m830 (2006).
[11] J.C. MacDonald, P.C. Dorrestein, M.M. Pilley, M.M. Foote, J.L. Lundburg, R.W. Henning, A.J. Schultz, J.L. Manson. *J. Am. Chem. Soc*, **122**, 11692 (2000).
[12] J.C. MacDonald, T.J.M. Luo, G.T.R. Palmore. *Cryst. Growth Des*, **4**, 1203 (2004).
[13] Stoe & Cie. X−Area (Version 1.18) and X−Red32 (Version 1.04). Stoe & Cie, Darmstadt, Germany (2002).
[14] G.M. Sheldrick. *SHELXS97 and SHELXL97*, University of Göttingen, Germany (1997).
[15] L.J. Farrugia. *J. Appl. Crystallogr.*, **30**, 565 (1997).
[16] K. Guven, S. Ilhan, M.B. Mutlu, F. Colak. *Fresenius Environ. Bull*, **17**, 303 (2008).
[17] National Committee for Clinical Laboratory Standards (NCCLS). Performance standards for antimicrobial disk susceptibility tests. Approved Standard (M2-A4) National Committee for Clinical Laboratory Standards Villanova, PA, (1990).
[18] A. Moghimi, A. Shokrollahi, M. Shamsipur, H. Aghabozorg, M. Ranjbar. *J. Mol. Struct*, **701**, 49 (2004).
[19] Z. Vargova, V. Zeleoak, I. Cisaova, K. Györyova. *Thermochim. Acta*, **423**, 149 (2004).
[20] M.V. Kirillova, M.F.C.G. Da Silva, A.M. Kirillov, J.J.R.F. Da Silva, A.J.L. Pombeiro. *Inorg. Chim. Acta*, **360**, 506 (2007).
[21] C. Ma, C. Chen, Q. Liu, D. Liao, L. Li. *Eur. J. Inorg. Chem*, **2003**, 1227 (2003).
[22] M. Devereux, M. McCann, V. Leon, V. McKee, R.J. Ball. *Polyhedron*, **21**, 1063 (2002).
[23] A. Moghimi, S. Sheshmani, A. Shokrollahi, M. Shamsipur, G. Kickelbick, H. Aghabozorg. *Z. Anorg. Allg. Chem*, **631**, 160 (2005).
[24] A.K. Singh, S. Kumari, K.R. Kumar, B. Sridhar, T.R. Rao. *Polyhedron*, **27**, 1937 (2008).
[25] C. Ma, C. Fan, C. Chen, Q. Liu. *Acta Crystallogr*, **C58**, m553 (2002).
[26] V.S. Shivankar, R.B. Vaidya, S.R. Dharwadkar, N.V. Thakkar. *Synth. React. Inorg. Met.-Org. Chem.*, **33**, 1597 (2003).