4,4′-Bipyridinium diaquabis(pyridine-2,5-dicarboxylato-κ^2N,O^2)zincate(II)

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Hydrothermal reaction of $Zn(NO_3)_2 \cdot 6H_2O$ with pyridine-2,5-dicarboxylic acid, 4,4′-bipyridine and pyridine in a 1:1:1:2 molar ratio affords the title complex, $(C_{10}H_{10}N_2)[Zn(C_7H_3NO_4)_2(H_2O)_2]$, in which both ions are centrosymmetric. The Zn^{II} atom is octahedrally coordinated by two pyridine-2,5-dicarboxylate chelating ligands and two water molecules in a distorted octahedral geometry. 4,4′-Bipyridinium, acting as counter-ion, has hydrogen-bonding interactions with pyridine-2,5-dicarboxylate, forming a three-dimensional structure.

Comment

In preparing metal complexes, carboxylate and pyridine ligands have been frequently employed (Erxleben, 2003). Pyridine-2,5-dicarboxylate has two carboxylate groups and one pyridine N atom, which can display different coordination modes to afford mono- or polynuclear complexes (Liang *et al.*, 2001; Shiu *et al.*, 2003; Zhang *et al.*, 2005; Zhao *et al.*, 2006). We report here the synthesis and crystal structure of a new pyridine-2,5-dicarboxylate (pydc) mononuclear zinc(II) complex, (I).
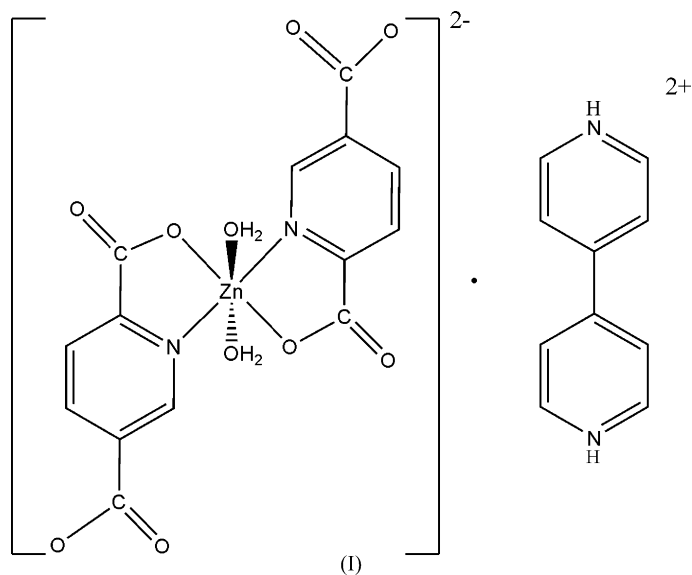
The asymmetric unit of (I) consists of a mononuclear $[Zn(pydc)_2(H_2O)_2]^{2-}$ anion and one 4,4′-bipyridinium counter-ion (Fig. 1), both of which are centrosymmetric. The Zn^{II} atom is in an octahedral environment (Table 1). Two pydc ligands chelate to the Zn atom, forming the equatorial plane of the octahedron. Two coordinated water molecules occupy the axial positions of the octahedron.
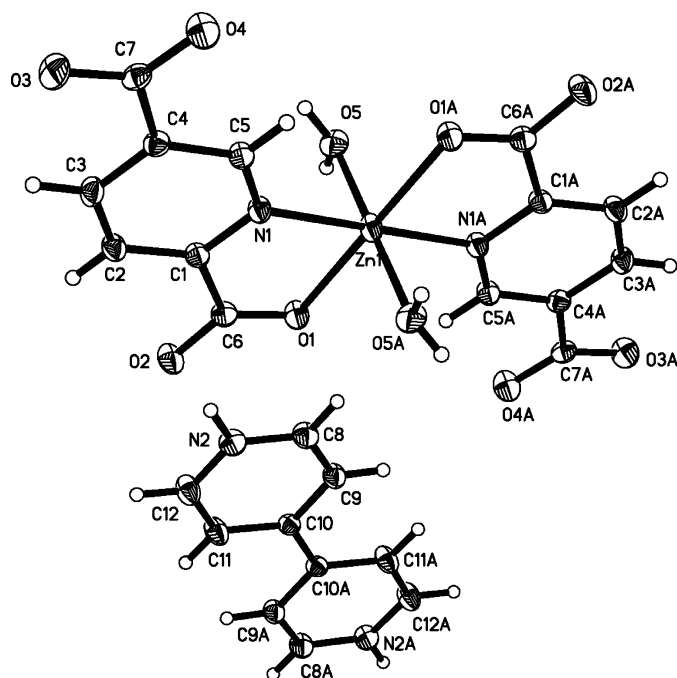
Figure 1
The structure of (I). Displacement ellipsoids are drawn at the 30% probability level. In the cation, symmetry code (A): $1 - x, 2 - y, 1 - z$; in the anion, symmetry code (A): $1 - x, 1 - y, 2 - z$.
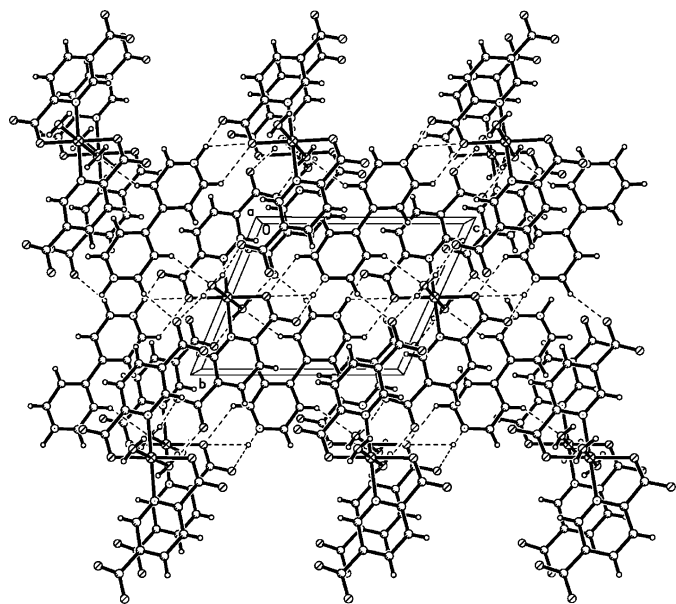

Figure 2
A packing diagram of (I) with the intermolecular hydrogen bonds shown as dashed lines.

There are hydrogen-bonding interactions involving the coordinated carboxylate group and the 4,4′-bipyridinium, and the uncoordinated carboxylate group and the water, which help to consolidate the crystal structure (Table 2). The distance between adjacent pyridine aromatic rings is *ca* 3.50 Å, indicating some π–π stacking interactions that leads to a supramolecular architecture (Fig. 2).

Experimental

A mixture containing $Zn(NO_3)_2 \cdot 6H_2O$ (0.149 g, 0.5 mmol), 2,5-H_2pydc (0.084 g, 0.5 mmol), 4,4′-bipyridine (0.078 g, 0.5 mmol) and pyridine (0.079 g, 1.0 mmol) in 8 ml H_2O was sealed in a 15 ml Teflon-lined stainless steel reactor. The reaction system was heated at 413K for 3 d under autogenous pressure. Upon cooling to room temperature at a rate of 10 K h^{-1}, light-yellow crystals of (I) suitable for X-ray diffraction were harvested.

Crystal data

$(C_{10}H_{10}N_2)[Zn(C_7H_3NO_4)_2(H_2O)_2]$
$M_r = 589.81$
Triclinic, $P\bar{1}$
$a = 7.0178 (12)$ Å
$b = 8.6945 (15)$ Å
$c = 10.4753 (18)$ Å
$\alpha = 112.469 (2)°$
$\beta = 90.395 (2)°$
$\gamma = 106.127 (2)°$

$V = 562.78 (17)$ Å^3
$Z = 1$
$D_x = 1.740$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 1.16$ mm^{-1}
$T = 273 (2)$ K
Block, light yellow
$0.30 \times 0.30 \times 0.20$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.722$, $T_{max} = 0.801$

2945 measured reflections
1960 independent reflections
1897 reflections with $I > 2\sigma(I)$
$R_{int} = 0.011$
$\theta_{max} = 25.1°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.063$
$S = 1.06$
1960 reflections
190 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0356P)^2 + 0.217P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—N1	2.1040 (14)	C6—O2	1.257 (2)
Zn1—O1	2.1089 (12)	C7—O4	1.243 (2)
Zn1—O5	2.1170 (15)	C7—O3	1.247 (2)
C6—O1	1.251 (2)	C10—C10^i	1.487 (3)
N1^{ii}—Zn1—N1	180	N1^{ii}—Zn1—O5	89.04 (6)
N1^{ii}—Zn1—O1	100.63 (5)	N1—Zn1—O5	90.96 (6)
N1—Zn1—O1	79.37 (5)	O1—Zn1—O5	89.84 (6)
O1^{ii}—Zn1—O1	180	O1—C6—O2	125.07 (16)

Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (ii) $-x + 1, -y + 1, -z + 2$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O5—H5$A\cdots$O4^{iii}	0.78 (3)	1.90 (3)	2.657 (2)	164 (3)
O5—H5$B\cdots$O3^{iv}	0.81 (3)	1.89 (3)	2.677 (2)	164 (3)
N2—H2$A\cdots$O2	0.873 (18)	1.728 (19)	2.600 (2)	176 (3)
N2—H2$A\cdots$O1	0.873 (18)	2.60 (3)	3.177 (2)	125 (3)

Symmetry codes: (iii) $x, y + 1, z$; (iv) $-x, -y, -z + 2$.

In complex (I), atoms H5A and H5B of the water molecule and the NH atom H2A were located in difference Fourier maps and refined freely. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2000).

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