trans-Diaqua{5,5′-[(E,E)-pyridine-2,6-diylbis(methylidynenitrilo)]bis-[pyrimidine-2,4(1H,3H)-dione]}-zinc(II) nitrate hexafluorophosphate trihydrate

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The title compound, $[Zn(C_{15}H_{11}N_7O_4)(H_2O)_2](NO_3)(PF_6)\cdot$ $3H_2O$, contains a mononuclear zinc(II) complex. The Zn^{2+} centre is seven-coordinated in a slightly distorted pentagonal–bipyramidal geometry, with the two water O atoms located in the apical positions, and the pyridine N atom, the two imine N atoms and two carbonyl O atoms of the uracil groups located in the equatorial plane. The charge is balanced by PF_6^- and NO_3^- anions.

Comment

Complexes of macrocyclic ligands derived from 2,6-diformyl-pyridine are of great interest because they can mimic the structural features of macrocyclic biological molecules (Hueso-Ureña et al., 2003). Mixed-ligand complexes of a variety of metals, including Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}, have been screened for their antimicrobial acitivities (Mohamed & Abd El-Wahab, 2005). Some tridentate Fe^{II} and Co^{II} complexes of bulky substituted arylimine units have been reported to be extremely active and long lived catalysts for the polymerization of ethylene (Small et al., 1998). The coordinative interaction between Zn and naphthalene-labelled diimine pyridine ligands, inducing the formation of light-emitting intra-complex charge-transfer species, has also been investigated (Boiocchi et al., 2003). Although a number of studies have been carried out with 2,6-diformylpyridine complexes (Owens et al., 2003; Lisowski & Starynowicz, 2000; Mazurek & Lisowski, 2003; Bligh et al., 2001), the chemistry of uracil-containing 2,6-diformylpyridine ligands with metal complexes has not been studied thoroughly. To the best of our knowledge, the title compound, (II), is the first complex of zinc with the ligand 5,5′-[(E,E)-pyridine-2,6-diylbis(methylidynenitrilo)]bis[pyrimidine-2,4(1H,3H)-dione], (I), to be crystallographically char-

acterized. In order to establish the coordination geometry and to determine the structural parameters, we present here the synthesis and structure of (II).
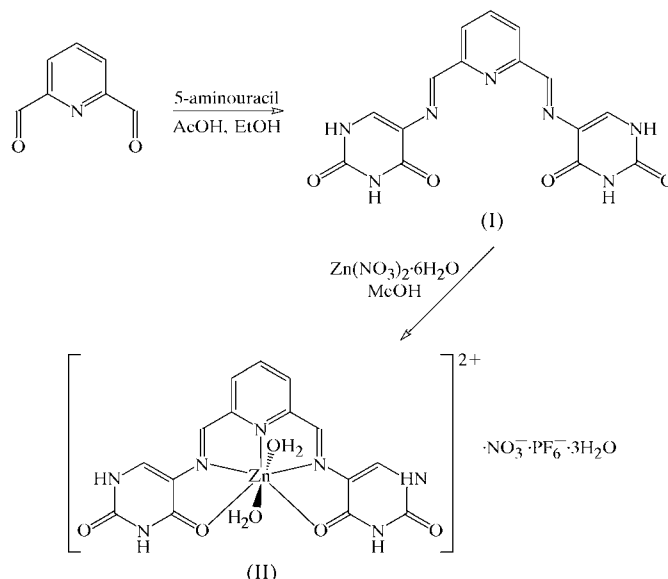
The mononuclear cation contains ligand (I) with a Zn centre and two aqua ligands. The cationic complex crystallizes with one nitrate anion, one hexafluorophosphate anion and three water molecules in the asymmetric unit, and ligand (I), with its two imine groups in ortho positions with respect to the pyridine N atom, behaves as a symmetrical N,N′,N,O,O′-pentadentate chelate. The Zn ion is seven-coordinated by two imine N atoms, one pyridine N atom, two carbonyl O atoms and two water O atoms (Fig. 1).

The Zn ion adopts a pentagonal–bipyramidal geometry. Three N atoms and two O atoms of ligand (I) (N1, N2, N5, O4 and O6) form a pentagon, while the axial sites are occupied by atoms O1 and O2, which subtend an angle of 169.84 (6)° at the metal centre. For an ideal pentagonal–bipyramidal complex, each of the five angles subtended at the equatorial plane should be 72° (Table 1). The angles around the Zn atom defined by adjacent donor atoms in the equatorial plane are not equivalent and lie in the range 70.92 (5)–73.12 (4)°. It should be pointed out here that, for an ideal pentagonal array of donor atoms, a cyclic ligand with identical donor atoms and bond lengths is required. As can be seen from the angles, the coordination polyhedra around the Zn ion can be visualized as being slightly distorted, with O_{water}—Zn—O,N angles in the range 84.90 (5)–94.96 (6)°. The angle between the MN_3O_2 plane and the plane including the metal and the two axial O atoms is 89.12 (12)°. This ligand disposition in (II) is consistent with approximate C_{2v} point-group symmetry for the molecule.

Although the azomethine N atoms are typically stronger donors than pyridine, the two $Zn—N_{imine}$ bond distances in the present complex are longer than the $Zn—N_{pyridine}$ distance, the formal double-bond character of the imino linkages N2=C6 and N5=C11 having been retained. This is probably due to the geometric requirements of the N_3O_2-pentadentate ligand, and the fact that the pyridine N-atom

donor occupies the central position of the pentadentate ligand and is forced into a shorter than normal interaction with the metal because of the restraints of the two chelating arms either side of the coordinating atom. The fact that the Zn—O$_{water}$ bond distances are shorter than the Zn—O$_{uracil}$ bond distances reflects the stronger donor capability of the water molecules.

There are several structures reported in the literature containing various transition metal complexes of 2,6-di-formylpyridine-based ligands (Gregoliński *et al.*, 2006; Valencia *et al.*, 2001). Inspection of the *M*—N bond distances in (II) and in these examples shows that the two *M*—N$_{imino}$ bonds are *ca* 0.1–0.2 Å longer than the corresponding *M*—N$_{pyridine}$ bond within each metal–tridentate chelate unit. Moreover, it is observed that the N$_{imino}$—*M*—N$_{pyridine}$ bond angle for the five-membered chelate rings of 2,6-diformyl-pyridine-based complexes is inversely related to the magnitude of the *M*—N$_{pyridine}$ bond. As the *M*—N$_{pyridine}$ distance increases from 2.1672 (15) in (II) to 2.281 (6) (*M* is Cd; Valencia *et al.*, 2001) to 2.325 (4) (*M* is Ag; Valencia *et al.*, 2001) to 2.671 (2) Å (*M* is La; Gregoliński *et al.*, 2006), the corresponding inner 'bite' angle decreases continually from 71.34 (average) to 69.2 (average) to 68.45 (average) to 60.99° (average).

The C—N bond lengths in the uracil rings (Table 1) range from 1.354 (3) to 1.368 (2) Å for the C7–C10/N3/N4 ring and from 1.350 (3) to 1.378 (2) Å for the C12–C15/N6/N7 ring, which are shorter than a C—N single-bond length (*ca* 1.443 Å; Allen *et al.*, 1987), but longer than a typical C=N bond length (*ca* 1.269 Å), indicating delocalization. The most notable feature of the crystal structure of (II) is the unexpected metallation of the C=O group at the 4-position of the uracil units. Although few examples of transition metal complexes containing uracil residues have been described so far (Burrows *et al.*, 1996; Hueso-Ureña *et al.*, 2000), the arrange-ment found in (II), where the nucleobases metallate through one carbonyl group, is very unusual (Fillaut *et al.*, 2002). The C10=O4 and C15=O6 bond lengths of the carbonyl groups involved in the intramolecular interaction with the Zn atom, even if slightly longer than in free uracil [1.227 (2) Å; Taylor & Kennard, 1982], do not significantly differ from that observed in the known uracil derivatives containing metal complexes (Burrows *et al.*, 1996; Hueso-Ureña *et al.*, 2000; Fillaut *et al.*, 2002). This points to a weak interaction between the uracil unit and the Zn atom.

In order to analyse the influence of the coordination of the two uracil carbonyl groups to the zinc centre, the bond lengths of the two uracil rings in (II) have been compared with those determined for the free ligand. The 'distal' C9=O3 and C14=O5 separations, which are in the usual range for a C=O double bond (Etter & Reutzel, 1991), are slightly shorter and longer, respectively, in (II) than in the free uracil molecule [1.218 (2) Å]. The C8—N3/C13—N6 and C10—N4/C15—N7 bond lengths are shorter in (II) than in free uracil [1.380 (2) and 1.383 (2) Å, respectively], while the C7—C8 and C12—C13 distances are longer with respect to the free nucleobase [1.338 (2) Å]. The C7—C10 and C12—C15 bond lengths are intermediate between a single C—C bond (*ca* 1.54 Å) and a C=C double bond (*ca* 1.34 Å), and the equivalent bond distance for these bonds in free uracil is 1.440 (2) Å. Finally, it is observed that the N3—C9 and N4—C9 bond distances are notably shorter in (II) than in free uracil [1.379 (2) and 1.373 (2) Å, respectively], and slight differences are observed for the N6—C14 and N7—C14 bonds.

Experimental

Crystal data

[Zn(C$_{15}$H$_{11}$N$_7$O$_4$)(H$_2$O)$_2$]-(NO$_3$)(PF$_6$)·3H$_2$O	$\beta = 77.957$ (6)°
$M_r = 715.74$	$\gamma = 73.665$ (6)°
Triclinic, $P\bar{1}$	$V = 1291.22$ (18) Å^3
$a = 8.8127$ (7) Å	$Z = 2$
$b = 11.5868$ (9) Å	Mo $K\alpha$ radiation
$c = 13.5365$ (11) Å	$\mu = 1.13$ mm^{-1}
$\alpha = 81.433$ (6)°	$T = 296$ K
	$0.64 \times 0.43 \times 0.24$ mm

Data collection

Stoe IPDSII diffractometer	18919 measured reflections
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)	6038 independent reflections
	5161 reflections with $I > 2\sigma(I)$
$T_{min} = 0.669$, $T_{max} = 0.836$	$R_{int} = 0.034$

Refinement

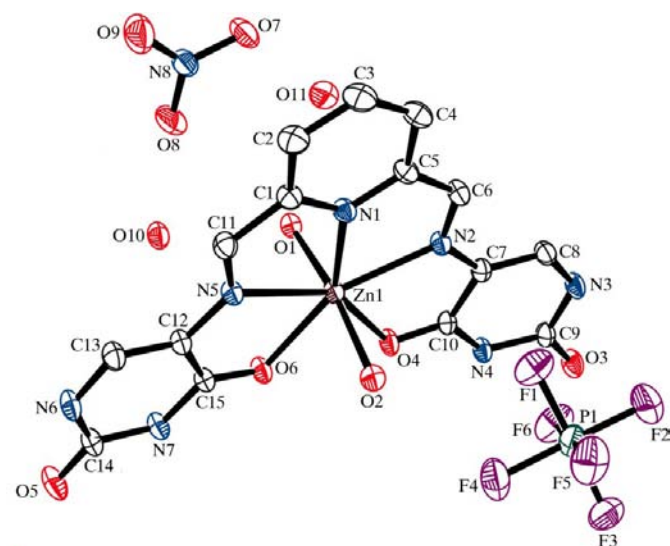|	
$R[F^2 > 2\sigma(F^2)] = 0.030$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.083$	
$S = 1.04$	
6038 reflections	$\Delta\rho_{max} = 0.35$ e Å^{-3}
429 parameters	$\Delta\rho_{min} = -0.34$ e Å^{-3}

Figure 1
A view of (II), showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

Table 1
Selected geometric parameters (Å, °).

Zn1—O1	2.0917 (14)	N3—C8	1.357 (2)
Zn1—O2	2.1168 (15)	N4—C9	1.364 (2)
Zn1—N1	2.1672 (15)	N4—C10	1.368 (2)
Zn1—O6	2.2419 (13)	N5—C11	1.268 (2)
Zn1—N2	2.2443 (14)	N5—C12	1.389 (2)
Zn1—N5	2.2732 (14)	N6—C13	1.350 (3)
Zn1—O4	2.2896 (13)	N6—C14	1.363 (3)
O3—C9	1.225 (2)	N7—C15	1.363 (2)
O4—C10	1.232 (2)	N7—C14	1.378 (2)
O5—C14	1.212 (2)	C7—C8	1.350 (2)
O6—C15	1.234 (2)	C7—C10	1.437 (3)
N2—C6	1.268 (2)	C12—C13	1.347 (2)
N2—C7	1.401 (2)	C12—C15	1.441 (2)
N3—C9	1.354 (3)		
O1—Zn1—N1	94.96 (6)	O2—Zn1—N5	87.47 (5)
O2—Zn1—N1	94.72 (6)	N1—Zn1—N5	70.92 (5)
O1—Zn1—O6	84.90 (5)	O6—Zn1—N5	72.15 (5)
O2—Zn1—O6	85.51 (6)	O1—Zn1—O4	87.17 (5)
O1—Zn1—N2	93.27 (5)	O2—Zn1—O4	86.83 (5)
O2—Zn1—N2	92.68 (6)	O6—Zn1—O4	73.12 (4)
N1—Zn1—N2	71.81 (5)	N2—Zn1—O4	72.05 (5)
O1—Zn1—N5	92.78 (5)		

The coordinates of the H atoms of the water molecules were determined from a difference map and refined isotropically subject to a restraint of O—H = 0.82 (1) Å. All other H atoms were positioned geometrically and refined with a riding model, fixing the C—H and N—H bond lengths at 0.93 and 0.86 Å, respectively. The $U_{iso}(H)$ values were constrained to $1.2U_{eq}$(parent atom).

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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