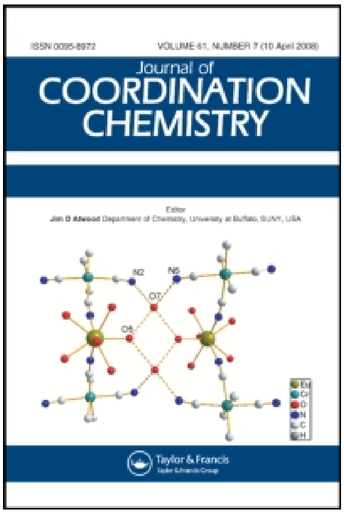

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Doubly bridged molecular ribbons in the structure of an ionic complex, hydronium zinc(II) pyrazine-2,3-dicarboxylate

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The structure of dihydronium [*catena*-bis(μ-pyrazine-2,3-dicarboxylato-N,O,O′)zinc(II)], (H3O)2[Zn(2,3PZDC)2], is composed of polyanionic ribbons of zinc(II) ions linked by double bridging 2,3-PZDC ligand molecules. Each ligand uses an N,O bonding moiety formed by one carboxylic group [Zn–O 2.071(2) Å; Zn–N 2.184(2) Å] and a monodentate oxygen atom of the other carboxylate group [Zn–O 2.092(2) Å]. Coordination around the zinc(II) ion is strongly distorted octahedral. Hydronium cations $(H_3O)^{1+}$ link the ribbons by hydrogen bonds.

Keywords: Pyrazine-2,3-dicarboxylic acid; Zinc complex; X-ray structure analysis

1. Introduction

The pyrazine-2,3-dicarboxylate (2,3-PZDC) ligand, with six potential chelating sites, can bridge metal ions to form polymetallic complexes. The number of complexes formed for a particular metal depends on the conditions of the chemical procedures adopted. For example, three copper complexes with different crystal structures have been reported: Cu[H(2,3-PZDC)]Cl [1], Cu(2,3-PZDC)$(H_2O)_2 \cdot 2H_2O$ [2,3] and Cu[H(2,3-PZDC)$_2$]$\cdot 2H_2O$ [2–4]. The structures of three Ca(II) complexes are also known [5–7]. Two zinc compounds have been obtained and their structures determined: Zn(2,3-PZDC)(H_2O) [8] and Zn(2,3-PZDC)$(H_2O)_3$[9]. In the course of our systematic structural studies of metal complexes with diazine dicarboxylate ligands, we report here a new zinc(II) complex obtained with the 2,3-PZDC ligand and its crystal structure determined by X-ray diffraction.

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Table 1. Crystal data and structure refinement details for (H3O)2[Zn(2,3-PZDC)2].

Empirical formula	$C_6H_5N_2O_5Zn$
Formula weight	267.5
Temperature	293 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions	$a = 14.478(3)$ Å $b = 8.439(2)$ Å $c = 12.861(3)$ Å $\beta = 114.66(3)^\circ$ $V = 1428.05$ Å^3
Z	4
Calculated density	2.026 g cm^{-3}
μ(Mo Kα)	1.79 mm^{-1}
$F(000)$	880.0
Crystal size	$0.26 \times 0.28 \times 0.30$ mm^3
Max 2θ for data collection	60.11°
Index range	$0 \le h \le 19$, $-11 \le k \le 0$, $-16 \le l \le 16$
No. of measured reflections	1986
No. of unique reflections with $F_o > 4\sigma(F_o)$	1628
R_{int}	0.0256
Method of structure solution	Direct method
Method of structure refinement	Full-matrix least-squares on F^2
No. of parameters refined	143
Goodness-of-fit on F^2	1.104
Final $R1$ $[F_o > 4\sigma(F_o)]$	0.0334
Final $wR2$ index	0.1045
Largest diff. peak and hole	0.84 and −0.38 e Å^{-3}
Weight parameters (A, B)	0.0683, 1.14
Mean shift/esd	0.054

2. Experimental

The title compound was synthesized by mixing aqueous solutions of zinc chloride (Aldrich) and pyrazine-2,3-dicarboxylic acid dihydrate (Aldrich), each containing 1 mmol of the reagent in 50 mL of hot water. The mixture was boiled for 1 h and then left to crystallize at room temperature. Rectangular, colorless single crystals were deposited after a few days. The dimensions of a single crystal used for X-ray data collection are given in table 1.

X-ray reflections were measured at room temperature using a KUMA KM4 four-circle diffractometer operating in the ω–2θ mode. Unit cell parameters were obtained by least-squares fit to 25 reflections ($15^\circ < 2\theta < 30^\circ$). Reflections were processed using profile analysis and corrected for Lorentz factor and polarization effects. Nonhydrogen atoms were located by the direct method using the SHELXLS [10] program and hydrogen atoms were found by successive Fourier syntheses. Final refinement on F^2 by the full-matrix least-squares method was performed on positional parameters of all atoms, anisotropic temperature factors of all nonhydrogen atoms and isotropic temperature factors of hydrogen atoms. The weighting scheme used was of the form $w = 1/[\sigma^2(F_o^2) + (AP)^2 + BP]$, where $P = [\max(F_o^2,0) + 2F_c{}^2]/3$. The A and B parameters and other experimental details are listed in table 1. Calculations were carried out using the SHELXL97 program [11]. Selected bond lengths and angles are given in table 2.

Table 2. Selected interatomic distances (Å) and bond angles (°) in (H3O)2[Zn(2,3-PZDC)2].

Zn coordination				
Zn–O1	2.071(2)	O1–Zn–O3	105.94(6)	
Zn–O1$^{\mathrm{I}}$	2.071(2)	O3–Zn–O1$^{\mathrm{I}}$	88.11(6)	
Zn–O3	2.092(2)	O1$^{\mathrm{I}}$–Zn–N1$^{\mathrm{I}}$	77.27(6)	
Zn–N1$^{\mathrm{I}}$	2.184(2)	N1$^{\mathrm{I}}$–Zn–O1	91.73(6)	
Zn–N1	2.184(2)	N1–Zn–O1	77.27(6)	
Zn–O3$^{\mathrm{I}}$	2.092(2)	O3$^{\mathrm{I}}$–Zn–O1	88.11(6)	
Pyrazine-2,3-dicarboxylate ligand				
N1–C2	1.337(2)	C6–N1–C2	118.5(2)	
C2–C3	1.387(3)	N1–C2–C3	120.8(2)	
C3–N2	1.340(2)	C2–C3–N2	120.9(2)	
N2–C5	1.328(3)	C3–N2–C5	117.8(2)	
C5–C6	1.392(3)	N2–C5–C6	121.5(2)	
C6–N1	1.330(3)	C5–C6–N1	120.6(2)	
C2–C7	1.510(3)			
C7–O1	1.244(2)	O1–C7–O2	126.0(2)	
C7–O2	1.250(2)			
C3–C8	1.517(3)			
C8–O3	1.236(2)	O3–C8–O4	125.(2)	
C8–O4	1.247(2)			
Hydrogen bonds				
D–H···A	D–A	D–H	H···A	D–H–A
O10–H2···O2$^{\mathrm{II}}$	2.501(3)	1.03(4)	1.48(4)	177(4)
O10–H11···N2$^{\mathrm{III}}$	2.745(3)	0.88(4)	1.87(4)	175(4)
O10–H12···O4$^{\mathrm{IV}}$	2.496(3)	0.86(8)	1.81(7)	136(7)

Symmetry codes: $^{\mathrm{I}}-x+1, y, -z+1/2$; $^{\mathrm{II}}x, y-1, z+1$; $^{\mathrm{III}}x-1/2, y-1/2, z+1$; $^{\mathrm{IV}}x-1/2, -y+3/2, z+1/2$.

3. Discussion

The structure of the title compound is composed of polyanionic ribbons in which Zn(II) ions are bridged by two 2,3-PZDC ligand molecules. This mode of bridging is illustrated in figure 1 and the atom numbering scheme is shown in figure 2. Each zinc(II) ion is *cis*-coordinated by N,O bonding moieties donated by two ligand molecules and two monodentate carboxylate oxygen atoms, each belonging to a different ligand. In this way, extended ribbons of zinc ions linked by double bridging 2,3-PZDC molecules are formed. The metal ion nitrogen and oxygen atoms form a strongly distorted octahedron with the basal plane formed by N1$^{\mathrm{I}}$, O1, O1$^{\mathrm{I}}$, O3 and Zn atoms, with atoms N1 and O3$^{\mathrm{I}}$ located at the apices. Maximum and minimum shifts from the basal plane are −0.273(1) (O$^{\mathrm{I}}$ atom) and −0.000(1) Å (Zn atom), respectively. Mean deviation from the plane is 1.190 Å. An interesting feature is the absence of any coordinated water oxygen atoms, in contrast to the structures reported in Refs [8] and [9]. Pyrazine ring atoms are coplanar with a mean deviation from the plane of 0.009 Å. The plane of the carboxylate group, which contributes one of its oxygen atoms to the N,O bonding moiety, makes the dihedral angle with the plane of the pyrazine ring 7.67°. The plane of the second carboxylate group, which donates one of its oxygen atoms for coordination, makes a dihedral angle of 74.5° with the plane of the pyrazine ring. This geometry of the 2,3-PZDC moiety as well as bond distances and angles within it are close to those reported for the parent acid H_2(2,3-PZDC) · $2H_2O$ [12].

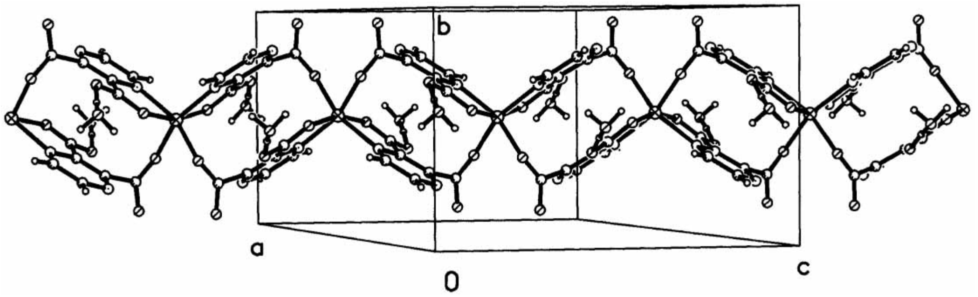

Figure 1. Packing diagram of the structure of (H3O)2[Zn(2,3-PZDC)2]. Broken lines indicate hydrogen bonds. For clarity, only two ribbons are shown.

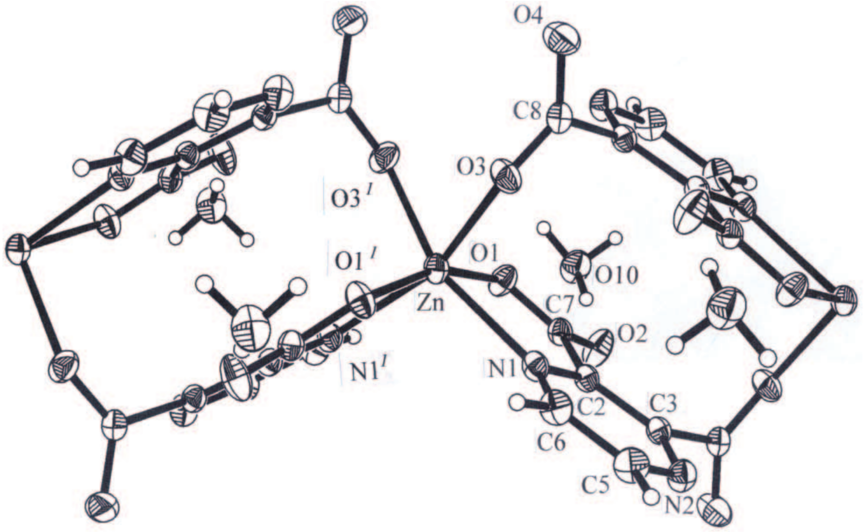

Figure 2. (H3O)2[Zn(2,3-PZDC)2] structural unit with atom numbering scheme. Hydrogen atoms attached to the pyrazine ring are not shown. The nonhydrogen atoms are represented by 50% probability ellipsoids.

A surprising feature of the structure of the title compound is the position of the hydrogen atom, which should be attached to one of the ligand carboxylic groups to maintain the charge balance. However, repeated examination of the Fourier maps indicated that this hydrogen atom is shifted to the solvation water molecule, forming a hydronium cation. In this way the ribbons acquire negative charge and the structure of the title compound can be visualized as composed of polyanionic ribbons with hydronium cations between them (see figure 1). The latter act as donors in hydrogen bonds [O–H$\cdots$O 2.50(1) Å] to the unbonded carboxylic oxygen atoms and in a hydrogen bond to the hetero ring nitrogen atom [O–H$\cdots$N 2.74(1) Å]. Each of these atoms belongs to a different adjacent ribbon.

It is interesting to compare the molecular pattern observed in the title compound with those reported in the structures of triclinic Zn(2,3-PZDC)$(H_2O)_3H_2O$ [8] and monoclinic Zn(2,3-PZDC)$(H_2O)_2H_2O$ [9]. The former was obtained by reacting the parent acid with zinc acetate dihydrate, the latter with zinc nitrate hexahydrate. In both, one ligand molecule is bridging adjacent metal(II) ions using an N,O bonding moiety donated by one carboxylate group and two oxygen atoms from the other carboxylate group. In the structure reported in Ref. [8], these oxygen atoms act in a bidentate mode, each being coordinated to two different adjacent zinc(II) ions. In this way a flat molecular ribbon is formed. Two water oxygen atoms complete the number of atoms coordinated to the zinc(II) ion to six, forming a fairly regular octahedron. Another molecular pattern has been discovered in the structure of the compound described [9], in which only one oxygen atom is bidentate, thus giving rise to a zigzag catenated pattern. The coordination number is also six, because there are three water oxygen atoms linked to the zinc(II) ion.

The tendency to form complexes with the 2,3-PZDC ligand exhibiting different structures is characteristic of divalent metal ions. For example, two series of 3d transition metal compounds have been reported. The first exhibits a 1:1 metal ion to ligand ratio, and the second a 1:2 ratio. In the latter, the ligand molecule is singly deprotonated. Both zinc(II) complexes reported [8,9] belong to the first series, in which the 2,3-PZDC molecules are doubly deprotonated. The molecular pattern observed in the structure of the title compound is the same as that observed in the manganese(II) complex (H3O)2[Mn(2,3-PZDC)2] [13] but differs from that reported for the copper compound $Cu[H(2,3\text{-PZDC})]_2 \cdot 2H_2O$ [2,4], in which Cu(II) ions are coordinated in the *trans* mode and the ribbons are neutral because a hydrogen atom remains attached to one carboxylate group of each ligand molecule.

Supplementary data

Listings of fractional atomic coordinates and equivalent isotropic displacements as well as the observed and calculated structure factors and anisotropic thermal parameters can be obtained on request from the authors. Detailed data on the structure of the title compound have also been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 243661. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http:\\www.ccdc.cam.ac.uk).

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