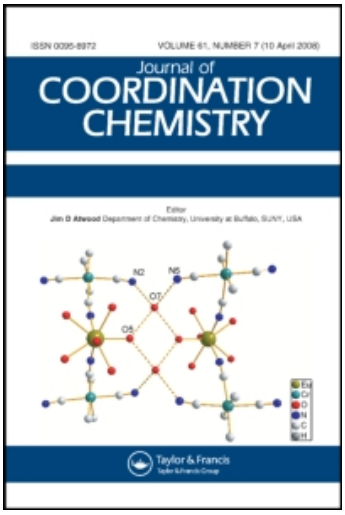

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MOLECULAR CHAINS IN THE STRUCTURE OF A ZINC(II) COMPLEX WITH PYRAZINE-2,6-DICARBOXYLATE AND WATER LIGANDS

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Crystals of *catena*-[diaqua-(μ-pyrazine-2,6-dicarboxylato-N,O,O′-μ-N′)]zinc(II) contain molecular chains in which the Zn(II) ions are bridged by pyrazine-2,6-dicarboxylate ligands via two symmetry-related oxygen atoms, each donated by a different carboxylic group [Zn–O(1) and O(1)^{I}: 2.182(2) Å] and the hetero-ring nitrogen atom [Zn–N(1): 2.049(3) Å] situated between them on one side and the second hetero-ring nitrogen atom [Zn–N(2)^{II} 2.118(3) Å] from the adjacent ligand on the other. The Zn(II) ion and four coordinating atoms are coplanar. Two symmetry related water molecules [Zn–O3 and O: 2.116(2) Å] situated above and below this plane complete the coordination around the Zn(II) ion to six atoms forming a distorted octahedron.

Keywords: Zinc complex; Pyrazine-2,6-dicarboxylate ligand; X-ray diffraction

INTRODUCTION

Diazine-dicarboxylate ligands, with six potential chelating atoms, form complexes exhibiting a large variety of polymeric molecular patterns, observed, for example, in alkaline earth [1–3] and 3d metal [4–12] compounds with pyrazine-2,3-dicarboxylate (2,3-PZDC) and water ligands, a strontium(II) complex with pyrazine-2,5-dicarboxylate (2,5-PZDC) and water ligands [13], calcium(II) [14] and strontium(II) [15] complexes with pyrazine-2,6-dicarboxylate (2,6-PZDC) and water ligands. Continuing these studies we report in this article the crystal structure of a zinc(II) complex with the latter ligands.

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EXPERIMENTAL

Colorless single crystals of the title compound were found in the mother liquor by evaporating at room temperature an aqueous solution containing zinc(II) nitrate hexahydrate and pyrazine-2,6-dicarboxylic acid dihydrate in the stoichiometric ratio 1 : 1. The dimensions of the sample crystal used for collecting X-ray diffraction data are given in Table I.

X-ray reflections were measured at room temperature using a KUMA KM4 four-circle diffractometer operating in 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. Non-hydrogen atoms were then located by the Patterson method using the SHELXLS program [16] and hydrogen atoms found by successive Fourier syntheses. Final refinement on F^2 by full-matrix least-squares was done on positional parameters of all atoms, anisotropic temperature factors of all non-hydrogen atoms and isotropic temperature factors of hydrogen atoms. A weighting scheme was used in the form: $w = 1/[\sigma^2(F_o^2) + (AP)^2 + BP]$, where $P = [\mathrm{Max}(F_o^2,0) + 2F_c^2]/3$. A, B are the parameters listed in Table I. Calculations were carried out using the SHELXL97 program [17]. Selected bond lengths and angles are listed in Table II. Detailed data on the structure reported in this article have been deposited with Cambridge Crystallographic Data Centre under code number CCDC 198905.

TABLE I Crystal data and structure refinement details for $Zn(2,6\text{-}PZDC)(H_2O)_2$

Empirical formula	$C_6H_6N_2O_{16}Zn$
Formula weight	267.5
Temperature (K)	293
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions (Å)	$a = 13.257(3)$ $b = 6.880(1)$ $c = 10.080(2)$ $\beta = 118.92(3)^\circ$
V (Å^3)	804.71
Z	4
Calculated density (g cm^{-3})	2.208
μ (MoKα) (mm^{-1})	3.07
$F(000)$	536.0
Crystal size (mm^3)	$0.26 \times 0.28 \times 0.30$
Max 2θ for data collection	60.12°
Index range	$-13 \le h \le 18,\ -9 \le k \le 0,\ -13 \le l \le 14.$
No. of measured reflections	1262
No. of unique reflections with $F_o > 4\sigma(F_o)$	903
R_{int}	0.0264
Method of structure solution	Patterson
Method of structure refinement	Full-matrix least squares on F^2
No. of parameters refined	82
Goodness-of-fit on F^2	1.070
Absorption correction	ψ-scan
Min. and max. transmission factors	0.402, 0.455
Final $R1$ [$F_o > 4((F_o)$]	0.0301
Final $wR2$ index	0.0854
Largest diff. peak and hole (e Å^{-3})	1.35 and −0.58
Weight parameters (A, B)	0.0618, 0.32
Mean shift/esd	0.004

TABLE II Selected bond lengths (Å) and angles (°) in [Zn(2,6-PZDC)$(H_2O)_2$

Zinc(II) ion coordination			
Zn–O(1)[O(1)^{I}]	2.182(2)	O(1)–Zn–N(2)^{II}	104.69(5)
Zn–O3 [O(3)^{I}]	2.116(2)	O(1)–Zn–N(1)	75.31(5)
Zn–N(1)	2.049(3)	O(3)–Zn–O(3)^{I}	176.1(1)
Zn–N(2)^{II}	2.118(3)	O(3)–Zn–N(1)	91.93(5)
		N(1)–Zn–N(2)^{II}	180
Pyrazine-2,6-dicarboxylate ligand			
N(1)–C(2)	1.325(2)	C(2)^{I}–N(1)–C(2)	121.6(3)
C(2)–C(3)	1.389(3)	N(1)–C(2)–C(3)	119.2(2)
C(3)–N(2)	1.340(3)	C(2)–C(3)–N(2)	120.4(2)
C(2)–C(7)	1.516(3)	O(1)–C(7)–O(2)	126.9(2)
C(7)–O(1)	1.265(3)		
C(7)–O(2)	1.231(3)		
Hydrogen bonds			
D–H · · · A	D–A	H · · · A	D–H–A
O(3)–H(31)–O(2)^{III}	2.746(3)	1.95(4)	173.7(3.8)
O(3)–H(32)–O(2)^{IV}	2.710(3)	1.88(4)	172.0(3.8)

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

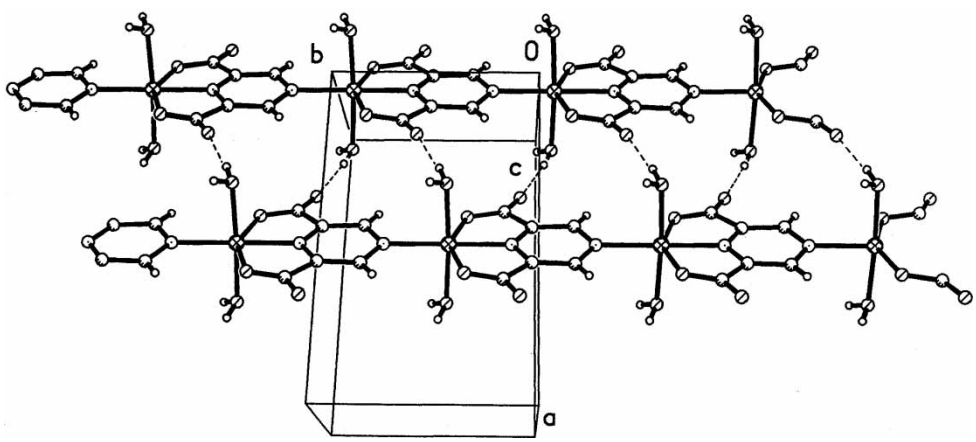

FIGURE 1 The alignment of the molecular chains in the structure of Zn (2,6-PZDC)$(H_2O)_2$. Dashed lines indicate the hydrogen bonds

DISCUSSION

The structure of the title compound can be visualized as composed of molecular chains propagating along the *b* axis of the unit cell (Fig. 1). The chain is built up by Zn(II) ions linked through the pyrazine ligand molecules. The bridging proceeds *via* two carboxylate oxygen atoms, each donated by a separate carboxylate group, and the hetero-ring nitrogen atom located between them (the N,O bonding moiety) on one side and the second hetero-ring nitrogen atom on the other. Figure 2 shows the enviroment of a Zn(II) ion with the atom labelling scheme. The coordination around the metal ion is distorted octahedral. The Zn(II) ion, two chelating carboxylate oxygen atoms and the two hetero-ring nitrogen atoms are coplanar. The observed Zn–O and Zn–N bond distances are typical for zinc coordination compounds with carboxylate ligands;

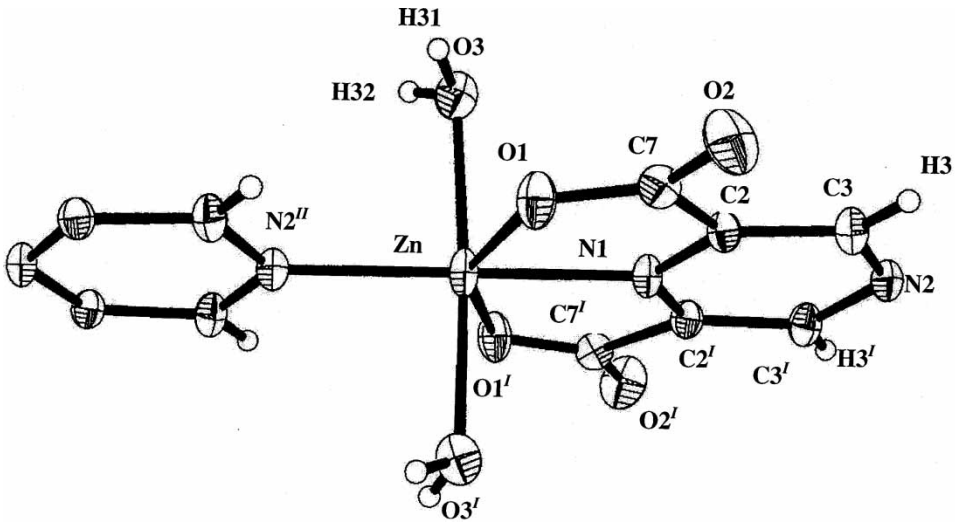

FIGURE 2 A fragment of the molecular chain in Zn(2,6-PZDC)$(H_2O)_2$ with numbering of atoms. The non-hydrogen atoms are shown at 50% probability level. Symmetry code: $^{I}-x+1, y, -z+1/2$; $^{II}x, y+1, z$.

however, the bond angles within the above plane deviate considerably from 90° (see Table II) indicating a distortion of the coordination polyhedron. Two symmetry-related water oxygen atoms, one above and the other below the base form the apices of an octahedron. The O(3)–Zn–O(3)^{I} angle is 176.1(1)° also indicating a distortion. The pyrazine ring of the ligand molecule deviates only slightly from planarity, since its carbon atoms are shifted from the mean plane by ±0.021(1) Å. On the other hand, the carboxylate group atoms are shifted by: C(7): 0.131(4) Å; O1: 0.170(4) Å and O2: 0.216(5) Å. The bond lengths and angles within the pyrazine ring fall in the same range as in the parent acid [18].

A simple hydrogen-bond scheme which holds together the molecular chains in the structure of the title compound consists of moderately strong bonds of 2.7 Å (for details see Table II) that link the coordinated water molecules with the unbonded carboxylate oxygen atoms in the adjacent chains (see Fig. 2).

The most interesting feature of the structure of the title compound is the use of both hetero-ring nitrogen atoms of the ligand molecule to bridge the zinc ions. The use of both pyrazine ring nitrogen atoms has been previously observed only in the structure of the strontium complex with pyrazine-2,5-dicarboxylate and water ligands [13]; however, in this structure two N,O bonding moieties of the ligand molecule are active in bridging, while in the title compound, apart from the N,O,O moiety, only a single hetero-ring N atom is bridging.

The coordination mode observed in the title compound also differs from that operating in two Zn(II) complexes with pyrazine-2,3-dicarboxylate ligands. In both compounds molecular ribbons have been detected, formed by Zn(II) ions bridged by ligand molecules via the N,O bonding moiety donated by one carboxylate group on one side and the oxygen atoms of the second carboxylate group on the other. In the triclinic complex Zn(2,3-PZDC)$(H_2O)_2 \cdot H_2O$ [5], the second carboxylate group is bidentate donating both its oxygen atoms, each to coordinate a different Zn(II) ion, forming a "closed" ribbon. In the monoclinic complex Zn(2,3-PZDC)$(H_2O)_3 \cdot H_2O$

[12], only one oxygen atom of the second carboxylate group coordinates the adjacent Zn(II) ion resulting in an "open" ribbon. The structure of the tetragonal compound $K_2Zn(2,3,5,6\text{-PZTC})(H_2O)\cdot 2.25H_2O$ [19] (2,3,5,6-PZTC = pyrazine-2,3,5,6-tetracarboxylate ligand) also contains molecular ribbons reminiscent of those observed in the triclinic complex [5]. The coordination of the Zn(II) ion in the above three compounds is distorted octahedral because the bridging bidentate carboxylate groups make angles of 85.4, 83.3 and 80°. with the plane of the pyrazine N,O bonding moiety in the triclinic, monoclinic and tetragonal complexes, respectively. Water oxygen atoms complete the coordination to six in each compound.

Since the pyrazine-2,6-dicarboxylate ligand has the same shape and dimensions as the pyridine-2,6-dicarboxylate (dipicolinate or 2,6-PDDC) ligand it is interesting to mention that in contrast to the structure of the title compound, the structure of a zinc dipicolinate $Zn[H_2(2,6\text{-PDDC})]_2\cdot 3H_2O$ contains monomeric units $Zn[H_2(2,6\text{-PDDC})]_2$ in which the Zn(II) ions are octahedrally coordinated by two N,O,O bonding moieties, each belonging to a different ligand molecule. The planes of the ligands are nearly perpendicular to each other giving rise to a distortion of the coordination octahedron [20–22]. In the compound $Zn_2(H_2O)_5(2,6\text{-PDDC})_2\cdot 2H_2O$ [20] one zinc (II) ion is coordinated in the same manner as in the previous complex; the other is chelated by five water oxygen atoms and an oxygen atom donated by one of the carboxylate groups coordinated to the first zinc(II) ion. This oxygen atom bridges the distorted zinc coordination octahedral, forming a dimeric unit.

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