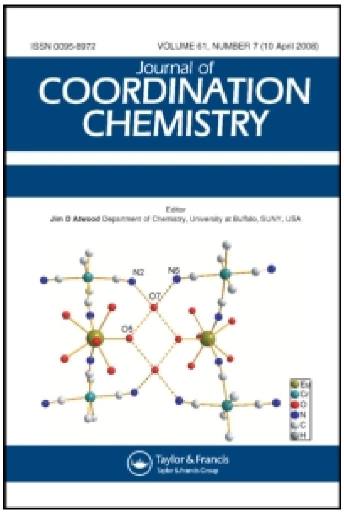

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Crystal and molecular structure of pyridazine-3-carboxylic acid hydrochloride and zinc(II) pyridazine-3-carboxylate tetrahydrate

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CRYSTAL AND MOLECULAR STRUCTURE OF PYRIDAZINE-3-CARBOXYLIC ACID HYDROCHLORIDE AND ZINC(II) PYRIDAZINE-3-CARBOXYLATE TETRAHYDRATE

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Crystals of pyridazine-3-carboxylic acid hydrochloride contain almost planar molecular sheets in which the cations, composed of acid molecules each with a hydrogen atom attached to one of the ring-nitrogen atoms, interact with chloride anions via a network of weak hydrogen bonds. Van der Waals interactions between sheets are indicated by the intersheet spacing of 3.47 Å. The crystal structure of di(aqua-*O*)bis(*trans*-pyridazine-3-carboxylato-*N*,*O*)zinc(II) dihydrate is composed of monomeric molecules in which the zinc(II) ion at the center of symmetry is coordinated by two ligand molecules each via its *N*,*O* bonding moiety. The ligand molecules and the metal ion form a *trans*-planar configuration. Two water oxygen atoms, above and below the plane, complete a distorted octahedron. A network of weak hydrogen bonds holds the monomers together.

Keywords: Pyridazine-3-carboxylic acid hydrochloride; Zinc(II) complex; Crystal structure

INTRODUCTION

Diazine carboxylate ligands, due to the number of their potential chelating sites, can form various polymeric molecular patterns in their compounds with metal ions. This ability is well illustrated by the structures of divalent metal complexes with pyrazine mono-, di- and tetracarboxylate ligands. Pyridazine carboxylate ligands also belong to this category since, in addition to the same number of potential chelating sites, they show different configurations, so that one may expect an influence on the observed coordination modes. As a part of our studies on the crystal chemistry of coordination compounds of divalent metal ions with diazine carboxylate ligands we report the crystal structures of the pyridazine-3-monocarboxylic acid hydrochloride and zinc(II) pyridazinate tetrahydrate determined by X-ray diffraction.

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EXPERIMENTAL

Single crystals of pyrazidine-3-carboxylic acid (**1**) suitable for X-ray data collection were obtained by recrystallization from 1 M hydrochloric acid, since the crystallization from aqueous solution provided thin needle-like specimens unsuitable for X-ray data collection. Zinc(II) pyridazinate tetrahydrate (**2**) was obtained by reacting hot aqueous solutions of zinc(II) acetate tetrahydrate and pyridazine-3-carboxylic acid in molar proportions of 1 : 2. After boiling under reflux for 2 h the solution was left at room temperature overnight to afford pale yellow single crystals.

X-ray reflections were measured at room temperature using a KUMA KM4 four-circle diffractometer operating in ω–2θ mode. Two standard reflections were monitored every 200 reflections. Unit cell dimensions and standard deviations were obtained by a least-squares fit to 25 reflections ($15^\circ < 2\theta < 30^\circ$). Reflections were processed using profile analysis and corrected for Lorentz and polarization effects. An empirical absorption correction based on a ψ-scan was applied. Nonhydrogen atoms were located by direct methods for **1** and by Patterson synthesis for **2** using the SHELXLS program [1] and hydrogen atoms were then found by successive Fourier syntheses. A final refinement on F^2 by a full-matrix least-squares method (SHELXL-97 [2]) was performed on the positional parameters of all atoms, anisotropic vibrational parameters of all non H-atoms and isotropic temperature factors of hydrogen atoms. The weighting scheme used was of the form $w = 1/[\sigma^2(F_o^2) + (A \times P)^2 + B \times P]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$. The parameters A and B (Table I), final atomic coordinates and equivalent isotropic displacements (Tables II and III) and selected bond lengths and angles (Tables IV and V) are given below. The observed and calculated structure factors and anisotropic thermal parameters can be obtained from the authors on request. Detailed data on the structures reported in this article have been deposited with Cambridge Crystallographic Data Centre under the code numbers CCDC 212611 (**1**) and CCDC 212612 (**2**).

RESULTS AND DISCUSSION

The packing diagram of compound **1** (Fig. 1) indicates that the structure is composed of molecular sheets aligned almost parallel to the (101) plane. The sheets contain molecules of pyridazine-3-carboxylic acid and hydrochloride molecules. Figure 2 shows a fragment of the sheet with an atomic labeling scheme. An interesting feature of this structure is the role of HCl. Its hydrogen atom is attached to one of the ring-nitrogen atoms (N1) and forms a weak hydrogen bond in which the latter is a donor and the chlorine atom acts as an acceptor (Table IV). In this way the pyridazine-3-carboxylic acid molecule gains a positive charge and acts as a $[H(C_4H_3N_2COOH)]^+$ cation while Cl^- is an anion. The observed N1–H1 bond length is 0.81(5) Å; the N–H bond length in the pyrrolidine ring of L-hydroxyproline was found to be 0.77(10) Å [3]. The atoms forming the pyridazine ring and the carboxylate carbon atom are almost coplanar, since the maximum displacements from the least-squares plane are +0.010(2) and −0.009(2) Å for the N2 and N1 atoms, respectively. However, the carboxylate oxygen atoms and the attached H11 hydrogen atoms deviate from the mean plane by +0.510(2), −0.463(2) and +0.500(2) Å, respectively. Also, the chloride is shifted from the mean plane by +0.466(2) Å. The hydrogen atom H1 involved in the

TABLE I Crystal data and structure refinement details for pyridazine-3-carboxylic acid hydrochloride (**1**) and zinc(II) pyridazinate tetrahydrate (**2**)

	Compound ***1***	*Compound* ***2***
Empirical formula	$C_5H_5N_2O_2Cl$	$C_{10}H_{14}N_4O_8Zn$
Formula weight	160	383.62
T (K)	293	
λ (Å)	0.71073	
Crystal system	Triclinic	Triclinic
Space group	$P(-1)$	$P(-1)$
Unit cell dimensions		
a (Å)	6.567(1)	5.366(1)
b (Å)	6.855(2)	7.563(1)
c (Å)	7.768(2)	9.672(2)
α (°)	109.17(3)	79.20(3)
β (°)	99.48(3)	89.03(3)
γ (°)	92.59(3)	71.33(3)
V (Å^3)	323.93	355.24
Z	2	1
D_{cald} (g cm^{-3})	1.646	1.793
μ(MoKα) (mm^{-1})	0.52	1.78
F(000)	164.0	196.0
Crystal size (mm^3)	$0.20 \times 0.25 \times 0.30$	$0.20 \times 0.30 \times 0.40$
Max. 2θ for data collection (°)	60.11	84.54
Index range	$-9 \le h \le 9$	$-9 \le h \le 10$
	$0 \le k \le 9$	$0 \le k \le 13$
	$-10 \le l \le 10$	$-12 \le l \le 12$
No. of measured reflections	1768	3491
No. of unique reflections with $F_o > 4\sigma(F_o)$	1710	3111
R_{int}	0.0106	0.0244
Method of structure solution	Direct method	Patterson
Method of structure refinement	Full-matrix least-squares on F^2	
No. of parameters refined	111	134
Goodness-of-fit on F^2	1.164	1.074
Final $R1$ [$F_o > 4\sigma(F_o)$]	0.0358	0.0370
Final $wR2$ index	0.0986	0.1000
Absorption correction	Ψ-scan	
Max. and min. transmission factors	0.855, 0.835	0.700, 0.669
Largest diff. peak and hole (eÅ^{-3})	0.29 and −0.37	1.77 and −1.28
Weight parameters (A, B)	0.0553, 0.08	0.0765, 0.00
Mean shift/esd	0.001	0.000

TABLE II Fractional atomic coordinates and equivalent isotropic displacements (Å^2) for pyridazine-3-carboxylic acid hydrochloride

Atom	x	y	z	U_{eq}
Cl	0.72570(5)	0.71900(6)	0.71597(4)	0.0352(1)
N1	0.1369(2)	0.7519(2)	−0.0287(2)	0.0336(3)
N2	0.0543(2)	0.7478(2)	0.1149(2)	0.0318(2)
C3	0.1878(2)	0.7575(2)	0.2644(2)	0.0292(3)
C4	0.4038(2)	0.7688(2)	0.2757(2)	0.0336(3)
C5	0.4792(2)	0.7680(2)	0.1218(2)	0.0361(3)
C6	0.3364(2)	0.7596(2)	−0.0347(2)	0.0357(3)
C7	0.0968(2)	0.7585(2)	0.4303(2)	0.0326(3)
O1	−0.0945(2)	0.6686(2)	0.3841(2)	0.0426(3)
O2	0.1952(2)	0.8360(2)	0.5849(2)	0.0487(3)
H1	0.049(4)	0.742(3)	−0.120(4)	0.058(6)
H4	0.483(3)	0.768(3)	0.384(3)	0.047(5)
H5	0.623(3)	0.767(3)	0.121(3)	0.049(6)
H6	0.367(3)	0.758(3)	−0.156(3)	0.055(6)
H11	−0.145(5)	0.677(4)	0.482(4)	0.078(8)

TABLE III Fractional atomic coordinates and equivalent isotropic displacements (Å^2) for zinc(II) pyridazinate tetrahydrate

Atom	*x*	*y*	*z*	U_{eq}
Zn	0	0.5	0	0.0270(6)
N1	0.4982(2)	0.1519(2)	0.0991(1)	0.0296(2)
N2	0.2582(2)	0.2524(2)	0.1317(1)	0.0249(1)
C3	0.1522(2)	0.1952(2)	0.2497(1)	0.0254(2)
C4	0.2807(3)	0.0238(2)	0.3446(2)	0.0358(2)
C5	0.5258(3)	−0.0843(2)	0.3106(2)	0.0406(3)
C6	0.6271(3)	−0.0127(2)	0.1867(2)	0.0353(2)
C7	−0.1176(2)	0.3311(2)	0.2734(1)	0.0272(2)
O1	−0.2193(2)	0.4750(1)	0.1759(1)	0.0314(2)
O2	−0.2181(2)	0.2888(2)	0.3869(1)	0.0379(2)
O3	0.1648(2)	0.6889(2)	0.0903(1)	0.0332(2)
O4	0.2527(3)	0.5213(2)	0.3737(2)	0.0474(3)
H4	0.200(5)	−0.015(3)	0.426(2)	0.031(5)
H5	0.626(6)	−0.197(4)	0.366(3)	0.044(6)
H6	0.811(6)	−0.078(4)	0.156(3)	0.049(7)
H31	0.246(7)	0.724(5)	0.047(4)	0.064(9)
H32	0.212(5)	0.643(4)	0.164(3)	0.040(6)
H41	0.234(6)	0.568(4)	0.450(3)	0.054(8)
H42	0.402(7)	0.458(5)	0.370(4)	0.054(8)

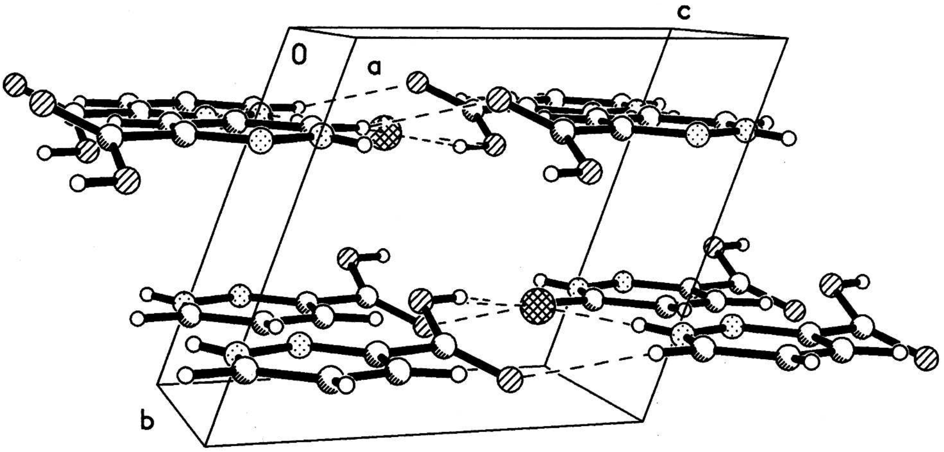

FIGURE 1 Packing diagram of pyridazine-3-carboxylic acid hydrochloride (**1**).

hydrogen bond to the chloride anion and the other hydrogen atoms attached to the pyridazine ring carbon atoms show displacements in the range 0.01–0.09 Å.

Within a sheet, each chloride anion is an acceptor in two weak hydrogen bonds. In the first, the carboxylate oxygen atom (O1) is the donor, while in the second it is the ring-nitrogen atom (N1) donated by the adjacent acid molecule. In this way, the chloride acts as a bridge and molecular ribbons propagating in the [010] direction can be visualized. Since the shortest distance observed between two atoms belonging to adjacent sheets amounts to 3.47 Å, van der Waals interactions can be expected.

Molecules of **2** occur in the structure as monomeric units, each composed of a zinc(II) ion at the center of symmetry coordinated by two ligand molecules in *trans*-planar positions, both ligands chelating via the *N*,*O* bonding moieties. Two water-oxygen atoms in

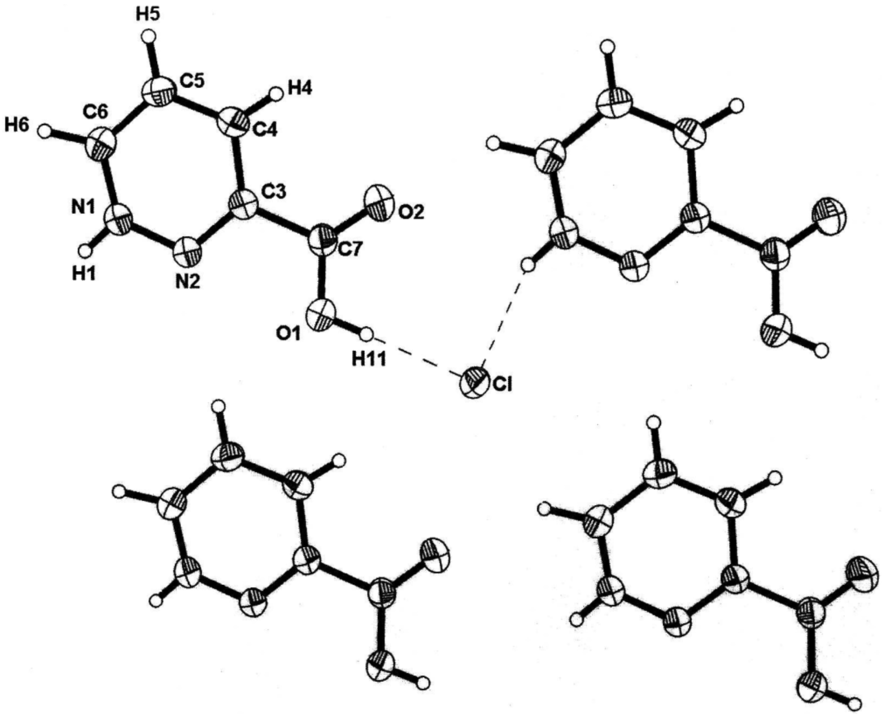

FIGURE 2 A fragment of a molecular sheet observed in the crystals of **1** with atom labeling. Dashed lines represent the hydrogen bonds. Nonhydrogen atoms are shown as 50% ellipsoids.

TABLE IV Selected bond lengths (Å) and bond angles (°) for pyridazine-3-carboxylate hydrochloride

N1–N2	1.326(2)	C6–N1–N2	123.8(1)	
N2–C3	1.316(2)	N1–N2–C3	115.1(1)	
C3–C4	1.390(2)	N2–C3–C4	123.8(1)	
C4–C5	1.366(2)	C3–C4–C5	117.8(1)	
C5–C6	1.391(2)	C4–C5–C6	117.6(1)	
C6–N1	1.318(2)	C5–C6–N1	119.2(1)	
C3–C7	1.505(2)	O1–C7–O2	126.2(1)	
C7–O1	1.313(2)			
C7–O2	1.198(1)			
Hydrogen bonds				
D–H···A	D–A	D–H	H···A	D–H–A
N1–H1···Cl[a]	3.027(14)	0.82(3)	2.26(3)	156(3)
O1–H11···Cl[b]	2.935(13)	0.86(3)	2.07(3)	175(3)

Symmetry code: $^{a}x-1, y, z-1$; $^{b}x-1, y, z$.

the axial position complete a slightly distorted octahedron around the metal ion. This is illustrated in Fig. 3, which also shows the atom labeling scheme. The relevant bond distances and angles are listed in Table V. The metal ion and the pyridazine ring and carboxylate atoms are almost planar, since the maximum deviations from the least-squares plane are −0.085(1) Å (Zn atom) and +0.080(2) Å (N2 atom). The packing diagram (Fig. 4) shows how the monomers interact via hydrogen bonds that link the solvation

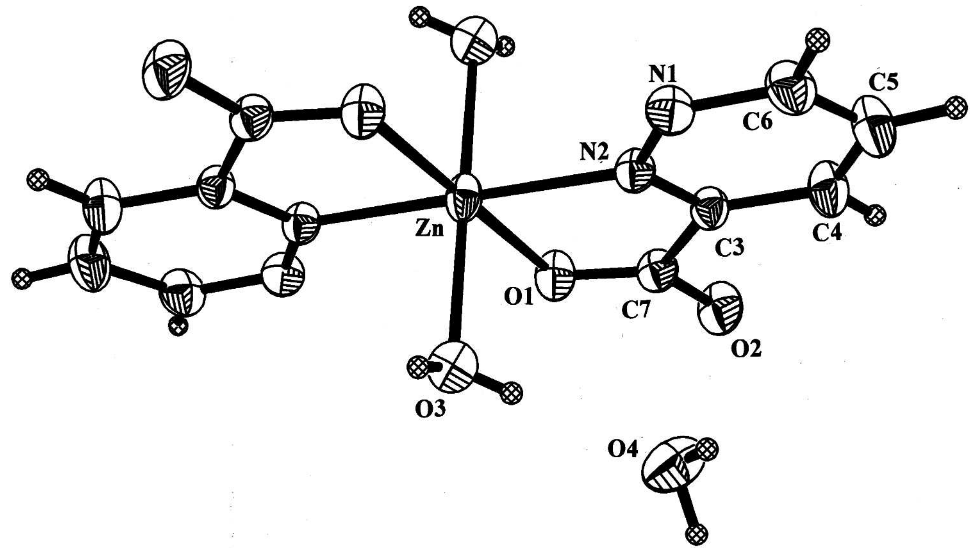

FIGURE 3 Di(aqua-*O*)bis(*trans*-pyridazine-3-carboxylato-*N*,*O*)zinc(II) molecule, showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level.

TABLE V Selected bond distances (Å) and angles (°) for zinc(II) pyridazinate tetrahydrate

Zinc(II) ion coordination				
Zn–O1 (O1^a)	2.066(1)	O1–Zn–N2	78.51(4)	
Zn–N2 (N2^a)	2.107(1)	O1–Zn–O3	89.56(5)	
Zn–O3 (O3^a)	2.179(1)	O1–Zn–N2^a	101.49(4)	
Pyridazine-3-carboxylate ligand				
N1–N2	1.330(1)	C3–N2–N1	121.7(1)	
N2–C3	1.324(2)	N2–N1–C6	117.9(1)	
C3–C4	1.394(2)	N2–C3–C4	122.3(1)	
C4–C5	1.373(2)	C3–C4–C5	116.7(1)	
C5–C6	1.390(2)	C4–C5–C6	117.8(1)	
C6–N1	1.328(2)	C5–C6–N1	123.6(1)	
C3–C7	1.516(2)	O1–C7–O2	126.3(1)	
C7–O1	1.258(2)			
C7–O2	1.246(1)			
Hydrogen bonds				
D–H···A	D···A	D–H	H···A	D–H–A
O3–H31···N1^b	2.905(2)	0.68(4)	2.23(4)	178(4)
O3–H32···O4	2.768(2)	0.74(3)	2.04(3)	167(3)
O4–H41···O2^c	2.896(X)	0.86(3)	2.04(3)	170(3)
O4–H42···O2^d	2.798(2)	0.79(3)	2.01(3)	173(3)

Symmetry code: $^a -x, -y+1, -z$; $^b -x+1, -y+1, -z$; $^c -x, -y, -z+1$; $^d x+1, y, z$.

water molecules with the uncoordinated carboxylate oxygen atoms in the adjacent monomers, as well as the coordinated water molecules and the ring-nitrogen atoms (Table V).

The title compound **2** is isostructural with manganese(II) pyridazinate tetrahydrate [4], which has the same space group, almost the same lattice parameters and the

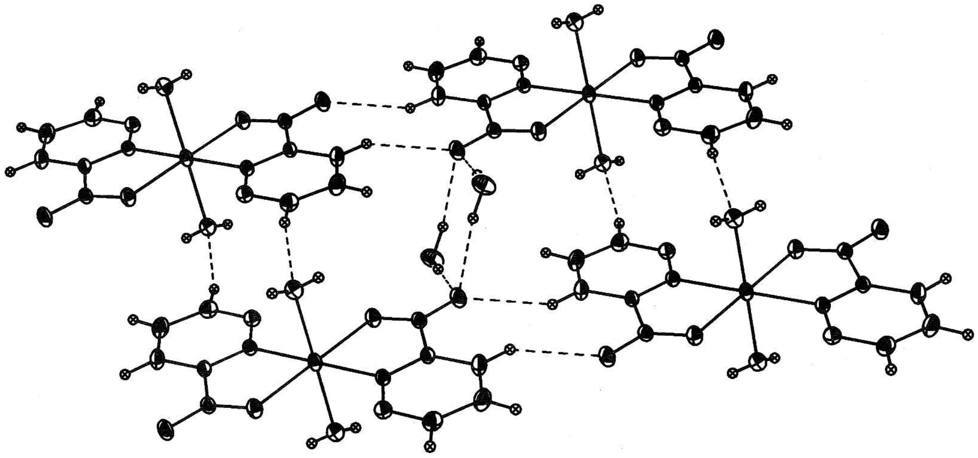

FIGURE 4 Packing diagram of zinc(II) pyridazinate tetrahydrate with hydrogen bonds represented as dashed lines.

metal ion in the unit cell is at the center of symmetry. The isostructurality index Π [5] is 0.00053.

The observed coordination mode in **2** is also the same as that previously reported in the structures of zinc(II) picolinate tetrahydrate [6] and zinc(II) pyrazinate tetrahydrate [7].

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