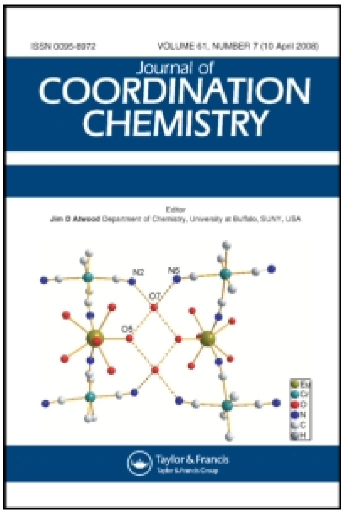

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Two-dimensional molecular pattern in the structure of a calcium(II) complex with pyrazine-2,3-dicarboxylate and water ligands

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Two-dimensional molecular pattern in the structure of a calcium(II) complex with pyrazine-2,3-dicarboxylate and water ligands

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The structure of di(aquo-*O*)(pyrazine-2,3-dicarboxylato-*N*,*O*; -*O*′,*O*″) calcium(II) hydrate [$Ca(2,3\text{-}PZDC)(H_2O)_2 \cdot H_2O$] contains molecular sheets in which Ca(II) ions are bridged by the carboxylate groups of the ligand molecules. Two bridging paths are evident. In the first, an N,O-bonding moiety formed by a hetero-ring nitrogen atom and the carboxylate oxygen atom nearest to it and both oxygen atoms of the second carboxylic group are active. The second path is formed by the other oxygen atom from the carboxylic group involved in the N,O-bonding moiety and an oxygen atom from the second carboxylic group. The latter atom is bidentate. A two-dimensional molecular pattern is formed. Each Ca(II) ion is also coordinated by two water oxygen atoms, making the number of coordinated atoms eight. The coordination polyhedron is a distorted pentagonal bipyramid with an oxygen atom at the apex on one side of the equatorial plane and two oxygen atoms forming the apices on the other side.

Keywords: Pyrazine-2,3-dicarboxylate; Calcium(II); Structure; Molecular sheets

1. Introduction

In the course of our structural studies of calcium(II) complexes with pyridine dicarboxylate ligands, we have found that, depending on the conditions of chemical preparation, complexes with different crystal structures are obtained [1, 2]. This tendency would also be expected in complexes with pyrazine dicarboxylate ligands. Hence, we prepared three calcium compounds containing the pyrazine-2,6-dicarboxylate ligand and their crystal structures were reported recently in the literature [3, 4]. Attempts to obtain complexes with the pyrazine-2,3-dicarboxylate (2,3-PZDC) ligand have also been successful. Depending on the Ca(II) compound used for the synthesis, two complexes were obtained and their crystal structures determined: $\{Ca[H(2,3\text{-}PZDC)](H_2O)_4\}^+Cl^-$ [5] and $\{Ca[H(2,3\text{-}PZDC)](H_3O)_3(NO_3)\}\{Ca[H(2,3\text{-}PZDC)](H_2O)_4\}^+(NO_3)^-$ [6]. In the course of recrystallization of the latter compound,

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single crystals of a new Ca(II) complex with the 2,3-PZDC ligand formed. Its crystal structure is reported in this article.

2. Experimental

Hot aqueous solutions, one containing 1 mmol of pyrazine-2,3-dicarboxylic acid (Aldrich) and the other containing 2 mmol of calcium(II) nitrate tetrahydrate, were mixed and boiled for 1 h. After evaporation to dryness at room temperature, single crystals were extracted from the mass of polycrystalline material. The crystals were identified by X-ray diffraction to be the compound $\{Ca[H(2,3\text{-}PZDC)](H_3O)_3(NO_3)\}\{Ca[H(2,3\text{-}PZDC)](H_2O)_4\}^+(NO_3)^-$ [6]. In an attempt to obtain more single crystals of this complex, the polycrystalline material was dissolved in boiling water and left to recrystallize. Well-formed, colorless single crystals appeared overnight in the mother liquid. Most of the crystals turned out to be twinned, but a few selected crystals could be isolated from the batch suitable for X-ray diffraction resulting in well-shaped diffraction peaks. Single-crystal X-ray crystallography has shown that these crystals represent a novel complex with a different structure. The crystal data and structure refinement details are given in table 1.

Table 1. Crystal data and structure refinement details for $Ca(2,3\text{-}PZDC)(H_2O)_2 \cdot H_2O$.

Empirical formula	$C_6H_8N_2O_7Ca$
Formula weight	260.22
Temperature	293 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 10.236(2)$ Å $b = 6.853(1)$ Å $c = 13.433(3)$ Å $\beta = 93.51(3)^\circ$ $V = 941.22$ Å^3
Z	4
Calculated density	1.836 g cm^{-3}
μ(Mo Kα)	0.69 mm^{-1}
$F(000)$	536.0
Crystal size	$0.10 \times 0.20 \times 0.23$ mm^3
Max. 2θ for data collection	60.12°
Index range	$-14 \le h \le 0,\ -9 \le k \le 0,\ -18 \le l \le 18$
No. of measured reflections	2747
No. of unique reflections with $F_o > 4\sigma(F_o)$	2465
R_{int}	0.0624
Method of structure solution	Direct method
Method of structure refinement	Full-matrix least-squares on F^2
No. of parameters refined	177
Goodness-of-fit on F^2	1.080
Absorption correction	Analytical
Min. and max. transmission factors	0.63394, 0.85863
Final $R1$ $[F_o > 4\sigma(F_o)]$	0.0440
Final $wR2$ index	0.1278
Largest diff. peak and hole	1.27 and −0.88 e/Å^3
Weight parameters (A, B)	0.0944, 0.34
Mean shift/esd	0.000

X-ray reflections were measured at room temperature using a KUMA KM4 four-circle diffractometer operating in the ω–2θ mode. Two standard reflections were monitored every 200 reflections. Unit cell dimensions and standard deviations were obtained by least-squares fit to 25 reflections in the 2θ range from 15 to 30°. Reflections were processed using profile analysis and corrected for Lorentz and polarization effects. An absorption correction based on the ψ-scan was applied. Nonhydrogen atoms were located by direct methods using the program SHELXLS [7] with the hydrogen atoms found by successive Fourier syntheses. Final refinement on F^2 by full-matrix least-squares methods using the program SHELXL97 [8] was carried out 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 was used in the form: $w = 1/[\sigma^2(F_o^2) + (AP)^2 + BP]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$. Values for the parameters A and B listed in table 1. Selected bond lengths and angles are given in table 2.

3. Discussion

The structure of the title compound contains molecular sheets in which the Ca(II) ions are bridged by the carboxylate groups of the ligand molecules. Figure 1 shows the packing diagram in which the two bridging paths can be easily recognized. Each ligand contributes both of its carboxylate groups in forming the bridge to adjacent Ca(II) ions: one group uses its N,O-bonding moiety [Ca–N1 2.587(1) Å; Ca–O1 2,410(1) Å], and the other uses both of its carboxylate oxygen atoms [Ca–O3 2.452(1) Å; Ca–O4 3.016(1) Å]. Figure 2 shows the atom-numbering scheme used. A catenated molecular assembly is formed in this way. However, a second bridging path operating between the chains can also be identified. It is formed by the second oxygen atom belonging to the carboxylate group participating in the N,O bonding, which is coordinated to the Ca(II) ion in the adjacent chain "above" [Ca–O2 2.466.(1) Å], while the oxygen atom of the other carboxylate group acting in bidentate mode coordinates the Ca(II) ion in the adjacent chain "below" [Ca–O4 3.017(2) Å]. A two-dimensional molecular sheet is formed in this way (see figure 1). In addition, each Ca(II) ion is surrounded by two water oxygen atoms [Ca–O5 2.446(1) Å; Ca–O6 2.367(1) Å], increasing the coordination number to eight. The coordination polyhedron is a distorted pentagonal bipyramid. The equatorial plane formed by the Ca, O1, O2, O3, O4, O4″ atoms is very distorted, as the maximum shifts from the average plane are +0.313(1) Å (for Ca) and −0.420(1) Å (for O4). The mean deviation from the plane is 0.254(1) Å. The O6 atom forms the apex on one side of the equatorial plane at 2.018(1) Å, while on the other side, the N1 and O5 atoms form two apices at 2.405(1) and 2.216(1) Å, respectively. The plane of the pyrazine ring also shows distortion, as indicated by the maximum shifts from the average plane: +0.219(1) (for C2) and −0.163(1) (for N1). The mean deviation from the plane is 0.138 Å. The planes of the carboxylate groups make the following angles with the average pyrazine ring plane: 96.0(1)° (for C7, O1, O2) and 51.9(1)° (for C8, O3, O4). The observed bond distances and angles in the title compound are close to those reported for the parent acid [9] and the Ca(II) coordination mode and the range of Ca–O bond lengths and angles agree with those most commonly reported for calcium complexes with carboxylate ligands [10].

Table 2. Selected bond lengths (Å) and angles (°) for Ca(2,3-PZDC)$(H_2O)_2 \cdot H_2O$.

Ca(II) coordination			
Ca–O1^{a}	2.410(1)	O1–Ca–O3	80.58(5)
Ca–N1	2.587(1)	O3–Ca–O4	46.22(4)
Ca–O2	2.466(1)	O4–Ca–O4^{a}	66.60(4)
Ca–O4	3.016(2)	O4^{a}–Ca–O2	82.93(4)
Ca–O4^{a}	2.322(2)	O2–Ca–O1^{a}	82.51(5)
Ca–O5	2.446(1)	O6–Ca–O1^{a}	86.02(5)
Ca–O3	2.452(1)	O6–Ca–O3	85.97(5)
Ca–O6	2.367(1)	O6–Ca–O4	66.79(4)
		O6–Ca–O4^{a}	78.72(4)
		O6–Ca–O2	82.93(4)
Ligand molecule			
N1–C2	1.336(2)	C6–N1–C2	117.7(1)
C2–C3	1.394(2)	N1–C2–C3	121.0(1)
C3–N2	1.334(2)	C2–C3–N2	121.0(1)
N2–C5	1.336(2)	C3–N2–C5	117.9(1)
C5–C6	1.384(2)	N2–C5–C6	120.9(2)
C6–N1	1.331(2)	C5–C6–N1	121.7(1)
C2–C7	1.512(2)		
C7–O1	1.258(2)	O1–C7–O2	126.8(1)
C7–O2	1.245(2)		
C3–C8	1.512(2)		
C8–O3	1.250(2)	O3–C8–O4	125.0(1)
C8–O4	1.239(2)		
Coordinated water molecules			
O5–H51	0.89(4)	H51–O5–H52	103(3)
O5–H52	0.76(3)		
O6–H61	0.75(3)	H61–O6–H62	114(3)
O6–H62	0.81(3)		
Solvation water molecule			
O7–H71	0.71(4)	H71–O7–H72	112(3)
O7–H72	0.75(3)		
Hydrogen bonds			
D–H···A	d(D–H···A)	d(H···A)	(D–H–A)
O5–H51···O7^{d}	2.784(2)	2.07(4)	178(4)
O5–H52···O7^{b}	2.710(2)	1.87(4)	174(4)
O6–H61···O5^{a}	2.887(2)	2.15(3)	167(3)
O6–H62···O3^{c}	2.723(2)	1.92(3)	175(3)
O7–H71···O1	2.784(2)	2.07(4)	178(4)
O7–H72···N2^{e}	2.790(2)	2.04(3)	172(3)

Equivalent positions: $^{a}-x, -y, -z$; $^{b}x, y-1, z$; $^{c}-x, -y+1, -z$; $^{d}-x+1/2, y-1/2, -z+1/2$; $^{e}-x+1/2, y+1/2, -z+1/2$.

The bridging mode in the title compound is only slightly different from that reported earlier for the compound Ca(2,3-PZDC)$(H_2O)_2 \cdot 2H_2O$, which was obtained by reacting pyrazine-2,3-dicarboxylic acid dihydrate with calcium carbonate. The second oxygen atom of the carboxylic group engaged in forming the N,O-bonding moiety does not participate in bridging. The structure of this compound is also monoclinic (space group $P2_1$); however, the unit cell volume is smaller (923.5 Å^3) and the lattice parameters are different [11]. The same bridging mode has also been observed in the orthorhombic structure of the strontium complex with the 2,3-PZDC and water ligands [12]. Hence, the title compound is the third example of a two-dimensional structure among the complexes with the 2,3-PZDC ligand.

By contrast, the bridging in two other Ca(II) complexes with the 2,3-PZDC ligand occurs via both bonding moieties of the ligand molecule, giving rise to polycationic

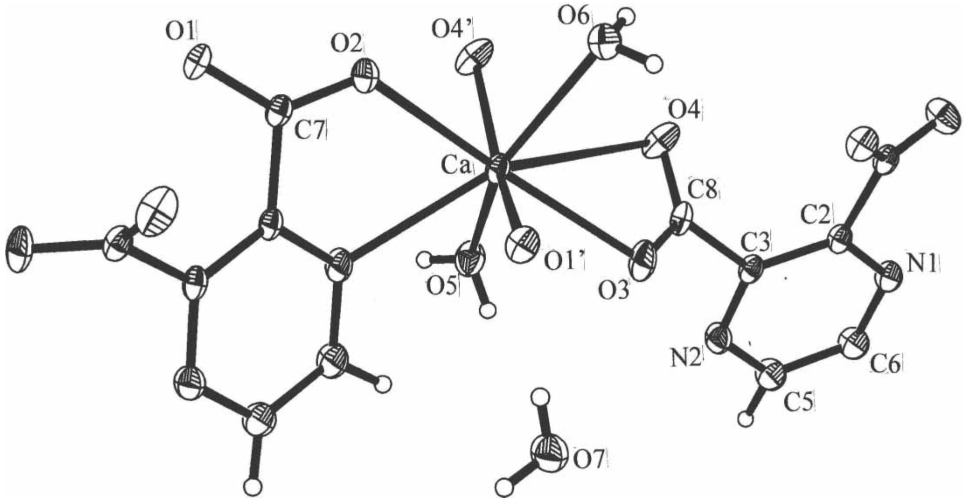

Figure 1. A fragment of a molecular sheet in the structure of Ca(2,3-PZDC)$(H_2O)_2 \cdot H_2O$.

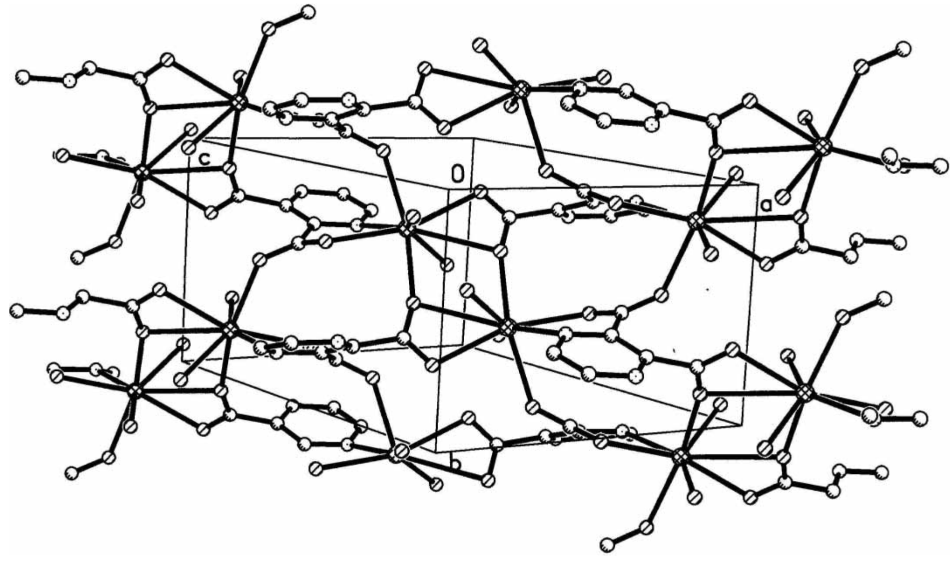

Figure 2. The structural unit of Ca(2,3-PZDC)$(H_2O)_2 \cdot H_2O$ with atom-labeling scheme. The nonhydrogen atoms are shown as 50% probability ellipsoids.

chains [5, 6]. A preferance to form catenated molecular patterns has been observed in the structures of many 3d transition metal complexes with the 2,3-PZDC ligand [6] and also in the magnesium(II) complex [13].

Acting as donors, the coordinated and solvation water molecules form a system of hydrogen bonds with bond distances ranging from 2.710(2) to 2.887(2) Å linking them with carboxylate oxygen and hetero-ring nitrogen atoms in adjacent molecular sheets. These bonds are responsible for the stability of the crystals. For detailed data, see table 2.

Supplementary data

Final atomic coordinates and equivalent isotropic displacements, as well as the observed and calculated structure factors and anisotropic thermal parameters, can be obtained from the authors on request. Detailed data on the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 246603.

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