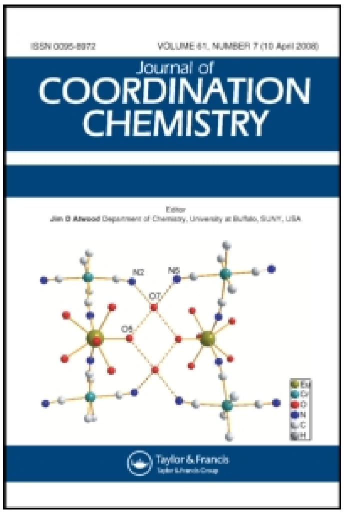

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Three-dimensional polymeric molecular pattern in the structure of a Ca(II) complex with pyrazine-2,3,5,6-tetracarboxylate and water ligands

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Three-dimensional polymeric molecular pattern in the structure of a Ca(II) complex with pyrazine-2,3,5,6-tetracarboxylate and water ligands

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Triclinic unit cell [space group $P\bar{1}$] of the calcium(II) complex with pyrazine-2,3,5,6-tetracarboxylate (2,3,5,6-PZTC) and water ligands [*poly*-bis(μ-aqua)di(μ-pyrazine-2,3,5,6-tetracarboxylate)tetracalcium(II)] contains four Ca(II) ions in two symmetry independent sites, two 2,3,5,6-PZTC ligands with their geometrical centers at the inversion centers at 0, 1/2, 1/2 and 0, 1/2, 0 and two coordinated water molecules. Metal ions are bridged by the ligand molecules *via* their N,O bonding moieties and carboxylate oxygen atoms as well as coordinated water oxygen atoms producing a densely packed three-dimensional molecular pattern. The Ca1 ion coordinates eight atoms at the corners of a distorted bicapped tetragonal bipyramid. The coordination number of the Ca2 ion is seven in a strongly distorted pentagonal bipyramid. The pyrazine ring planes of the ligands are parallel to each other forming molecular sheets stacked normal to the *a* axis. They are interconnected by carboxylate oxygen atoms coordinating calcium ions located between the adjacent sheets.

Keywords: Ca(II) complex; 2,3,5,6-PZTC; Ligand molecule

1. Introduction

Pyrazine-2,3,5,6-tetracarboxylate (2,3,5,6-PZTC) exhibits ten chelating sites: two hetero-ring nitrogen atoms and four potentially bidentate carboxylate groups. Therefore, one may expect formation of a variety of polymeric structures in metal coordination compounds with this ligand. Crystal structures of 3-d metal complexes with 2,3,5,6-PZTC confirm this expectation. Linear molecular ribbons with different bridging modes and the ligand molecules appearing as doubly or fully deprotonated have been reported [1–4]. Simple ionic structures consisting of $[Mn(H_2O)_6]^{2+}$ cations and doubly deprotonated $[H_2(2,3,5,6\text{-PZTC})]^{2-}$ anions [2], $[Mg(H_2O)_6]^{2+}$ cations and fully deprotonated $(2,3,5,6\text{-PZTC})^{4-}$ anions [5] have also been reported. In all above compounds the coordination around the metal ions is octahedral with coordination number six. We sought to study the bridging ability of the ligand when the metal ions show larger coordination numbers and more complicated coordination polyhedra.

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Therefore, in our research program on the crystal chemistry of calcium(II) coordination compounds with hetero-cyclic carboxylate ligands, an X-ray diffraction structural study has been undertaken on a Ca(II) complex with the title ligand. Infrared spectra at 293 K were also recorded.

2. Experimental

The title compound was obtained by reacting 50 mL of boiling aqueous solutions, one containing two mmols of calcium(II) acetate tetrahydrate, the other containing two mmols of pyrazine-2,3,5,6-tetracarboxylic acid. The mixture was boiled with stirring for one hour and then left to crystallize at room temperature. After a week, colorless well formed single crystals of the title compound were found in the mass of polycrystalline material. The dimensions of a crystal used for X-ray data collection are given in table 1.

Table 1. Crystal data and structure refinement details for $Ca_4(2,3,5,6\text{-PZTC})_2(H_2O)_2$.

Compound	$Ca_2(C_8N_2O_8)(H_2O)$
Color/shape	Colorless/rectangular block
Empirical formula	$C_8H_2N_2O_9Ca_2$
Formula weight	350.28
Temperature (K)	293(2)
Wavelength (Mo-Kα) (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	6.748(1)
b	9.368(2)
c	9.918(2)
α	75.68(3)
β	72.83(3)
γ	82.64(3)
V(Å^3)	560.11
Z	2
Calculated density (g cm^{-3})	2.005
μ (Mo-Kα) (mm^{-1})	1.04
F(000)	352.0
Crystal size (mm^3)	$0.12 \times 0.17 \times 0.51$
$\theta_{\min}$, $\theta_{\max}$ (°)	2.52, 30.09
Index range	$-9 \leq h \leq 0$, $-13 \leq k \leq 13$, $-13 \leq l \leq 13$
Total data/constraints/parameters	3398/0/198
Observed data with $[I > 4\sigma(I)]$	2772
R_{int}	0.0265
Goodness-of-fit on F^2	1.083
Final R_1 $[I > 4\sigma(I)]$	0.0490
Final wR_2 index	0.1492
Absorption correction	Analytical [6]
Min. and max. transmission	0.80657, 0.88075
Extinction correction	None
Largest diff. peak and hole (e Å^{-3})	1.20, −0.44
Weight parameters (A, B)	0.0911, 0.55
Mean shift/esd	0.000

X-ray diffraction data were collected 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 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 analytical absorption correction [6] was applied. Non-hydrogen atoms were located by direct methods and hydrogen atoms then found by successive Fourier syntheses. Final refinement on F^2 by full-matrix least squares method was performed on positional parameters of all atoms, anisotropic vibrational parameters of all non H-atoms and isotropic temperature factors of hydrogen atoms. Weighting scheme was used in the form: $w = 1/[\sigma^2(F_o^2) + (A * P)^2 + B * P]$, where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$. Structure solution and refinement were carried out using *SHELX97 and SHELXL97* program packages [7]. Data collection and refinement parameters are collected in table 1; selected bond lengths and angles in table 2.

Infrared spectra in the range from 400–4000 cm^{-1} were recorded at room temperature using a sample capsuled in a KBr disc. The sample was obtained by grinding the crystals extracted from the mother liquid. A Bruker Equinox 55 FTIR spectrometer with a resolution of 1 cm^{-1} was used. Observed intense bands with their assignments are listed in table 3.

3. Results and discussion

Centrosymmetric, triclinic unit cell of the title compound contains four (in two symmetry independent sites) Ca(II) ions, two fully deprotonated 2,3,5,6-PZTC ligand

Table 2. Selected bond distances (Å) and angles (°) for $\mathrm{Ca_2(2,3,5,6\text{-}PZTC)(H_2O)}$.

Ca1 coordination			
Ca1–O10$^{\mathrm{III}}$	2.824(3)	O10$^{\mathrm{III}}$–Ca1–O14$^{\mathrm{VIII}}$	70.15(7)
Ca1–O14$^{\mathrm{VIII}}$	2.958(2)	O11$^{\mathrm{VIII}}$–Ca1–N11	105.75(6)
Ca1–N11	3.160(2)	N11–Ca1–O24$^{\mathrm{IX}}$	87.42(7)
Ca1–O24$^{\mathrm{IX}}$	2.881(2)	O24$^{\mathrm{IX}}$–Ca1–O10$^{\mathrm{III}}$	74.51(9)
Ca1–O22$^{\mathrm{IV}}$	2.990(2)	O22$^{\mathrm{IV}}$–Ca1–O10$^{\mathrm{III}}$	59.81(5)
Ca1–O14$^{\mathrm{X}}$	2.697(2)	O12$^{\mathrm{VII}}$–Ca1–O14$^{\mathrm{X}}$	64.18(6)
Ca1–O12$^{\mathrm{VII}}$	2.847(2)	O22$^{\mathrm{IV}}$–Ca1–O11	66.21(5)
Ca1–O11	2.724(2)	O11–Ca1–N11	54.19(5)
Ca2 coordination			
Ca2–O10$^{\mathrm{III}}$	2.831(3)	O21–Ca2–O13$^{\mathrm{XI}}$	81.45(7)
Ca2–O22$^{\mathrm{IV}}$	2.890(2)	O13$^{\mathrm{XI}}$–Ca2–O23$^{\mathrm{XII}}$	72.92(6)
Ca2–O21	2.854(2)	O23$^{\mathrm{XII}}$–Ca2–O10$^{\mathrm{III}}$	71.37(7)
Ca2–O13$^{\mathrm{XI}}$	2.824(2)	O10$^{\mathrm{III}}$–Ca2–O22$^{\mathrm{IV}}$	61.05(6)
Ca2–O23$^{\mathrm{XII}}$	2.750(2)	O22$^{\mathrm{IV}}$–Ca2–O21	76.15(7)
Ca2–N21	2.843(2)	N21–Ca2–O23$^{\mathrm{IV}}$	136.55(5)
Ca2–O23$^{\mathrm{IV}}$	2.695(2)	O22$^{\mathrm{I}}$–Ca2–N11	79.94(6)
		O22$^{\mathrm{IV}}$–Ca2–O23$^{\mathrm{IV}}$	64.53(6)
		O21–Ca2–N21	56.21(5)
		Ca1–O10$^{\mathrm{III}}$–Ca2	94.81(8)
Hydrogen bonds			
O10–H101 ··· O14$^{\mathrm{VIII}}$	3.046(3)	O10–H101–O14$^{\mathrm{VIII}}$	121
O10–H102 ··· O12$^{\mathrm{VII}}$	2.736(3)	O10–H102–O12$^{\mathrm{VII}}$	160

Symmetry code (in respect to the inversion center located at 0,0,0): $^{\mathrm{I}}x, y, z-1$; $^{\mathrm{II}}x, y-1, z$; $^{\mathrm{III}}-x+1, -y+2, -z+1$; $^{\mathrm{IV}}-x+1, -y+1, -z+2$; $^{\mathrm{V}}-x+1, -y+2, -z+2$; $^{\mathrm{VI}}x-1, y, z$; $^{\mathrm{VI}}-x+1, -y+1, -z+1$; $^{\mathrm{VII}}-x, -y+2, -z+1$; $^{\mathrm{IX}}-x, -y+2, -z+1$; $^{\mathrm{X}}x+1, y, z$; $^{\mathrm{XI}}x, y, z+1$; $^{\mathrm{XII}}x, y+1, z$; $^{\mathrm{XIII}}-x, -y+1, -z+1$; $^{\mathrm{XIV}}-x, -y+2, -z+2$.

Table 3. Observed IR vibration frequencies (cm^{-1}) for Ca_2(2,3,5,6-PZTC)(H_2O) and their assignments.

Frequency (cm^{-1})	Intensity	Assignment
447	Medium	
550	Medium	Deformation modes of the
771	Strong	COO group
840	Strong	
900–1300	Broad band	Vibration modes of the pyrazine ring
1408	Medium	Stretching vibrations of the COO
1750	Strong	Group
3479	Strong	Vibration modes of the coordinated
3670	Strong	Water molecules

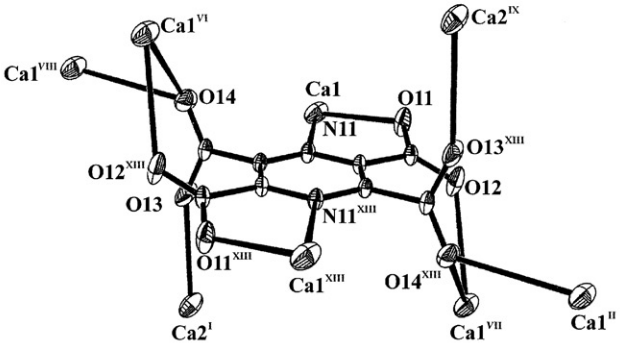

Figure 1. The bridging pathway *via* ligand molecule 1 in the structure of Ca_2(2,3,5,6-PZTC)(H_2O). For symmetry code, see table 2.

molecules with their geometrical centers in the inversion centers at 0, 1/2, 1/2 (molecule 1) and 0, 1/2, 0 (molecule 2) and two water molecules coordinated to the metal ions. All potential chelating sites of both ligand molecules are engaged in bridging the metal ions giving rise to a three-dimensional molecular network. Three bridging pathways are observed. The first, *via* the ligand molecule 1, the second *via* the ligand molecule 2 and the third *via* the coordinated water molecule.

N,O and N^{XIII}, O^{XIII}-bonding moieties of the ligand molecule 1 chelate the Ca1 and $Ca1^{XIII}$ ions, while the second oxygen atoms O12 and $O12^{XIII}$ are coordinated to $Ca1^{VII}$ and $Ca1^{VI}$ ions, respectively. Belonging to the remaining carboxylate groups oxygen atoms O13 and $O13^{XIII}$ are bonded to $Ca2^{I}$ and $Ca2^{IX}$ ions, respectively, and the O14 and $O14^{XII}$ oxygen atoms, each bidentate are bonded to the $Ca1^{VI}$ and $Ca1^{VIII}$ ions (O14) and $Ca1^{II}$ and $Ca1^{VII}$ ions ($O14^{XIII}$). Thus, ligand molecule 1 bridges six Ca1 ions and two Ca2 ions. This bridging pathway with the atom labelling in respect to the inversion center at 0, 0, 0 is shown in figure 1.

Having its geometrical center at the inversion center at 0, ½, 0, ligand molecule 2 chelates ten Ca ions. Figure 2 illustrates the bridging with atom labelling in respect to the inversion center at 0, 0, 0. The N,O-bonding moieties composed of N21, O21 and $N21^{IX}$, $O21^{IX}$ atoms coordinate the Ca2 and $Ca2^{IX}$ ions, respectively, while the second carboxylate oxygen atoms O22 and $O22^{IX}$ bidentate are linked to $Ca2^{IV}$, $Ca1^{IV}$, $Ca2^{VI}$, and $Ca1^{VI}$ ions, respectively. Oxygen atoms of the carboxylate groups which do not

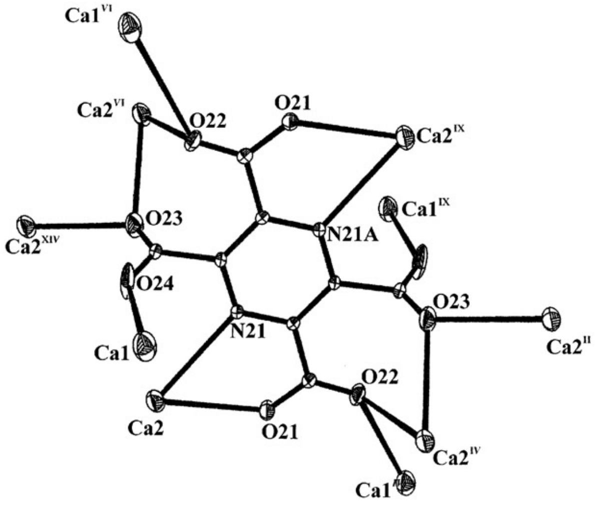

Figure 2. The bridging pathway *via* ligand molecule 2 in the structure of Ca_2(2,3,5,6-PZTC)(H_2O). For symmetry code, see table 2.

form the N,O bonding moieties are also bidentate: O23 chelates Ca2^{IV} and Ca2^{II}, while the O23^{IX} atom – Ca2^{VI} and Ca2^{XIV}. The O24 and O24^{IX} atoms are bonded to Ca1^{IV} and Ca1^{XIV} ions, respectively. In this way, the ligand molecule 2 bridges six Ca2 and four Ca1 ions.

The bridging pathways *via* ligand molecules 1 and 2 are interconnected by carboxylate oxygen atoms O13 and O13^{IX} donated by the ligand molecule 1 to the coordination polyhedron around Ca2, O22 and O24 coordinate Ca1 (see table 2 and figures 3 and 4).

In the third bridging pathway, the coordinated water oxygen atom O10 joins two adjacent Ca1 and Ca2 ions. Since the Ca1–O10–Ca2 angle is 94.81(8)°, a catenated zig-zag motif is observed. The water molecule O10 as a donor also provides an additional pathway *via* very weak hydrogen bonds to carboxylate O14^{VIII} and O12^{VII} atoms. The geometrical parameters of these hydrogen bonds are listed in table 2.

Symmetry independent Ca(II) ions show different coordination modes. The Ca1 coordinates eight atoms at the corners of a distorted bicapped tetragonal bipyramid (figure 3). Its equatorial plane is composed of N11, O24^{IX}, O10^{III} and O14^{VIII} with maximum shifts from the mean plane: $+0.0063(1)$ Å (O24^{IX} atom) and $-0.0223(1)$ Å (O1O^{III} atom); r.m.s. 0.0174(1) Å. The O11 and O22^{IV} atoms form a double apex on one side and O14^{X} and O12^{VII} a double apex on the other side of the equatorial plane. The Ca1 atom is shifted by 0.0373(1) Å from the equatorial plane in the direction of the double apex formed by O11 amd O22^{IV}.

The coordination number of Ca2 is seven. Five atoms are provided by ligand molecule 2, one oxygen atom O13^{XI} by ligand molecule 1, the seventh atom O10^{III} is donated by coordinated water. Atoms O21, O13^{XI}, O23^{XII}, O10^{III} and O22^{IV} form a strongly distorted equatorial plane: maximum shifts from the mean plane are $+0.3809(1)$ (O23^{XII}), $-0.3314(1)$ Å (O13^{IX}); r.m.s. 0.1991(1) Å. Atoms N21 and O23^{IV} form single apices of a strongly distorted pentagonal bipyramid. Figure 4 shows the coordination around Ca2 viewed along a direction normal to the mean

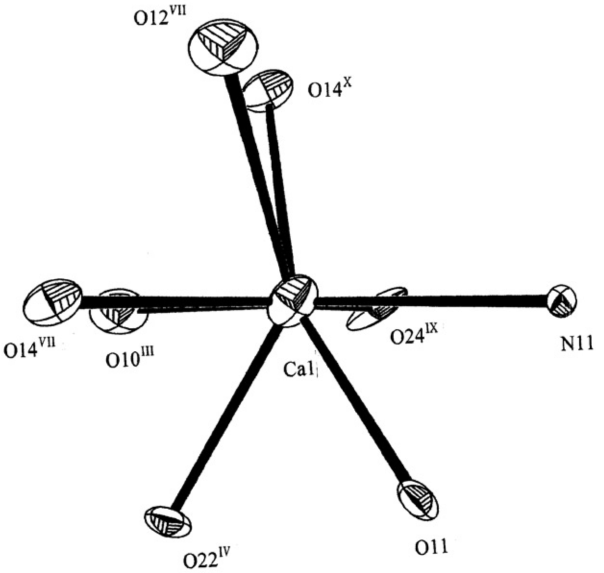

Figure 3. The coordination of Ca1 viewed along the direction normal to the tetragonal equatorial plane. Displacement ellipsoids are drawn at 50% probability. For symmetry code, see table 2.

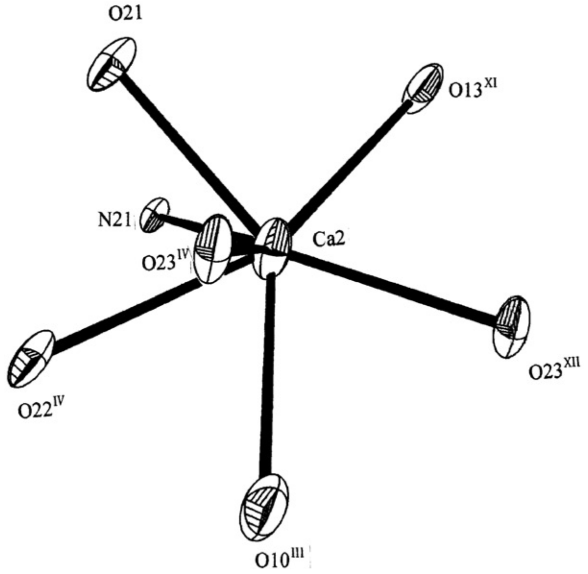

Figure 4. Coordination of Ca2 viewed along the direction normal to the pentagonal equatorial plane. Displacement ellipsoids are drawn at the 50% probability. For symmetry code, see table 2.

equatorial plane. Relevant bond distances and angles for both polyhedra are listed in table 2.

The observed Ca–Ca distances are in the range 3.854(1) to 4.163(1) Å, so that intermetal interaction is improbable.

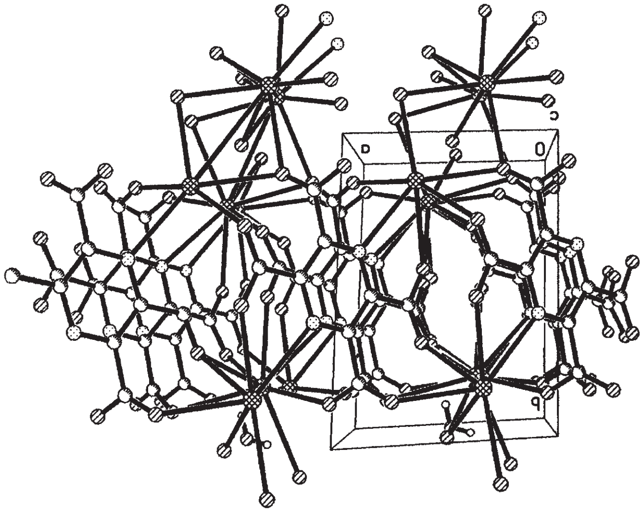

Figure 5. The packing of atoms in the structure of $Ca_2(2,3,5,6\text{-PZTC})(H_2O)$ viewed along the *c* axis.

The pyrazine rings of both ligands are planar to within 0.0009(1) Å (molecule 1) and 0.0013(2) Å (molecule 2). In ligand molecule 1, the carboxylate group O17, O11, O12 and C18, O13, O14 deviate from the ring plane by 21.0(1)° and 84.6(1)°, respectively. In ligand molecule 2, the relevant angles are 2.0(1)° (C27, O21, O22) and 103.7(1)° (C28, O23, O24). The bond lengths and angles within the ligand molecules are similar to those reported for other complexes with the title ligand [1–4].

The pyrazine ring planes of ligands 1 and 2 are parallel to each other forming molecular sheets stacked normal to the *a* axis. They are interconnected by carboxylate oxygen atoms coordinating calcium ions located between the adjacent sheets. The packing of sheets as viewed along the c axis and displayed in figure 5 reveals a dense packing of the molecules in the crystal. This may be the reason that the observed Ca–O and Ca–N bond distances in the structure of the title compound are ca 0.3–0.4 Å longer than those reported in less dense structures, as for example, in the two-dimensional polymeric structure of a Ca(II) complex with pyrazine-2,3-dicarboxylate and water ligands [8].

Sharp, intense bands observed on the IR spectrum were identified as vibrations of the deprotonated carboxylic groups. Two intense bands at 3479 and 3637 cm^{-1} are assigned to the vibrations of the coordinated water molecules (see table 3). This assignment is supported by IR data reported for polymeric Mn(II) and Fe(II) complexes with the title ligand [1, 3]. An interesting feature of the title compound spectrum is the absence of a broad band around 2000 cm^{-1} observed on the spectrum of the Mn(II) complex and assigned to the vibrations of hydrogen bonds [3].

An interesting feature of the title structure is the occurence of two symmetry independent Ca(II) ions, each with a different coordination mode. A short comparison of Ca(II) coordination modes observed in the structures of complexes with pyrazine dicarboxylate ligands (PZDC) shows, all but one, coordination number eight and a more or less distorted pentagonal bipyramidal environment. As an example, figure 3 shows the coordination of Ca1 ion in the title structure. In all structures of Ca(II) complexes with pyrazine dicarboxylate ligands the coordinated atoms are carboxylate oxygen atoms, water oxygen atoms and hetero-ring nitrogen atoms. Coordination number eight is also shown for one of the Ca ions in an ionic complex $\{\mathrm{Ca[H(2,3\text{-}PZDC)](H_2O)_3(NO_3)}\}\{\mathrm{Ca[H(2,3\text{-}PZDC)](H_2O)_4}\}^{+1}(\mathrm{NO_3})^{-1}$. The other is nine-coordinate with a pentagonal bipyramid with two apices on both sides of the equatorial plane. Apart from two hetero-ring nitrogens, two carboxylate and three water oxygens, the metal is coordinated by two oxygen atoms of the nitrate group [9].

Stereochemical features of Ca(II) complexes with carboxylate ligands were analyzed over a quarter of century ago [11]. A more recent study confirmed the conclusions drawn from this analysis: coordination number eight is shown by 45% of surveyed structures, 25% exhibit coordination number seven but only 5% – coordination number nine [12]. Coordination modes observed in the structures of Ca(II) complexes with pyrazine dicarboxylate and tetracarboxylate ligands conform with this analysis.

The available structural data also permit an attempt to compare the bridging modes operating in the title compound with those observed in structures of Ca(II) complexes with pyrazine dicarboxylate ligands. As shown above, the title ligand donates all possible donating sites to coordination producing a three-dimensional, densely packed structure. The pyrazine-2,5-dicarboxylate ligand molecule also has an inversion center. However, the structure of a Ca(II) complex still remains unknown. One may only guess, that like in the structure of the Sr(II) complex with this ligand both N,O-bonding groups are used for bridging. This would be supported by the bridging mode observed in this compound; the inversion center of the ligand coincides with the inversion center of a triclinic unit cell and bridging of the Sr(II) ions proceeds *via* both N,O-bonding groups of the ligand molecule. In addition, coordinated water oxygens are also engaged in bridging, giving rise to a three-dimensional molecular framework [13]. In the structures of two Ca(II) complexes with pyrazine-2,3-dicarboxylate only one N,O-bonding group is active in bridging. In $\mathrm{Ca(2,3\text{-}PZDC)(H_2O)_2 \cdot 2H_2O}$ the second oxygen of the carboxylate group forming the N,O-bonding moiety and the second hetero-ring nitrogen atom remain uncoordinated. The other carboxylate group coordinates the Ca(II) ion using both oxygens. One bidentate ligand also chelates an adjacent metal ion. Molecular layers are formed in this way [14]. A similar pattern has been reported in the structure of the $\mathrm{Ca(2,3\text{-}PZDC)(H_2O)_2 \cdot H_2O}$ compound, however, in this case the second oxygen of the carboxylate group forming the N,O-bonding moiety is monodentate [8]. In both structures water oxygen atoms do not participate in bridging. In two other known Ca(II) complexes with the 2,3-PZDC ligand, the second oxygen atom of each singly deprotonated carboxylate group participates in a short symmetric intramolecular hydrogen bond while both N,O-bonding groups link adjacent metal ions producing catenated ribbons with $\mathrm{Cl^-}$ or $\mathrm{NO_3}^-$ anions located in the space between adjacent ribbons [9, 14]. In 2,6-PZDC both carboxylate groups are situated close to only one hetero-ring nitrogen. Consequently, a N,O,O-bonding group is active in coordination, the second carboxylate oxygen and the second hetero-ring nitrogen atom being inactive. This chelation mode is reflected in all three known complexes of this ligand with Ca(II). In each, the Ca(II) ion is chelated by a N,O,O-bonding group donated by one ligand, however, one of the oxygen atoms active in the bonding is bidentate, coordinating an adjacent Ca(II) ion. Dimeric assembly is formed in this way. The dimers are bridged by three water oxygen atoms coordinated to each Ca(II) giving catenated molecular columns. Two of the complexes differ by the amount of solvation water molecules in the unit cell [15], the third contains, in addition, a molecule of pyrazine-2,6-dicarboxylic acid [16].

This short survey indicates that the flexibility of Ca(II) to adopt coordination numbers from 6 to 9 [10, 11], as well as the geometry of the respective molecule, are the main factors influencing coordination and bridging modes, consequently the formation of observed molecular patterns.

Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 611839. Copies of the available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-(0)1223-336033 or Email: teched@chemcrys.cam.ac.uk).

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