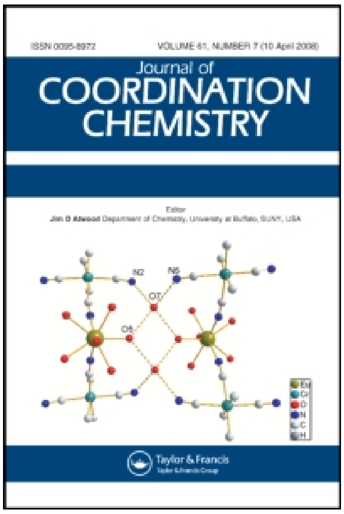

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W. Starosta[a]; B. Ptasiewicz-Bak[a]; J. Leciejewicz[a]
[a] Institute of Nuclear Chemistry and Technology, Warszawa, Poland

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POLYMERIC MOLECULAR PATTERN IN THE CRYSTALS OF A CALCIUM(II) COMPLEX WITH PYRIDINE-3,4-DICARBOXYLATE AND WATER LIGANDS

W. STAROSTA, B. PTASIEWICZ-BĄK and J. LECIEJEWICZ*

Institute of Nuclear Chemistry and Technology, ul.Dorodna 16,
03-195 Warszawa, Poland

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Crystals of triaquamono (μ-pyridine-3,4-dicarboxylato-O,O′,O,O′)(aqua-O)calcium(II) contain molecular ribbons in which two adjacent calcium ions are bridged *via* oxygen atoms donated by the carboxylate group attached to carbon atom "3" in the pyridine ring. Both oxygen atoms are bidentate, each being coordinated to two calcium ions. In addition, every second pair of calcium(II) ions is bridged by a water oxygen atom. The coordination polyhedron around the calcium(II) ion is pentagonal bipyramidal; its equatorial plane is composed of two bridging oxygen atoms each belonging to the carboxylate group of the adjacent ligands, the bridging water oxygen atom and two coordinated water molecules. Another coordinated water oxygen atom constitutes the apex of the pyramid on one side of the pentagon, while two bridging carboxylate oxygen atoms donated by the same carboxylate group make two apices on the other side of the pentagon. The pyridine hetero-ring nitrogen atom does not participate in coordination to the central ion. Both oxygen atoms of the carboxylate group attached to the carbon atom in position "4" of the pyridine ring are not directly coordinated to the calcium(II) ion and act only as acceptors in the hydrogen bond system.

Keywords: Pyridine-3,4-dicarboxylic acid; Calcium complex; X-ray structure analysis

INTRODUCTION

Calcium(II) is known for its bonding flexibility in complexes with carboxylate ligands and coordinates from five to nine oxygen donor ligands,

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*Corresponding author. Tel.: 48228111313, Fax: 48228111532, e-mail: jlec@orange.ichtj.waw.pl showing irregular geometry and Ca–O bond distances ranging from 2.2 to 2.8 Å. In Ca(II) complexes with ligands which contain pyridine or pyrazine rings, hetero-ring nitrogen atoms are also often involved in coordinating the central ion, in most cases forming a N, O bonding moiety comprising the hetero-ring nitrogen and nearest carboxylate oxygen atoms. The Ca(II) coordination modes have also been found to be influenced by the size of the ligand. This effect is illustrated by structures of calcium compounds with pyrazine carboxylate ligands; while crystals of calcium complex with pyrazine-2-carboxylate ligand [1] contain monomeric molecules, its compounds with 3-aminopyrazine-2-carboxylate [2] and 5-methylpyrazine-2-carboxylate [3] ligands exhibit polymeric molecular patterns. The structure of calcium nicotinate (pyridine-3-carboxylate) has been reported to be polymeric with only carboxylate oxygen atoms active in coordination [4]. On the other hand, crystals of calcium isonicotinate (pyridine-4-carboxylate) contain monomeric molecules, in which, apart from carboxylate oxygen atoms, the hetero-ring nitrogen atom is active as a chelating site, however, without any conjunction with the carboxylate oxygen atom [5]. Therefore, we are interested in studying calcium coordination modes in the crystals of its complexes with pyridine dicarboxylate ligands, particularly those, in which the carboxylate groups are distant from the hetero-ring nitrogen atom. As the first step we have determined the crystal structure of the calcium(II) complex with pyridine-3,4-dicarboxylate (3,4-PDDC) ligand. The results are reported in this paper.

EXPERIMENTAL

The title compound was obtained by mixing hot solutions, one containing 1 millimol of calcium nitrate (analytical grade) in 50 mL of water, the second – 1 millimol of pyridine 3,4-dicarboxylic acid (ALDRICH) in 100 mL of water. After boiling for one hour, the mixture was left to evaporate to dryness at ambient temperature. Colorless single crystals in the form of rectangular plates were found after a few days. The dimensions of a crystal taken for collecting X-ray diffraction data are given in Table I.

X-ray reflections were measured at room temperature using a KUMA KM4 (MoK_α radiation) four circle diffractometer operating in $\omega-2\theta$ mode. Two sets of equivalent reflections were collected $(-8 < k < 8)$. Two standard reflections were monitored every 200 reflections. They remained constant throughout the data collection process. Unit cell dimensions and standard deviations were obtained by least-squares fit to 25 reflections

TABLE I Crystal data and structure refinement details for $Ca(3,4\text{-}PDDC)(H_2O)_{1/2}(H_2O)_3$

Empirical formula	$C_7H_{10}NO_{7.5}Ca$
Formula weight	268.24
Temperature	293 K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	P2/c
Unit cell dimensions	$a = 10.744(2)$ Å $b = 7.541(2)$ Å $c = 13.204(3)$ Å $\beta = 94.12(3)°$ $V = 1067.03$ Å^3
Z	4
Calculated density	1.670 g cm^{-3}
μ(MoKα)	0.61 mm^{-1}
$F(000)$	556.0
Crystal size	$(0.2 \times 0.2 \times 0.4)$ mm^3
Max 2θ for data collection	49.97°
Index range	$-12 \leq h \leq 12$, $-8 \leq k \leq 8$, $0 \leq l \leq 15$
No. of measured reflections	3223
No. of unique reflections with $F_o > 4\sigma(F_o)$	1559
R_{int}	0.019
Method of structure solution	direct method
Method of structure refinement	full-matrix least squares on F^2
No. of parameters refined	191
Goodness-of-fit on F^2	1.111
Final $R1$ $[F_o > 4\sigma(F_o)]$	0.0355
Final $wR2$ index	0.0954
Absorption correction	ψ-scan
Min. and max. transmission factors	0.572, 0.699
Largest diff. peak and hole	0.79 e/Å^3 and -0.34 e/Å^3
Weight parameters (A, B)	0.0452, 1.26
Mean shift/esd	0.051

$(15° < 2\theta < 30°)$. Reflections were processed using profile analysis and corrected for Lorentz factor and polarization effects. An empirical absorption correction based on ψ-scan was applied. Non-hydrogen ions were located by direct methods using a SHELXLS program [6] and hydrogen atoms then found by successive Fourier syntheses. Final refinement on F^2 by least squares was done on positional parameters of all atoms, anisotropic temperature factors of all non H-atoms and isotropic temperature factors of hydrogen atoms. A weighting scheme was used in the form: $w = 1/[\sigma^2(F_o^2) + (A * P)^2 + B * P]$, where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$. A, B are refined parameters listed in Table I. Calculations were carried out using SHELXL97 program [7]. Final atomic coordinates and equivalent isotropic displacements are listed in Table II, bond lengths and angles in Table III. Listings of the observed and calculated structure factors and anisotropic thermal parameters can be obtained on request from the authors.

TABLE II Fractional atomic coordinates and equivalent isotropic displacement (Å^2) for Ca(3,4-PDDC)$(H_2O)_{1/2}(H_2O)_3$

Ca	0.57588(1)	0.13751(1)	0.12900(1)	0.0182(2)
O1	0.3734(2)	0.0747(3)	0.1910(1)	0.0253(4)
O2	0.3791(2)	−0.0652(3)	0.0441(1)	0.0296(5)
O3	0.3156(2)	−0.3911(3)	0.1939(2)	0.0467(6)
O4	0.2236(2)	−0.5035(3)	0.05179(2)	0.0353(5)
O5	0.50000(0)	0.3751(4)	0.25000(0)	0.0285(6)
O6	0.44611(3)	0.3401(4)	0.0242(2)	0.0316(5)
O7	0.7642(4)	0.3081(7)	0.1325(3)	0.080(2)
O8	0.6603(4)	−0.1584(4)	0.1409(2)	0.0575(9)
N1	−0.0240(2)	0.0384(4)	0.1259(2)	0.0369(6)
C2	0.1001(2)	0.0740(4)	0.1278(2)	0.0252(6)
C3	0.1870(2)	−0.0612(4)	0.1229(2)	0.0185(5)
C4	0.1446(2)	−0.2365(4)	0.1169(2)	0.0201(5)
C5	0.0176(3)	−0.2653(4)	0.1135(2)	0.0297(6)
C6	−0.0625(4)	−0.1285(6)	0.1185(3)	0.0297(9)
C7	0.3229(2)	−0.0167(3)	0.1194(2)	0.0192(5)
C8	0.2351(2)	−0.3894(4)	0.1203(2)	0.0240(6)
H2	0.131(3)	0.194(4)	0.130(2)	0.028(8)
H5	−0.009(3)	−0.378(4)	0.108(2)	0.031(8)
H6	−0.100(3)	−0.144(5)	0.119(3)	0.00(1)
H51	0.440(3)	0.449(5)	0.232(3)	0.044(9)
H61	0.371(4)	0.373(5)	0.046(3)	0.041(9)
H62	0.474(6)	0.396(8)	0.011(5)	0.10(3)
H71	0.723(3)	0.363(5)	0.135(3)	0.000(9)
H72	0.82(1)	0.38(2)	0.054(6)	0.45(9)
H81	0.663(4)	−0.241(6)	0.197(4)	0.07(1)
H82	0.599(2)	−0.178(4)	0.152(2)	0.000(8)

TABLE III Selected bond distances (Å) and angles (°) for Ca(3,4-PDDC)$(H_2O)_{1/2}(H_2O)_3$

Calcium(II) environment:			
Ca–O1	2.425(3)	O1–Ca–O2	49.7(1)
Ca–O2	2.779(2)	O2–Ca–O2^{I}	72.2(1)
Ca–O1^{II}	2.447(2)	O1–Ca–O5	66.1(1)
Ca–O2^{I}	2.433(2)	O5–Ca–O1^{II}	65.8(1)
Ca–O5	2.572(2)	O5–Ca–O6	73.8(1)
Ca–O6	2.433(2)	O6–Ca–O2^{I}	75.6(1)
Ca–O7	2.395(4)	O6–Ca–O7	97.0(1)
Ca–O8	2.409(3)	O7–Ca–O8	100.5(2)
		O8–Ca–O1^{II}	72.6(1)
		O8–Ca–O2^{I}	75.8(1)
The bridging system:			
O5–Ca	2.572(2)	Ca–O5–Ca^{II}	91.7(1)
O5–Ca^{II}	2.572(2)		
O1–Ca	2.425(2)	Ca–O1–Ca^{II}	98.5(1)
O1–Ca^{II}	2.447(2)		
O2–Ca^{I}	2.443(2)	Ca–O2–Ca^{I}	107.8(1)
O2–Ca	2.779(2)		
The ligand molecule:			
N1–C2	1.359(4)	C6–N1–C2	119.3(3)
C2–C3	1.387(4)	N1–C2–C3	121.1(3)
C3–C4	1.399(4)	C2–C3–C4	118.7(2)
C4–C5	1.379(4)	C3–C4–C5	117.9(3)

TABLE III (Continued)

C5–C6	1.348(5)	C4–C5–C6	120.7(3)		
C6–N1	1.326(5)	C5–C6–N1	122.2(4)		
C3–C7	1.502(3)	O1–C7–O2	123.2(2)		
C7–O1	1.261(3)				
C7–O2	1.254(3)				
C4–C8	1.506(4)	O3–C8–O4	125.6(3)		
C8–O3	1.256(4)				
C8–O4	1.248(4)				
Water molecules:					
O5–H51	0.87(3)				
O6–H61	0.94(4)	H61–O6–H62	114(7)		
O6–H62	0.56(5)				
O7–H71	0.61(3)	H71–O7–H72	99(9)		
O7–H72	10.95(8)				
O8–H81	0.96(5)	H81–O8–H82	70(3)		
O8–H82	0.70(2)				
Hydrogen bonds:					
O5–H51···O3^{III}	2.72(1)	H51···O3^{III}	1.84(1)	O5–H51–O3^{III}	179.3(1)
O6–H61···O4^{III}	2.71(1)	H61···O4^{III}	1.86(1)	O6–H61–O4^{III}	159.9(1)
O7–H71···O4^{I}	2.86(1)	H71···O4^{I}	2.43(1)	O7–H71–O4^{I}	135.2(1)
O8–H81···O3^{I}	2.78(1)	H81···O3^{I}	2.78(1)	O8–H81–O3^{I}	166.4(1)
O8–H82···O2^{I}	2.99(1)	H82···O2^{I}	2.43(1)	O8–H82–O2^{I}	177.1(1)

Symmetry code: ^{I} $-x+1,\ -y,\ -z$; ^{II} $-x+1,\ y,\ -z+0.5$; ^{III} $x,\ y+1,\ z$; ^{IV} $-x+1,\ -y+1,\ -z$.

DISCUSSION

The structure of the title compound is polymeric. The crystals contain molecular ribbons, in which calcium(II) ions are bridged by oxygen atoms contributed by only one carboxylate of the ligand and a water molecule. The ribbons are held together by a network of hydrogen bonds. Figure 1 shows a fragment of the ribbon with numbering of atoms; Figure 2 illustrates, how the ribbons are packed in the crystal. The bridging oxygen atoms are donated by only one carboxylate group which is attached to the carbon atom in position "3" of the pyridine ring. These oxygen atoms are bidentate, each being simultaneously bonded to two adjacent calcium(II) ions with Ca–O bond distances ranging from 2.425(2) to 2.779(3) Å (see Tab. III). In consequence, each calcium(II) ion is linked to four carboxylate oxygens belonging to three different ligand molecules. Thus, the coordinated carboxylate operates as a tetradentate group. This bridging is strengthened by an additional water oxygen atom O5 situated at the symmetry center. Therefore, only every second pair of Ca(II) ions is bridged by this water molecule [O5–Ca and O5–Ca^{II}, 2.572(2) Å]. The other potentially chelating

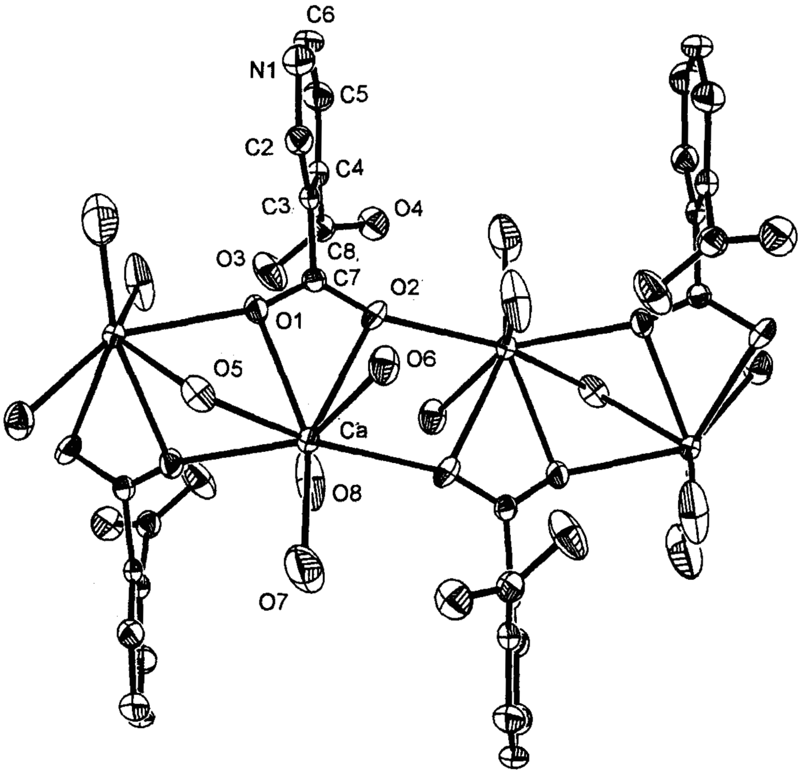

FIGURE 1 A fragment of the molecular ribbon in $Ca(3,4\text{-}PDDC)(H_2O)_{1/2}(H_2O)_{1/2}(H_2O)_3$ with numbering of atoms. The non hydrogen atoms are shown as 50% probability ellipsoids. For clarity, hydrogen atoms are omitted.

atoms: two oxygen atoms of the second carboxylate group attached to the pyridine ring carbon atom in position "4" as well as the hetero-ring nitrogen atom do not participate in chelating the metal ion.

Calcium(II) ion exhibits eight-fold coordination. Apart from the five oxygen atoms mentioned above, each Ca(II) ion is also coordinated by three water molecules $H_2O(6)$, $H_2O(7)$ and $H_2O(8)$ with bond distances as listed in Table III. The geometry of the coordination polyhedron is complex: the calcium ion and five oxygen atoms O1, O2, O5, O6 and O8 form a distorted pentagon with the maximum and minimum shifts from the mean plane of 0.351(2) Å ($O2^{I}$) and −0.305(2) Å (O6), respectively. The water oxygen atom O7 situated on one side of the pentagonal plane with the Ca−O7 bond almost perpendicular to it makes one apex. Carboxylate oxygen atoms O1 and O2 situated on the other side of the pentagon constitute two apices giving rise to a complex pentagonal bipyramid.

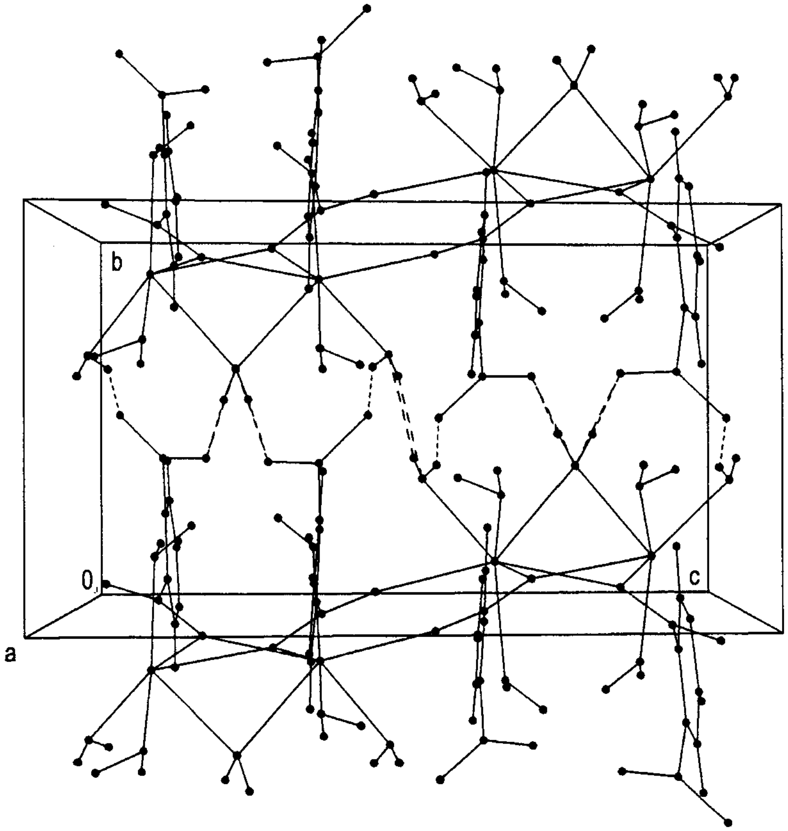

FIGURE 2 The packing of molecular ribbons in the structure of Ca(3,4-PDDC)$(H_2O)_{1/2}(H_2O)_3$. Broken lines indicate the hydrogen bonds.

The pyridine ring of the ligand molecule is planar with maximum shift from the average plane amounting to 0.009(2) Å (heteroring carbon atom C4). The determined bond lengths and angles within the ring are in fair agreement with those reported for the parent acid [8]. The plane of the bridging carboxylate plane defined by the atoms C7, O1 and O2 is inclined to the plane of the pyridine ring by 57.6(1)°; the values of the C7–O1 and C7–O2 bond distances of 1.261(3) and 1.254(3) Å, respectively, are similar to those observed in other Ca(II) complexes with pyridine carboxylate ligands [4, 5, 9]. The plane formed by the non-coordinated carboxylic group atoms C8, O3 and O4 makes an angle of 54.6(1)° with the plane of the pyridine ring. The observed equivalence of C8–O3 and C8–O4 bond distances 1.255(3) and 1.248(3) Å, respectively, indicates that they are stabilized by resonance like in the molecules of the parent acid, which was found to adopt the zwitter-ion form [8]. The oxygen atoms of this group are active as acceptors in the hydrogen bonds donated by the water molecules.

The molecular ribbons constituting the structure of the title compound are interconnected by a system of hydrogen bonds in which the water molecules act as donors. The bridging water molecule O5 situated in the center of symmetry links, *via* its two hydrogen atoms, two symmetry related non-coordinated carboxylate oxygen atoms O3 belonging to the ligand molecules in the adjacent ribbons [$\mathrm{O5-H51\cdots O3^{III}}$ 2.71(2) Å] – see Figure 2. The other non-coordinated oxygen atom of the same group $\mathrm{O4^{III}}$ is an acceptor in a hydrogen bond linking it with the water molecule O6 coordinated to the calcium ion in the adjacent ribbon, $\mathrm{O6-H61\cdots O4^{III}}$ 2.71(1) Å. The non-coordinated oxygen atom $\mathrm{O4^{II}}$ is also linked by a hydrogen bond to the water molecule O7 with an $\mathrm{O7-H71\cdots O^{II}}$ bond length of 2.86(1) Å, while the possible $\mathrm{O7-H72\cdots O}$ bonds are all longer than 3.3 Å. The water molecule O8 donates its hydrogen atoms to two bonds: one to the non-coordinated carboxylate oxygen atom $\mathrm{O3^{II}}$: $\mathrm{O8-H81\cdots O3^{II}}$ 2.78(1) Å; the other bond of 2.99(1) Å is to the bridging carboxylate oxygen atom $\mathrm{O2^{I}}$.

The molecular pattern detected in the crystals of the title compound is different compared to dimeric molecules which have been observed in the crystals of Ca(II) complexes with pyridine-2,6-dicarboxylate [9, 10] and pyridine-3,5-dicarboxylate [10] ligands.

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