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THE CRYSTAL STRUCTURES OF TWO POLYMORPHIC FORMS OF A CALCIUM(II) COMPLEX WITH PYRIDINE-2,6-DICARBOXYLATE, WATER AND NITRATE LIGANDS

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The calcium (II) complex: *catena*-mono(μ -pyridine-2,6-dicarboxylato-O:O:N;O') (diaqua-O)mono (nitrate-O:O)calcium(II) exists in two polymorphic forms. Each contains molecular ribbons in which adjacent Ca(II) ions are bridged by monodentate oxygen atoms donated by one carboxylate group of the pyridine-2,6-carboxylate ligand. Apart from this bridging oxygen atom, the Ca(II) ion is coordinated by two carboxylate oxygen atoms contributed by a different carboxylate group of the ligand molecule, the heteroring nitrogen atom, two water oxygen atoms and two oxygen atoms of a nitrate group giving rise to a distorted pentagonal bipyramid as a coordination polyhedron. The structures of the polymorphic modifications differ in the way in which the nitrate ligands are oriented with respect to the equatorial planes of the adjacent Ca(II) coordination polyhedra: the *trans* mode in the α -form; the *cis* mode in the β -form. In both forms, hydrogen bonds operate between the carboxylate oxygen atoms, water oxygen atoms and nitrate oxygen atoms.

Keywords: Pyridine-2,6-dicarboxylate acid; calcium complex; X-ray diffraction

INTRODUCTION

The structures of two calcium(II) complexes with pyridine-2,6-dicarboxylate (dipicolinate or 2,6-PDDC) have been solved. The crystals of the complex denoted by the authors as “calcium dipicolinate trihydrate” contain dimeric units composed of two calcium(II) ions and two 2,6-PDDC ligand molecules. The Ca(II) ions are bridged by two bidentate oxygen atoms donated by only one carboxylate group of each 2,6-PDDC ligand. In turn, the Ca(II) ions in adjacent dimers are bridged by two water oxygen atoms giving rise to a polymeric molecular pattern [1]. Discrete dimeric molecules have been also observed in the structure of another calcium(II) complex with 2,6-PDDC and water ligands in which free dipicolinic acid molecules have been

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found to be accommodated in the space between the dimers resulting in removal of the bridging via water molecules [2]. In the course of our structural studies of Ca(II) complexes with 2,6-PDDC ligand we have obtained single crystals of two polymorphic forms of a new calcium(II) complex with pyridine-2,6-dicarboxylate, water and nitrate ligands. The crystal structures of both forms are reported in this paper.

EXPERIMENTAL

The synthesis of one of the modifications (designated α -CADIP 2) was carried out by reacting 1 mmol of calcium nitrate tetrahydrate with 1 mmol of pyridine-2,6-dicarboxylic acid (ALDRICH), each dissolved in 100 mL of warm methanol. After boiling under reflux for one hour, the mixture was left at room temperature. Colorless single crystals in the form of rectangular plates separated from the mother liquid overnight. Some of them were removed and used for collection of x-ray data.

TABLE I Crystal data and structure refinement details for polymorphic forms of Ca(2,6-HPDDC)(H₂O)₂(NO₃)

Empirical formula	C ₇ H ₈ N ₂ O ₉ Ca	
Code name	α -CADIP 2	β -CADIP 2
Formula Weight	305.0	
Temperature	293 K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions	<i>a</i> = 7.789(2) Å <i>b</i> = 12.227(2) Å <i>c</i> = 13.242(3) Å β = 106.45° <i>V</i> = 1209.50 Å ³	8.070(2) Å 13.400(3) Å 11.000(2) Å 98.78(3)° 1175.58 Å ³
Z	4	4
Calculated density	1.671 g cm ⁻³	1719 g cm ⁻³
μ (MoK α)	0.56 mm ⁻¹	0.58 mm ⁻¹
<i>F</i> (000)	624.0	624.0
Crystal size	0.2 × 0.2 × 0.4 mm ³	0.2 × 0.2 × 0.5 mm ³
Max 2 θ for data collection	59.99°	60.03°
Index range	-10 ≤ <i>h</i> ≤ 10 -17 ≤ <i>k</i> ≤ 0, -13 ≤ <i>l</i> ≤ 0.	-12 ≤ <i>h</i> ≤ 0 0 ≤ <i>k</i> ≤ 18 -15 ≤ <i>l</i> ≤ 15
No. of measured reflections	2070	1962
No. of reflections with <i>F</i> _o > 4 σ (<i>F</i> _o)	1584	1383
<i>R</i> _{int}	0.0158	0.0180
Method of structure solution	direct method	
Method of structure refinement	full-matrix least squares on <i>F</i> ²	
No. of parameters refined	204	205
Goodness-of-fit on <i>F</i> ²	1.071	1.065
Final <i>R</i> 1 [<i>F</i> _o > 4 σ (<i>F</i> _o)]	0.0305	0.0308
Final w <i>R</i> 2 index	0.0889	0.0902
Absorption correction	ψ -scan	
Min. and max. transmission factors	0.297, 0.343	0.251, 0.287
Largest diff. peak and hole	0.32 e/Å ³ and -0.22 e/Å ³	0.27 e/Å ³ and -0.23 e/Å ³
Weight parameters (<i>A</i> , <i>B</i>)	0.0559, 0.00	0.0520, 0.00
Mean shift/esd	0.013	0.006

The mother liquid was subsequently evaporated to dryness at room temperature. The precipitate was then dissolved in warm water and evaporated to dryness at *ca.* 50°C in a water bath. Colorless, well-formed single crystals of the second form (β -CADIP 2) were found at the bottom of the crystallization pot, among a mass of unidentified polycrystalline material. The dimensions of the crystals chosen for collection of x-ray diffraction data are given in Table I.

X-ray reflections were measured at room temperature using KUMA KM4 (MoK $_{\alpha}$ radiation) 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 ($15^\circ < 2\theta < 30^\circ$). 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 method using the SHELXLS program [3] and hydrogen atoms then found by successive Fourier syntheses. Final refinement on F^2 by least squares method 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: $w = 1/[\sigma^2(F_o^2) + (A \times P)^2 + B \times P]$, where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$. A , B are the parameters listed in Table I. Calculations were carried out using the SHELXL97 program [4]. Final atomic coordinates and equivalent isotropic displacements are listed in Tables II and III and bond lengths and angles in Tables IV and V. Listings of the observed and calculated x-ray intensities are obtainable from the authors.

TABLE II Fractional atomic coordinates and equivalent isotropic displacements (\AA^2) for α -Ca(2,6-HPDDC) $(\text{H}_2\text{O})_2(\text{NO}_3)$. U_{eq} is defined as one third of the trace of the orthogonal U_q tensor

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Ca	0.71297(7)	0.41423(4)	0.21972(4)	0.0284(1)
N1	0.7187(3)	0.3561(1)	0.4046(2)	0.0269(4)
N3	0.3458(3)	0.4951(2)	0.1677(2)	0.0416(6)
C2	0.6791(3)	0.2533(2)	0.4260(2)	0.0279(5)
C3	0.6428(4)	0.2240(2)	0.5188(2)	0.0394(6)
C4	0.6509(5)	0.3041(2)	0.5934(2)	0.0469(7)
C5	0.6951(4)	0.4098(2)	0.5738(2)	0.0413(7)
C6	0.7275(3)	0.4324(2)	0.4781(3)	0.0289(5)
C7	0.8202(3)	0.6710(2)	0.1571(2)	0.0286(5)
C8	0.7691(3)	0.5467(2)	0.4473(2)	0.0313(5)
O1	0.8187(2)	0.5730(1)	0.1401(1)	0.0333(4)
O2	0.6826(3)	0.2145(1)	0.2524(1)	0.0396(5)
O3	0.8034(3)	0.6205(1)	0.5132(1)	0.0453(7)
O4	0.7629(3)	0.5573(1)	0.3512(1)	0.0433(5)
O31	0.4568(3)	0.5326(2)	0.1241(2)	0.0492(5)
O32	0.3960(3)	0.4177(2)	0.2310(2)	0.0521(5)
O33	0.1937(3)	0.5313(2)	0.1498(2)	0.0739(7)
O7	1.0223(3)	0.3762(2)	0.2697(2)	0.0446(5)
O8	0.6742(4)	0.3340(2)	0.0549(2)	0.0574(7)
H3	0.617(3)	0.148(2)	0.529(2)	0.038(7)
H4	0.621(4)	0.287(3)	0.653(3)	0.059(9)
H5	0.693(4)	0.466(2)	0.619(2)	0.043(8)
H21	0.704(6)	0.162(4)	0.208(3)	0.10(2)
H71	1.073(4)	0.367(3)	0.325(3)	0.05(1)
H72	1.091(5)	0.410(3)	0.242(3)	0.07(1)
H81	0.697(7)	0.282(4)	0.026(4)	0.11(2)
H82	0.655(5)	0.366(3)	0.013(3)	0.06(1)

TABLE III Fractional atomic coordinates and equivalent isotropic displacements (\AA^2) for β -Ca(2,6-HPDDC) $(\text{H}_2\text{O})_2(\text{NO}_3)$. U_{eq} is defined as one third of the trace of the orthogonal U_q tensor

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Ca	0.19150(8)	0.78322(4)	0.45025(5)	0.0288(2)
N1	0.2559(3)	0.5983(2)	0.4983(2)	0.0240(5)
N3	-0.0883(4)	0.8333(2)	0.5821(3)	0.0421(7)
C2	0.3607(4)	0.5698(2)	0.5985(2)	0.0263(4)
C3	0.3880(4)	0.4706(2)	0.6313(3)	0.0314(6)
C4	0.3045(5)	0.3975(2)	0.5571(3)	0.0370(7)
C5	0.1993(4)	0.4261(2)	0.4517(3)	0.0316(6)
C6	0.1779(4)	0.5272(2)	0.4267(2)	0.0252(6)
C7	0.4501(4)	0.6518(2)	0.6748(2)	0.0281(6)
C8	0.0614(4)	0.5636(2)	0.3140(2)	0.0274(6)
O1	0.0591(3)	0.8674(2)	0.2629(2)	0.0388(5)
O2	0.4021(3)	0.7414(1)	0.6400(2)	0.0357(5)
O3	-0.0057(3)	0.5045(2)	0.2366(2)	0.0403(6)
O4	0.0400(3)	0.6586(2)	0.3117(2)	0.0337(5)
O7	0.4320(3)	0.8012(2)	0.3519(2)	0.0458(6)
O8	0.2808(4)	0.9422(2)	0.5236(3)	0.0626(9)
O31	-0.0969(4)	0.8529(3)	0.4718(3)	0.0671(9)
O32	0.0312(3)	0.7783(2)	0.6307(2)	0.0497(6)
O33	-0.1896(4)	0.8670(3)	0.6426(3)	0.0773(9)
H3	0.456(5)	0.454(3)	0.710(4)	0.05(1)
H4	0.317(5)	0.337(3)	0.586(3)	0.04(1)
H5	0.154(4)	0.387(3)	0.403(3)	0.03(1)
H21	0.458(6)	0.784(4)	0.726(5)	0.09(2)
H71	0.446(7)	0.772(5)	0.293(5)	0.08(2)
H72	0.434(8)	0.860(6)	0.340(6)	0.12(2)
H81	0.331(7)	0.944(4)	0.588(5)	0.07(2)
H82	0.215(9)	0.985(5)	0.505(6)	0.11(2)

DISCUSSION

The molecular pattern observed in the crystals of both modifications of CADIP 2 is different from the patterns described previously [1,2]. The crystals of both polymorphic forms of CADIP 2 contain molecular ribbons, in which the structural units containing the Ca(II) ions are linked by carboxylate oxygen atoms, one per each ligand molecule. Figures 1 and 2 show the structural units of α -CADIP2 and β -CADIP2, respectively, with atom numbering schemes, and Figs. 3 and 4 illustrate the alignment of the molecular ribbons. In both structures, two adjacent Ca(II) ions are bridged by a single, monodentate carboxylate oxygen atom O1 with bond distance O1–Ca of 2.460(2) Å in α -CADIP 2 and 2.447(2) Å in β -CADIP 2. Molecular ribbons are formed in this way.

Similar to the compounds reported [1,2] the coordination around the Ca(II) ion is eight-fold. Apart from the bridging carboxylate oxygen atom O1, each metal ion is coordinated by two other carboxylate oxygen atoms: O4 donated by the carboxylate group used for bridging its second oxygen O1 and the oxygen atom donated by the second carboxylate group O2; the heteroring nitrogen atom N1; water oxygen atoms O7 and O8; and finally nitrate oxygen atoms O31 and O32. The three coordinated oxygen atoms, the heteroring nitrogen atom and one water oxygen atom O8 form a pentagonal base of a polyhedron. On one side of this base, water oxygen atom O7 is the apex and on the opposite side, two apices are constituted by nitrate oxygen

TABLE IV Selected bond distances (Å) and bond angles (°) for α -Ca(2,6-HPDDC)(H₂O)₂(NO₃)

<i>Calcium ions coordination:</i>					
Ca–N1	2.538(2)	N1–Ca–O2	62.39(6)		
Ca–O2	2.503(2)	O2–Ca–O8	76.00(8)		
Ca–O8	2.334(2)	O8–Ca–O1	84.32(8)		
Ca–O1	2.460(2)	O4–Ca–O1	74.50(6)		
Ca–O4	2.420(2)	O4–Ca–N1	63.47(6)		
Ca–O7	2.357(2)	O7–Ca–N1	86.35(8)		
Ca–O31	2.500(2)	O31–Ca–N1	116.40(7)		
Ca–O32	2.516(2)	O32–Ca–N1	72.35(7)		
		O31–Ca–O32	50.54(6)		
<i>Coordinated water molecules:</i>					
O7–H71	0.73(3)	H71–O7–H72	106(4)		
O7–H72	0.84(4)				
O8–H81	0.79(5)	H81–O8–H82	95(4)		
O8–H82	0.65(4)				
<i>Nitrate group:</i>					
N3–O31	1.255(3)	O31–N3–O32	117.4(2)		
N3–O32	1.251(3)	O32–N3–O33	120.3(3)		
N3–O33	1.224(3)	O33–N3–O31	122.3(3)		
<i>2,6-PDDC ligand molecule:</i>					
N1–C2	1.343(3)	N1–C2–C3	123.1(2)		
C2–C3	1.385(4)	C2–C3–C4	118.2(2)		
C3–C4	1.380(4)	C3–C4–C5	119.6(2)		
C4–C5	1.381(4)	C4–C5–C6	118.5(2)		
C5–C6	1.387(4)	C5–C6–N1	122.7(2)		
C6–N1	1.337(3)	C6–C7–O2	117.9(2)		
C2–C7	1.492(3)				
C7–O1	1.218(2)	O1–C7–O2	124.3(2)		
C7–O2	1.318(3)				
C6–C8	1.517(3)	O4–C8–O3	125.2(2)		
C8–O3	1.231(3)				
C8–O4	1.267(3)				
<i>Hydrogen bonds:</i>					
O2–H41...O4 ^I	2.467(2)	H21...O4 ^I	1.55(5)	O2–H21–O4 ^I	169(4)
O7–H71...O3 ^{II}	2.811(3)	H71...O3 ^{II}	2.10(4)	O7–H71–O3 ^{II}	166(3)
O7–H72...O32 ^{III}	3.137(3)	H72...O32 ^{III}	2.43(4)	O7–H72–O32 ^{III}	143(3)
O7–H72...O33 ^{III}	3.017(4)	H72...O33 ^{III}	2.21(4)	O7–H72–O33 ^{III}	162(4)
O8–H81...O3 ^I	2.783(4)	H81...O3 ^I	2.04(4)	O8–H81–O3 ^I	157(4)
O8–H82...O31 ^{IV}	2.818(3)	H82...O31 ^{IV}	2.17(4)	O8–H82–O31 ^{IV}	170(4)

Symmetry code used to generate equivalent atoms:

^I–x+3/2, y–1/2, –z+1/2; ^{II}–x+2, –y+1, –z+1; ^{III}x+1, y, z; ^{IV}–x+1, –y+1, –z.

atoms O31 and O32. The respective bond distances and angles are collected in Tables IV and V. The equatorial planes in both forms deviate strongly from planarity since the mean shifts from the best plane are 0.151(1) Å and 0.122(1) Å in the α and β forms, respectively. On the other hand, in both forms the 2,6-PPDC ligand molecule is almost planar showing a mean deviation from the average plane of 0.005(1) Å. In the structure of α -CADIP 2, the equatorial planes associated with adjacent Ca(II) ions make an angle of 24.4° to each other. This angle is 4.8° in the β form. Thus, the plane of the ribbon composed of equatorial planes of the Ca coordination polyhedra is almost flat in the β -form: it has a zig-zag character in the α -form (Figs. 3 and 4). This observation may be correlated with the mutual alignment of the nitrate ligands bonded to adjacent Ca(II) ions. All the nitrate ligands are located on one side of the ribbon in the β -form showing the *cis* mode, while in the α -form they are situated on the opposite sides of two

TABLE V Selected bond distances (Å) and bond angles (°) for β -Ca(2,6-HPDDC)(H₂O)₂(NO₃)

<i>Calcium ions coordination:</i>					
Ca–N1	2.571(2)	N1–Ca–O2	61.99(6)		
Ca–O2	2.545(2)	O2–Ca–O8	77.69(9)		
Ca–O8	2.352(2)	O8–Ca–O1	86.72(9)		
Ca–O1	2.447(2)	O4–Ca–O1	71.28(7)		
Ca–O4	2.456(2)	O4–Ca–N1	62.49(7)		
Ca–O7	2.374(2)	O7–Ca–N1	92.19(9)		
Ca–O31	2.562(3)	O31–Ca–N1	119.50(9)		
Ca–O32	2.530(3)	O32–Ca–O32	85.68(8)		
		O31–Ca–O32	49.77(8)		
<i>Coordinated water molecules:</i>					
O7–H71	0.79(6)	H71–O7–H72	110(6)		
O7–H72	0.80(8)				
O8–H81	0.76(5)	H81–O8–H82	117(6)		
O8–H82	0.79(7)				
<i>Nitrate group:</i>					
N3–O31	1.233(4)	O31–N3–O32	117.7(3)		
N3–O32	1.266(4)	O32–N3–O33	121.2(3)		
N3–O33	1.217(4)	O33–N3–O31	121.1(3)		
<i>2,6-PDDC ligand molecule:</i>					
N1–C2	1.339(3)	N1–C2–C3	122.9(3)		
C2–C3	1.386(4)	C2–C3–C4	118.8(3)		
C3–C4	1.383(4)	C3–C4–C5	118.7(3)		
C4–C5	1.382(4)	C4–C5–C6	118.6(3)		
C5–C6	1.388(4)	C5–C6–N1	123.2(2)		
C6–N1	1.332(3)	C6–N1–C2	117.8(2)		
C2–C7	1.499(3)				
C7–O1	1.232(2)	O1–C7–O2	124.6(2)		
C7–O2	1.301(3)				
C6–C8	1.517(3)	O4–C8–O3	125.6(2)		
C8–O3	1.285(3)				
C8–O4	1.228(3)				
<i>Hydrogen bonds:</i>					
O2–H21...O4 ^{II}	2.441(2)	H21...O4 ^{II}	1.31(5)	O2–H21...O4 ^{II}	169.2
O7–H71...O32 ^{II}	2.880(3)	H71...O32 ^{II}	2.11(6)	O7–H71...O32 ^{II}	165.0
O7–H72...O3 ^{III}	2.982(4)	H71...O3 ^{III}	2.22(5)	O7–H72...O3 ^{III}	159.2
O8–H81...O3 ^{II}	2.057(5)	H81...O3 ^{II}	2.06(5)	O8–H81...O3 ^{II}	160.0

Symmetry code used to generate equivalent atoms:

^I $x-1/2, -y+3/2, z-1/2$; ^{II} $x+1/2, -y+3/2, z+1/2$; ^{III} $-x+1/2, y+1/2, -z+1/2$.

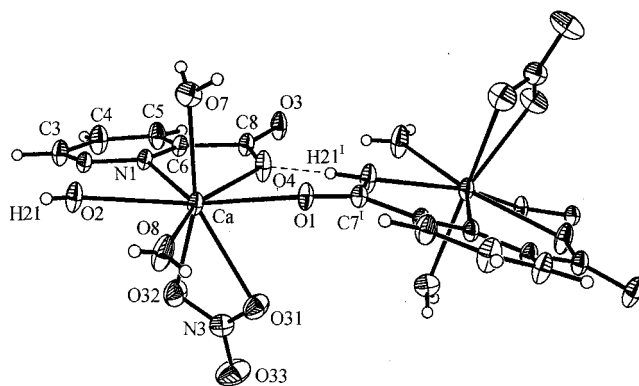


FIGURE 1 The α -Ca(2,6-HPDDC)(H₂O)₂(NO₃) structural unit with numbering of atoms. The non-hydrogen atoms are shown as 50% probability ellipsoids.

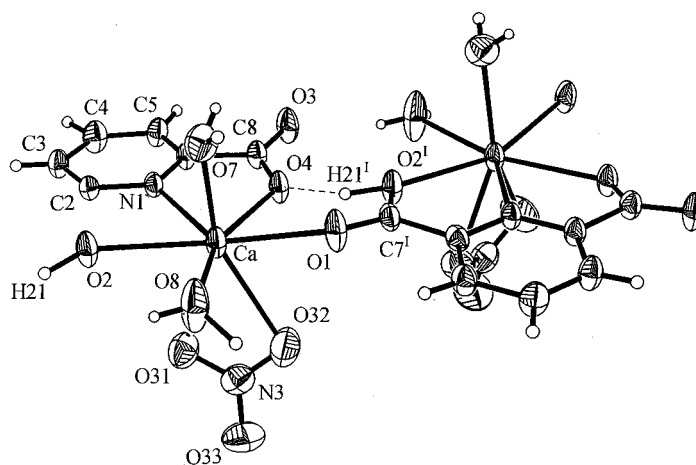


FIGURE 2 The structural unit of β -Ca(2,6-HPDDC)(H₂O)₂(NO₃) with numbering of atoms. The non-hydrogen atoms are shown as 50% probability ellipsoids.

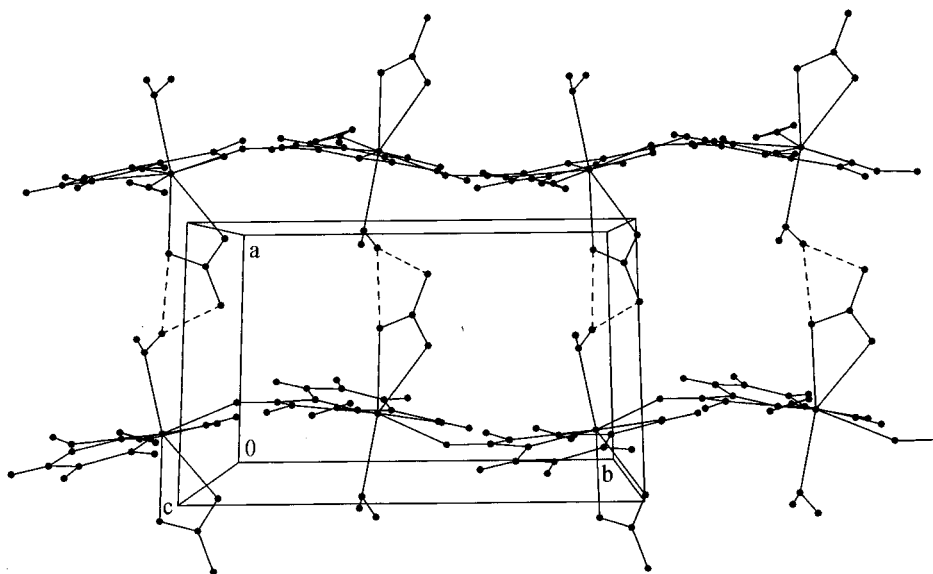


FIGURE 3 The alignment of molecular ribbons in the structure of α -Ca(2,6-HPDDC)(H₂O)₂(NO₃). Dashed lines indicate hydrogen bonds.

adjacent equatorial planes showing thus the *trans* mode. The latter alignment may be the cause of the ribbon deformation in the α -form.

The observed bond distances and angles within the pyridine ring in both forms fit well the values reported for the parent acid [5].

The molecular pattern in both polymorphic forms of CADIP 2 is entirely different from the patterns detected in the structures of the complexes described

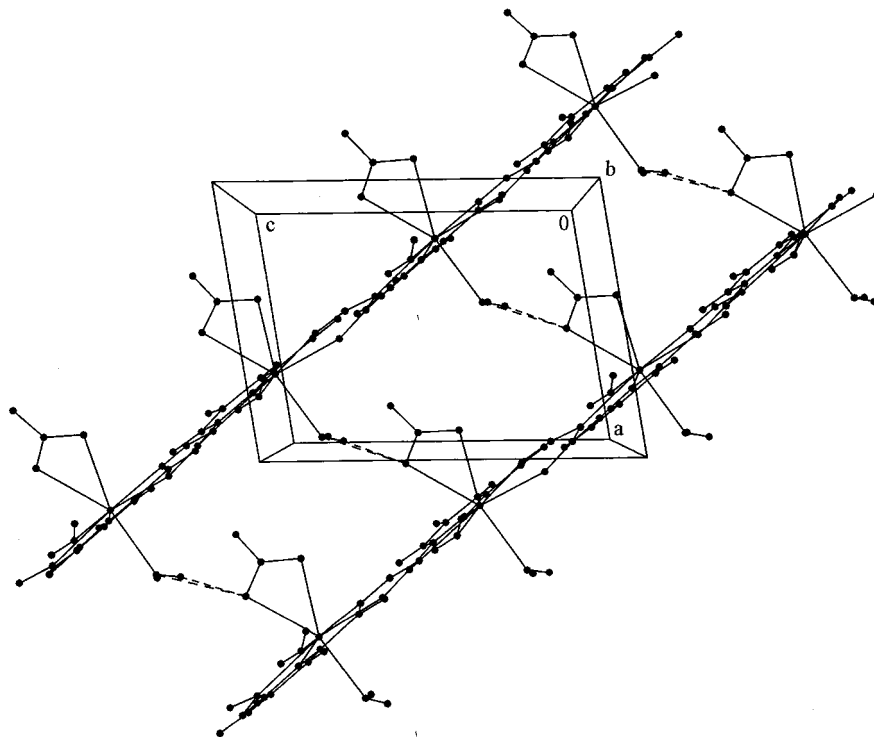


FIGURE 4 The alignment of molecular ribbons in the structure of β -Ca(2,6-HPDDC)(H₂O)₂(NO₃). Dashed lines indicate hydrogen bonds.

previously [1,2]. Instead of discrete dimeric molecules, infinite molecular ribbons are observed in which the Ca(II) ions are bridged by only one carboxylate oxygen atom.

In both modifications of CADIP 2, Fourier maps revealed unambiguously the presence of a hydrogen atom H21 attached to the coordinated carboxylate oxygen O2 which, apart from maintaining the charge balance, takes part in a fairly short hydrogen bond of 2.467(2) Å (α -CADIP 2) and 2.441(2) Å (β -CADIP(2)). This bond represents an additional bridging mode of adjacent Ca ions inside the ribbon.

Acting as donors, the coordinated water molecules form a system of hydrogen bonds with bond lengths ranging from 2.781(3) to 2.982(3) Å linking them with non-bonded carboxylate and nitrate oxygen atoms belonging to the adjacent CADIP 2 structural units. These bonds are responsible for the stability of the crystals. They are listed in detail in Tables IV and V.

The Ca(II) coordination scheme and the range of Ca–O_{carboxylate} bond lengths observed CADIP 2 calcium–carboxylate interaction modes agree well with those most commonly encountered in large number Ca(II) complexes with carboxylate ligands [6].

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