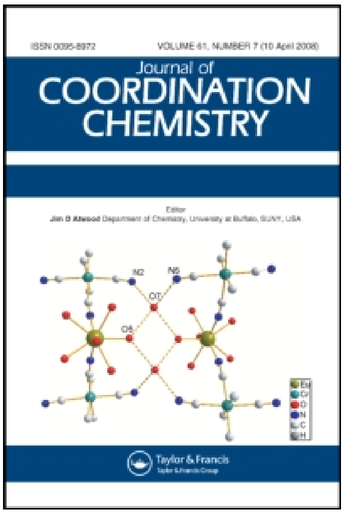

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Starosta, W. , Ptasiewicz-Bąk, H. and Leciejewicz, J.(2002) 'Molecular Chains in the Crystals of a Calcium(II) Complex with Pyridine-3,5-Dicarboxylate (Dinicotinate) and Water Ligands', Journal of Coordination Chemistry, 55: 9, 985 — 990

To link to this Article: DOI: 10.1080/0095897021000009947

URL: http://dx.doi.org/10.1080/0095897021000009947

J. Coord. Chem., 2002, Vol. 55(9), pp. 985–990

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MOLECULAR CHAINS IN THE CRYSTALS OF A CALCIUM(II) COMPLEX WITH PYRIDINE-3,5-DICARBOXYLATE (DINICOTINATE) AND WATER LIGANDS

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(Received 15 May 2001; Revised 2 July 2001; In final form 1 November 2001)

The crystal of pentaqua (*catena*-pyridine-3,5-dicarboxylato-O,O) calcium(II) contain zigzag molecular chains composed of Ca ions linked by two bridging oxygen atoms, each donated by one carboxylate group [Ca–O1 2.353(2) Å, Ca–O3^{III} 2.334(1) Å]. The Ca ions, the ligand molecules and one water oxygen atom coordinated by each metal ion [Ca–O5 2.410(2) Å] are coplanar. The coordination of the Ca ion is completed by four other water oxygen atoms situated above and below the plane of the chain [Ca–O6 2.475(1) Å, Ca–O7 2.371(2) Å]. The coordination number of the calcium(II) ion is seven. The water molecules act as donors in a system of hydrogen bonds.

Keywords: Calcium complexes; Pyridine-3,5-dicarboxylic acid; X-ray structure analysis

INTRODUCTION

Coordination compounds exhibiting different molecular patterns are formed by the calcium(II) ion and the dipicolinate (pyridine-2,6-discarboxylate) ligand [1–3]. Since the dinicotinate (pyridine-3,5-dicarboxylate or 3,5-PDDC) ligand has the same geometrical shape, we decided to investigate whether calcium also forms more than one complex with the dinicotinate ligand. Dimeric molecules have been detected in the crystals of a complex with the composition $Ca_2(3,5\text{-PDDC})_2(H_2O)_{10} \cdot 2H_2O$ [4]. We report in this paper the results of an X-ray crystal structure study of a new calcium dinicotinate complex which we have obtained while testing the reactions of dinicotinic acid with a number of different calcium(II) compounds.

EXPERIMENTAL

The title compound (compound 2) was obtained by mixing 1 mmol of calcium nitrate tetrahydrate dissolved in 20 mL of hot water with 100 mL of boiling aqueous solution

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ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/0095897021000009947

containing *ca.* 1 mmol of pyridine-3,5-dicarboxylic acid (Aldrich). The mixture was stirred and boiled for 1 h. Fairly large, well-formed, colorless, rectangular plate-like single crystals deposited in the mother liquid. They were identified as crystals of the compound, whose crystal structure is described in [4] (compound 1). However, in one experiment, we came across two kinds of single crystals: rectangular plates identified by X-ray analysis as crystals of compound 1 and elongated pillars being the crystals of the title compound. The dimensions of the crystal used for X-ray diffraction data collection are given in Table I.

X-ray reflections were measured at room temperature using a 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. Nonhydrogen ions were located by the direct method using the SHELXLS program [5] and hydrogen atoms then found by successive Fourier syntheses. Final refinement on F^2 by least

TABLE I Crystal data and structure refinement details for Ca(3,5-PDDC)(H_2O)$_5$

Empirical formula	$C_7H_{13}N_1O_9Ca$
Formula weight	305.0
Temperature	293K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	Pnma
Unit cell dimensions	$a = 15.451(3)$ Å $b = 7.086(1)$ Å $c = 11.000(2)$ Å $V = 1204.34$ Å^3
Z	4
Calculated density	1.628 g cm^{-3}
μ (Mokα)	056 mm^{-1}
F(000)	616.0
Crystal size	$0.1 \times 0.3 \times 0.4$ mm^3
Max 2θ for data collection	64.01°
Index range	$0 \leq h \leq 22$ $0 \leq k \leq 10$, $0 \leq l \leq 16$.
No. of measured reflections	1706
No. of reflection with $F_o > 4\sigma(F_o)$	1446
R_{int}	0.0665
Method of structure solution	direct method
Method of structure refinement	full-matrix least squares on F^2
No. of parameters refined	135
Goodness-of-fit on F^2	1.053
Final R1 [$F_o > 4\sigma(F_o)$]	0.0391
Final wR2 index	0.0966
Absorption correction	ψ-scan
Min. and max. transmission factors	0.614, 0.689
Largest diff. peak and hole	0.64 e/Å^3 and −0.64 e/Å^3
Weight parameters (A, B)	0.0700, 0.00
Mean shift/esd	0.014

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 $P = [\max(F_o^2, 0) + 2F_c^2]/3$, with A and B refined parameters listed in Table I. Calculations were carried out using the SHELXL97 program [6]. Selected bond lengths and angles are collected in Table II. Listings of the observed and calculated structure factors and anisotropic thermal parameters can be obtained on request from the authors.

TABLE II Selected bond lengths [Å] and angles [°] for Ca(3,5-PDDC)(H_2O)$_5$

Ca ion coordination					
Ca–O1	2.353(2)	O1–Ca–O3^{III}	141.30(5)		
Ca–O3^{III}	2.334(1)	O1–Ca–O5	73.84(6)		
Ca–O5	2.410(2)	O1–Ca–O3^{III}	141.30(5)		
Ca–O6	2.475(1)	O6–Ca–O6^{II}	95.09(7)		
Ca–O6^{II}	2.475(1)	O6–Ca–O7	82.13(6)		
Ca–O7	2.371(2)	O1–Ca–O6	69.74(4)		
Ca–O7^{II}	2.371(2)	O1–Ca–O7	124.87(4)		
		O5–Ca–O6	117.40(4)		
		O5–Ca–O7	79.21(5)		
		O3^{III}–Ca–O6	84.72(4)		
		O3^{III}–Ca–O7	77.26(4)		
Water molecules					
O5–H51	0.73(4)	H51–O5–H52	85(4)		
O5–H52	0.94(5)				
O6–H61	0.86(3)	H61–O6–H62	109(3)		
O6–H62	0.78(3)				
O7–H71	0.80(3)	H71–O7–H72	114(3)		
O7–H72	0.83(3)				
Dinicotinate ligand					
N–C2	1.344(3)	C6–N–C2	117.6(2)		
C2–C3	1.388(3)	N–C2–C3	123.7(2)		
C3–C4	1.390(3)	C2–C3–C4	118.2(2)		
C4–C5	1.395(3)	C3–C4–C5	119.7(2)		
C5–C6	1.393(3)	C4–C5–C6	117.7(2)		
C6–N	1.346(3)	C5–C6–N	123.4(2)		
C3–C7	1.508(2)				
C7–O1	1.242(2)	O1–C7–O2	124.9(2)		
C7–O2	1.263(2)				
C5–C8	1.512(2)				
C8–O3	1.240(2)	O3–C8–O4	124.7(2)		
C8–O4	1.265(2)				
Hydrogen bonds					
O5–H51…O4^{IV}	2.854(2)	H51…O4^{IV}	2.14(4)	O5–H51…O4^{IV}	168(4)
O5–H52…O2	2.787(3)	H52…O2	1.94(4)	O5–H52…O2	149(4)
O6–H61…O4^{V}	2.906(2)	H61…O4^{V}	2.05(3)	O6–H61…O4^{V}	171(3)
O6–H62…N^{VII}	2.948(2)	H62…N^{VII}	2.19(3)	O6–H62…N^{VII}	163(3)
O7–H71…O2^{VI}	2.700(2)	H71…O2^{VI}	1.93(3)	O7–H71…O2^{VI}	160(3)
O7–H72…O6^{VII}	2.902(2)	H72…O6^{VI}	2.08(3)	O7–H72…O6^{VI}	172(3)

Symmetry transformations used to generate equivalent atoms:
$^{I}x-\frac{1}{2}, y, -z+\frac{3}{2}$; $^{II}x, -y+\frac{1}{2}, z$; $^{III}x+\frac{1}{2}, y-z+\frac{3}{2}$; $^{IV}x, y, z+1$; $^{V}-x, -y, -z+1$; $^{VI}-x, -y, -z+2$; $^{VII}-x+\frac{1}{2}, -y, z+\frac{1}{2}$.

DISCUSSION

The title compound [pentaquo(*catena*-pyridine-3,5-dicarboxylato-O,O′)calcium(II)] contains zigzag molecular chains composed of Ca(II) ions bridged by the ligand molecules *via* their carboxylate oxygen atoms acting as monodentate ligands. The coordination around the Ca(II) ion includes five water molecules. Fig. 1 shows fragments of two adjacent chains with the atom numbering scheme projected on the plane of the layer; Fig. 2 illustrates, how the chains are packed in the crystal. The Ca(II) ion, the ligand molecule and one water oxygen atom (O5) are coplanar: four oxygen atoms (O6, $O6^I$ O7 and $O7^I$) are situated outside the plane of the chain and form the base of a bipyramid. The atoms which constitute the base are not coplanar: the shifts from the average plane are $+0.078$ Å for the O7 and $O7^I$ atoms, $+0.074$ Å for the O6 and $O6^I$ atoms and -0.304 Å for the Ca atom. The bridging O^{III} oxygen atom lies on the apex on one side of the basal plane, the water oxygen atom O5 and the bridging oxygen atom O1 form a double apex on the other side. The above atoms are coplanar. The second carboxylate atoms of the ligand molecule do not participate in coordinating the metal ion. Selected Ca–O bond distances and angles

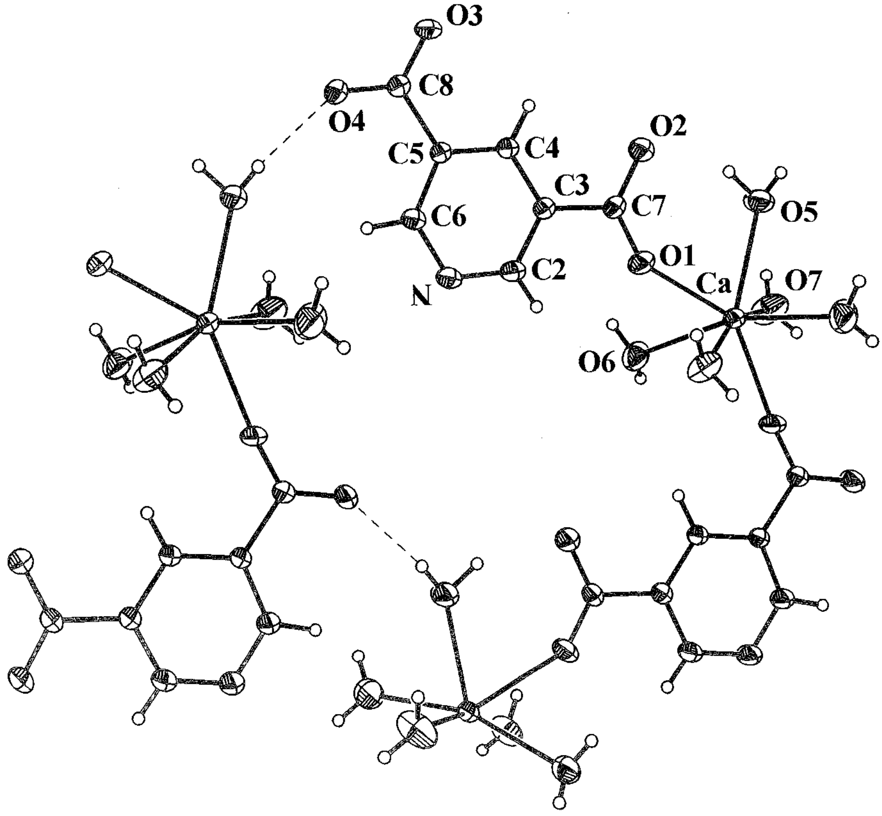

FIGURE 1 Fragments of two neighboring, coplanar molecular chains in the structure of Ca(3,5-PDDC)(H_2O)$_5$ with numbering of atoms. The nonhydrogen atoms are shown as 50% probability ellipsoids. Broken lines indicate the hydrogen bonds operating between the chains situated on the same plane.

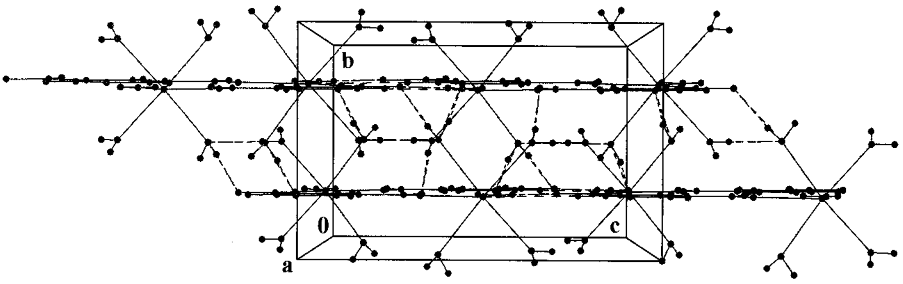

FIGURE 2 The packing of molecular chains in the crystal of Ca(3,5-PDDC)$(H_2O)_5$. Hydrogen bonds operating between two chains situated on neighboring planes are marked by broken lines.

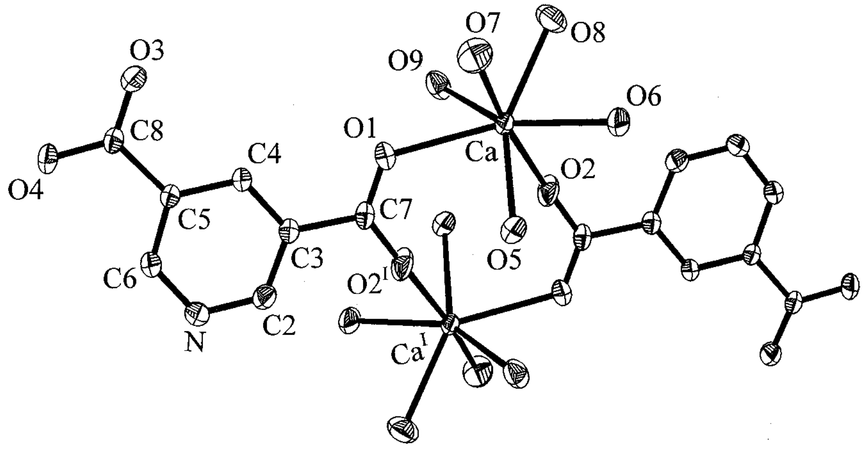

FIGURE 3 The dimeric molecule of Ca_2(3,5-PDDC)$_2$$(H_2O)_{10}$ (compound 1) after [4].

are listed in Table II. The bond distances and angles observed within the ligand molecule are in fair agreement with those reported for the parent acid [7].

All water molecules act as donors in a system of hydrogen bonds which links them with the carboxylate oxygen atoms (O2, O4) which do not participate in bridging the metal ions. These acceptor oxygen atoms belong either to the same coordination moiety (O5–H52$\cdots$O2) or to the adjacent molecular chains: O5–H51$\cdots$O4^{III}, O6–H61$\cdots$O4^{V}, O7–H71$\cdots$O2^{VI}. A hydrogen bond linking the water molecule O6 with the heteroring nitrogen atom N^{VII} of the ligand molecule in the neighboring chain is also observed. The respective bond length and the O–H–O angles are listed in Table II.

The calcium dinicotinate (compound 1) described in [4] and the compound constitute a pair of polymorphic compounds with the formula unit Ca(3,5-PDDC)$(H_2O)_5$. In both compounds each Ca(II) ion is coordinated by two bridging carboxylate oxygen atoms and five water oxygen atoms, however, the shapes of the coordination polyhedra are different: a distorted pentagonal bipyramid in compound 1 and a distorted bipyramid with a rectangular base and one apex on one side of the base and two apices on the other in the title compound. For comparison, the molecule of compound 1 is shown in Fig. 3.

The Ca–O bond distances observed in both compounds fall in the same range, characteristic for a large number of calcium complexes with carboxylate ligands [8].

The transformation from discrete dimeric molecules in compound 1 to the linear molecular pattern detected in the title compound proceeds by engaging an oxygen of each ‘‘free’’ carboxylate group of the ligand molecules in bridging the Ca(II) ions, resulting in ‘‘opening’’ of the dimer and formation of zigzag molecular chains, in which the Ca(II) ions, the ligand molecules and one water oxygen atom per each Ca ion are strictly coplanar. This transformation is accompanied by a drastic change in the shape of the Ca(II) coordination polyhedron although the number of coordinated oxygen atoms remains unaltered and amounts to seven in each compound.

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