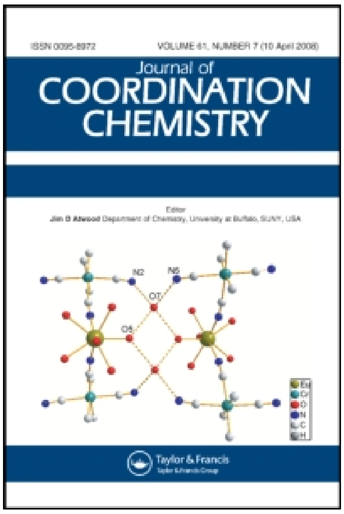

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Dimeric Molecules in the Crystals of a Calcium(II) Complex with Pyridine-2,6-Dicarboxylate and Water Ligands

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

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DIMERIC MOLECULES IN THE CRYSTALS OF A CALCIUM(II) COMPLEX WITH PYRIDINE-2,6-DICARBOXYLATE AND WATER LIGANDS

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

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

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The crystals of bis[μ-pyridine-2,6-dicarboxylato-O,N,O′)]bis[trisaqua-calcium(II)] di(pyridine-2,6-dicarboxylic acid) contain dimeric molecules composed of two calcium(II) ions and two ligand molecules. Calcium ions are bridged by two bidentate oxygen atoms each donated by one carboxylic group of the ligand [Ca—O 2.438(2) Å; Ca—O 2.409(2) Å]. Apart from the two bridging oxygen atoms, the coordination around each Ca(II) ion is composed of the heteroring nitrogen atom [Ca—N 2.467(2) Å], a monodentate oxygen atom of the second carboxylate group of the ligand [Ca—O 2.484(2) Å] and three oxygen atoms donated by the water molecules [mean Ca—O 2.388(2) Å]. The coordination polyhedron is a distorted pentagonal bipyramid. Acid molecules were found to be located in the space between the dimers and involved in an extended network of hydrogen bonds.

Keywords: Pyridine-2,6-dicarboxylic acid; Calcium complex; X-ray diffraction

INTRODUCTION

Two calcium complexes with pyridine-2,6-dicarboxylate (2,6-PDDC or dipicolinate) ligands have been reported. The crystal structure of one of them denoted by the authors as "calcium dipicolinate trihydrate" has been published. Only possible space group and lattice parameters have been given

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*Corresponding author. Tel.: 4822 811 1313, Fax: 4822 811 1532, e-mail: jlec@orange.ichtj.waw.pl

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for the second complex called "calcium dipicolinate sesquihydrate" [1]. In the course of our systematic X-ray diffraction structural studies of calcium complexes with pyridine dicarboxylate ligands we have obtained single crystals of a number of calcium dipicolinates. The crystal structure of one of them is described in this paper.

EXPERIMENTAL

The title compound (code name CADIP 1) was obtained by mixing 1 mmol of calcium nitrate tetrahydrate dissolved in 20 mL of hot water with 100 ml of boiling aqueous solution containing ca. 4 millimols of pyridine-2,6-dicarboxylic acid (ALDRICH). The mixture was stirred and boiled for one hour. After a week two kinds of colorless single crystals

TABLE I Crystal data and structure refinement details for $Ca_2(2,6\text{-PDDC})_2(H_2O)_6 \cdot 2(2,6\text{-}H_2PDDC)$

Code name	CADIP 1
Empirical formula	$C_{56}H_{56}N_8O_{44}Ca_4$
Formula weight	1705.41
Temperature	293K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 9.307(2) Å b = 14.880(3) Å c = 12.265(3) Å $\beta = 97.24(3)°$ V = 1685.01 $Å^3$
Z	4
Calculated density	1.681 gcm^{-3}
μ (MoKα)	0.44 mm^{-1}
F(000)	880.0
Crystal size	$0.2 \times 0.2 \times 0.4\,mm^3$
Max 2θ for data collection	56.05°
Index range	$-12 \le h \le 12,\ -19 \le k \le 19,\ 0 \le 1 \le 16$
No. of measured reflections	5962
No. of unique reflections with $F_o > 4\sigma(F_o)$	2698
R_{int}	0.0364
Method of structure solution	direct method
Method of structure refinement	full-matrix least squares on F^2
No. of parameters refined	310
Goodness-of-fit on F^2	1.115
Final Rl $[F_o > 4\sigma(F_o)]$	0.0407
Final wR2 index	0.1082
Absorption correction	Ψ-scan
Min. and max. transmission factors	0.205, 0.293
Largest diff. peak and hole	0.46 e/ $Å^3$ and -0.58 e/ $Å^3$
Weight parameters (A,B)	0.0709, 0.00
Mean shift/esd	0.013

were found in the mother liquid. One was identified as pyridine-2,6-dicarboxylic acid [2], the other as CADIP 1. Well-formed, fairly large crystals of CADIP 1 deposited also in the mother liquid, when anhydrous calcium chloride and an excess of 2,6-H_2PDDC were used as reagents. The dimensions of the crystal used for X-ray diffraction data collection are given in Table I.

TABLE II Fractional atomic coordinates and equivalent isotropic displacement (Å^2) for $Ca_2(2,6\text{-PDDC})_2(H_2O)_6 \cdot 2(2,6\text{-}H_2\ \text{PDDC})$

	x	y	z	U_{eq}
Ca	0.41150(5)	0.08050(3)	0.09747(4)	0.0273(1)
N1	0.5176(2)	0.2268(1)	0.0572(1)	0.0243(4)
C12	0.6011(2)	0.2326(1)	−0.0237(2)	0.0255(4)
C13	0.6579(3)	0.3138(1)	−0.0544(2)	0.0330(5)
C14	0.6284(3)	0.3907(2)	0.0017(2)	0.0389(6)
C15	0.5426(3)	0.3850(1)	0.0858(2)	0.0341(5)
C16	0.4886(2)	0.3016(1)	0.1113(2)	0.0261(4)
C17	0.6306(2)	0.1448(1)	−0.0793(2)	0.0257(4)
C18	0.3921(2)	0.2882(1)	0.2008(2)	0.0265(4)
O11	0.5779(2)	0.0742(1)	−0.0408(1)	0.0294(3)
O12	0.7038(2)	0.1483(1)	−0.1565(1)	0.0386(4)
O13	0.3588(2)	0.3539(1)	0.2544(1)	0.0355(4)
O14	0.3504(2)	0.2079(1)	0.2141(1)	0.0331(4)
O15	0.2414(2)	0.0216(1)	0.2012(2)	0.0447(5)
O16	0.2113(2)	0.0952(1)	−0.0551(2)	0.0359(4)
O17	0.6028(2)	0.0343(1)	0.2308(2)	0.0387(4)
H13	0.717(3)	0.313(2)	−0.106(3)	0.049(8)
H14	0.672(3)	0.445(2)	−0.015(2)	0.036(7)
H15	0.529(3)	0.436(2)	0.123(2)	0.034(7)
H51	0.208(5)	0.032(3)	0.248(4)	0.09(2)
H52	0.248(3)	−0.036(2)	0.199(3)	0.056(9)
H61	0.157(4)	0.127(3)	−0.034(3)	0.065(1)
H62	0.246(4)	0.109(2)	−0.098(3)	0.06(1)
H71	0.685(4)	0.058(2)	0.229(3)	0.052(9)
H72	0.607(4)	−0.019(3)	0.232(8)	0.06(1)
N2	0.0445(2)	0.2391(1)	0.0352(2)	0.0281(4)
C22	0.0843(2)	0.3252(1)	0.0226(2)	0.0292(5)
C23	0.0539(3)	0.3941(2)	0.0932(2)	0.0371(5)
C24	−0.0173(3)	0.3739(2)	0.1815(2)	0.0414(6)
C25	−0.0587(3)	0.2863(2)	0.1964(2)	0.0391(6)
C26	−0.0268(2)	0.2217(2)	0.1212(2)	0.0302(5)
C27	0.1652(3)	0.3477(2)	−0.0719(2)	0.0304(5)
C28	−0.0770(3)	0.1268(2)	0.13659(2)	0.0351(5)
O21	0.1987(2)	0.2789(1)	−0.1281(2)	0.0447(5)
O22	0.1964(3)	0.4248(1)	−0.0903(2)	0.0540(6)
O23	−0.0718(2)	0.0743(1)	0.0516(2)	0.0426(4)
O24	−0.1214(2)	0.1032(1)	0.2215(2)	0.0536(5)
H21	0.254(4)	0.287(3)	−0.186(3)	0.09(1)
H23	0.090(4)	0.454(2)	0.072(3)	0.06(1)
H24	−0.035(4)	0.418(2)	0.230(3)	0.06(1)
H25	−0.105(3)	0.273(2)	0.252(2)	0.037(7)
H231	−0.100(4)	0.025(3)	0.067(3)	0.07(1)

TABLE III Bond lengths (Å) and angles (°) for $Ca_2(2,6\text{-PDDC})_2(H_2O)_6 \cdot 2(2,6\text{-}H_2PDDC)$

Calcium(II) coordination:			
Ca—N1	2.467(2)	N1—Ca—O11	65.75(5)
Ca—O11	2.438(2)	O11—Ca—O11^{I}	73.12(5)
Ca—O11^{I}	2.409(2)	O11^{I}—Ca—O15	81.55(6)
Ca—O14	2.484(2)	O15—Ca—O14	75.60(6)
Ca—O15	2.324(2)	O14—Ca—N1	64.42(5)
Ca—O16	2.479(2)	O16—Ca—N1	93.04(6)
Ca—O17	2.362(2)	O17—Ca—N1	96.30(7)
		O16—Ca—O17	167.81(6)
2,6-*PDDC ligand*:			
N1—C12	1.338(3)	N1—C12—C13	122.2(2)
C12—C13	1.390(3)	C12—C13—C14	118.7(2)
C13—C14	1.380(3)	C13—C14—C15	119.4(2)
C14—C15	1.385(3)	C14—C15—C16	118.7(2)
C15—C16	1.389(3)	C15—C16—N1	121.9(2)
C16—N1	1.341(3)	C16—N1—C12	119.1(2)
C12—C17	1.514(3)		
C17—O11	1.276(2)	O11—C17—O12	126.4(2)
C17—O12	1.235(3)		
C16—C18	1.517(3)		
C18—O13	1.239(3)	O13—C18—O14	124.9(2)
C18—O14	1.273(3)		
Coordinated water molecules:			
O15—H51	0.71(4)	H51—O15—H52	106(4)
O15—H52	0.86(4)		
O16—H61	0.76(4)	H61—O16—H62	119(4)
O16—H62	0.68(4)		
O17—H71	0.84(4)	H71—O17—H72	112(3)
O17—H72	0.81(4)		
2,6-H_2 *PDDC acid molecule*:			
N2—C22	1.348(3)	N2—C22—C23	123.2(2)
C22—C23	1.394(3)	C22—C23—C24	119.0(2)

C23—C24	1.372(4)			C23—C24—C25	118.9(2)
C24—C25	1.379(4)			C24—C25—C26	118.7(2)
C25—C26	1.390(3)			C25—C26—N2	123.8(2)
C26—N2	1.341(3)			C26—N2—C22	116.4(2)
C22—C27	1.497(3)				
C27—O21	1.294(3)			O21—C27—O22	124.8(2)
C27—O22	1.211(3)				
O21—H21	0.93(4)				
C26—C28	1.506(3)				
C28—O23	1.307(3)			O23—C28—O24	124.0(2)
C28—O24	1.221(3)				
O23—H231	0.81(4)				
Intermolecular hydrogen bonds:					
O16—H62…O13^{II}	2.955(3)	H62…O13^{II}	2.28(4)	O16—H62—O13^{II}	176(4)
O17—H72…O13^{V}	2.712(3)	H72…O13^{V}	1.92(4)	O17—H72—O13^{V}	172(3)
Hydrogen bonds donated by the acid molecule:					
O21—H21…O13^{II}	2.965(3)	H21…O13^{II}	2.47(4)	O21—H21—O13^{II}	113(3)
O21—H21…O14^{II}	2.543(3)	H21…O14^{II}	1.61(4)	O21—H21—O14^{II}	174(4)
O23—H231—O16^{VII}	2.839(3)	H231…O16^{VII}	2.07(4)	O23—H231—O16^{VII}	161(4)
Hydrogen bonds accepted by the acid molecule:					
O15—H51…O22^{III}	2.761(3)	H51…O22^{III}	2.10(5)	O15—H51—O22^{III}	157(5)
O16—H61…O21	2.875(3)	H61…O21	2.60(4)	O16—H61—O21	104(3)
O16—H61…N2	2.942(3)	H61…N2	2.20(4)	O16—H61—N2	166(4)
O17—H71…O24^{IV}	2.780(3)	H71…O24^{IV}	1.94(4)	O17—H71—O24^{IV}	176(3)
Intramolecular hydrogen bonds:					
O15—H52…O12^{I}	2.649(3)	H52…O12^{I}	1.82(4)	O15—H52—O12^{I}	160(3)
C13—H13…O12	2.820(3)	H13…O12	2.52(3)	C13—H13—O12	100(2)
C23—H23…O22	2.790(3)	H23…O22	2.38(3)	C23—H23—O22	104(2)

Symmetry code used to generate equivalent positions: ^{I} −x + 1, −y, −z; ^{II} x, 1/2 − y, −1/2 + z; ^{III} x, 1/2 − y, 1/2 + z; ^{IV} 1 + x, y, z; ^{V} 1 − x, 1/2 + y, 1/2 − z; ^{VI} 1 − x, 1 − y, −z; ^{VII} −x, −y, −z; ^{VIII} −1 + x, 1/2 − y, 1/2 + z.

X-ray reflections were measured at room temperature using a KUMA KM4 (MoK_α 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 ($15° < 2\theta < 30°$). 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 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: $w = 1/[\sigma^2(F_o^2) + (A^*P)^2 + B^*P]$ where $P = [\max(F_o^2, 0) + 2F_c^2]/3$. A and B are refined parameters listed in Table I. Calculations were carried out using the SHELXL97 Program [4]. 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.

DISCUSSION

The crystals of CADIP 1 contain dimeric molecules consisting of two calcium(II) ions, two ligand molecules and six water molecules. The calcium ions are bridged by two oxygen atoms each donated by a different ligand molecule [Ca—O11 2.438(2) Å; Ca—O11^{I} 2.409(2) Å]. The bridging oxygen atom belongs to one carboxylic group of the ligand and is bidentate. The second oxygen atom of this group does not coordinate the metal ion. Apart from the two bridging oxygen atoms, the calcium ion is coordinated by an oxygen atom donated by the second carboxylic group of the ligand molecule [Ca—O14 2.484(2) Å], the heteroring nitrogen atom [Ca—N1 2.467(2) Å] and three oxygen atoms of water molecules [Ca—O15 2.324(2) Å; Ca—O16 2.479(2) Å; Ca—O17 2.362(2) Å]. The coordination around the metal ion is thus sevenfold – the respective coordination polyhedron is a distorted pentagonal bipyramid. Its equatorial plane is composed of three carboxylate oxygen atoms, the heteroring nitrogen atom and one water oxygen atom. The maximum deviation from the mean plane of 0.126(1) Å is for the oxygen atom O14. Water oxygen atoms O16 and O17 with Ca—O16 and

Ca—O17 bond distances of 2.479(2) and 2.362(2) Å respectively and O16—Ca—O17 angle of 167.81(6)° constitute the vertices of the bipyramid.

Maximum deviation from the mean plane of the ligand molecule is 0.073(1) Å (the bridging oxygen atom O11). The bond distances and angles in the ligand molecule are reasonably close to those reported for the parent acid [2]. A molecule of the dimer with numbering of atoms is displayed in Figure 1. An interesting feature of the structure is the ordered distribution of uncoordinated molecules of the ligand acid in the space between the dimers. This is illustrated in Figure 2. The pyridine ring of the acid molecule is planar: maximum deviation from the mean plane is 0.008(1) Å but the carboxylate oxygen atoms deviate from the mean plane from − 0.349(1) (O23) to + 0.152(1) Å (O24). The observed interatomic distances and angles do not differ from those reported for the pyridine-2,6-dicarboxylic acid [2]. These interstitial acid molecules play an important role in the network of hydrogen bonds in which they act both as donors and acceptors. For example, a fairly short hydrogen bond of 2.543(3) Å links the carboxylate oxygen atom O21 of the acid molecule with the coordinated carboxylate oxygen atom $O14^{II}$ of the adjacent dimer. The other hydrogen bond lengths are in the range from 2.75 to 2.96 Å. These bonds join the acid carboxylate oxygen atoms with the coordinated water molecules of the neighboring

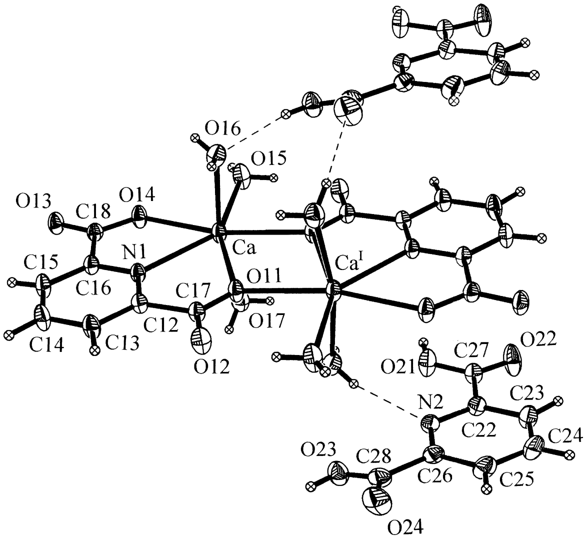

FIGURE 1 The view of the $Ca_2(2,6\text{-PDDC})_2(H_2O)_6$ dimer and two ($2,6\text{-}H_2PDDC$) molecules with atom numbering scheme. Non-hydrogen atoms are shown as 50% probability elipsoids.

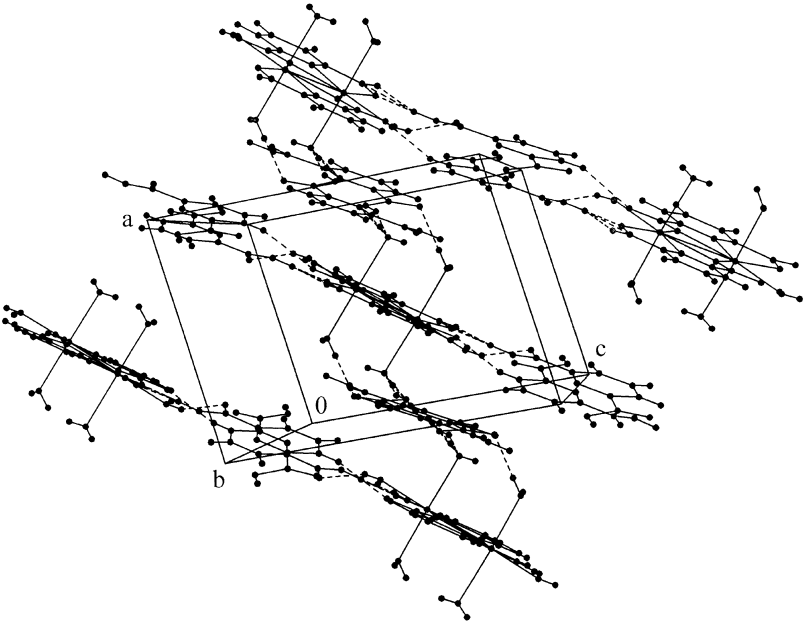

FIGURE 2 The packing diagram of $Ca_2(2,6\text{-PDDC})_2(H_2O)_6 \cdot 2(2,6\text{-}H_2PDDC)$ complex. Broken lines indicate hydrogen bonds.

dimers (see, Tab. III). The water oxygen atoms which constitute the apices of the pentagonal bipyramid around the calcium are interacting with unbonded carboxylate oxygen atoms of the adjacent ligand molecules. Intramolecular hydrogen bonds are also observed in the ligand molecule: one of them operates between the coordinated oxygen atom O15 of the water molecule and the unbonded carboxylate oxygen atom $O12^{I}$, the other one links the heteroring carbon atom C13 with the unbonded carboxylate oxygen atom O12. An intramolecular hydrogen bond (C23—H23…O22) of 2.790(3) Å is also observed in the acid molecule.

The bridging mode of two Ca(II) ions in the dimer of the title compound is the same as detected in the dimer of "calcium dipicolinate trihydrate" [1] however, the molecular patterns observed in the crystals of both compounds are entirely different. In the "calcium dipicolinate trihydrate" structure calcium ions in adjacent dimers are bridged by two water oxygen atoms forming molecular pillars. A fragment of this pillar is shown in Figure 3. Each calcium ion is coordinated by eight atoms: three oxygen atoms donated by carboxylate groups, a hetero-ring nitrogen atom and four water oxygen atoms, giving rise to a coordination polyhedron consisting of a

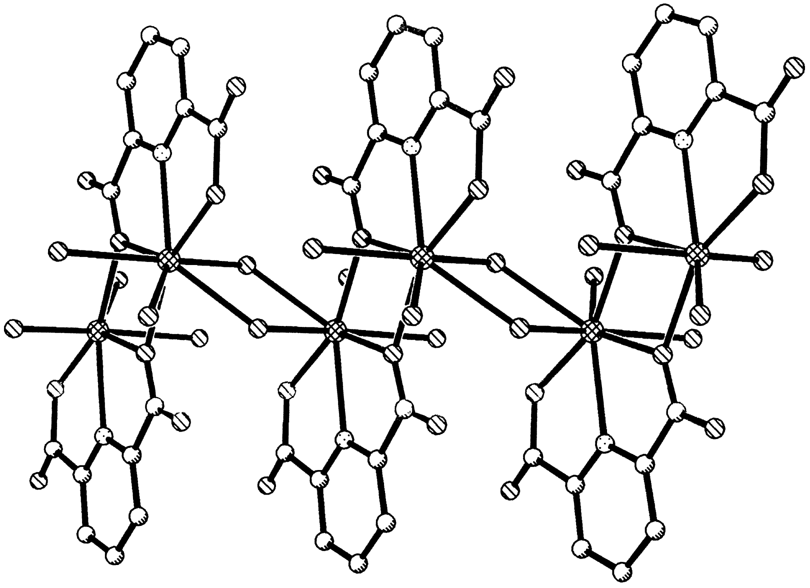

FIGURE 3 A fragment of the molecular pattern of "calcium dipicolinate trihydrate" drawn using atomic coordinates reported in Ref. [1]. Squared circles indicate calcium ions. For clarity, hydrogen atoms are not shown.

pentagonal equatorial plane, two apices represented by the bridging water oxygen atoms on one side of the pentagon and a single water oxygen atom forming the apex on the other side. The accomodation of fairly large flat molecules of the ligand acid in the crystal space of the title compound, apart from increasing the cell volume by ca. 65%, brings about the break of bridging the calcium ions belonging to neighbouring dimers, resulting in reduction of their coordination from eight to seven atoms.

In the title compound the observed calcium carboxylate interaction modes, Ca(II) coordination scheme and the range of Ca—$O_{carboxylate}$ bond lengths agree well with those most commonly encountered in Ca(II) complexes with carboxylate ligands [5].

Dimeric molecules with two calcium(II) ions bridged by carboxylate oxygen atoms have also been found in the crystals of the Ca(II) complex with pyridine-3,5-dicarboxylate (dinicotinate) ligand, which has the same geometrical shape and dimensions as the dipicolinate ligand. However, in the dinicotinate complex oxygen atoms belong to only one carboxylate group of the ligand and the hetero-ring nitrogen atom does not participate in coordination. Like in the title compound, the coordination around Ca(II) ion is sevenfold [6].

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