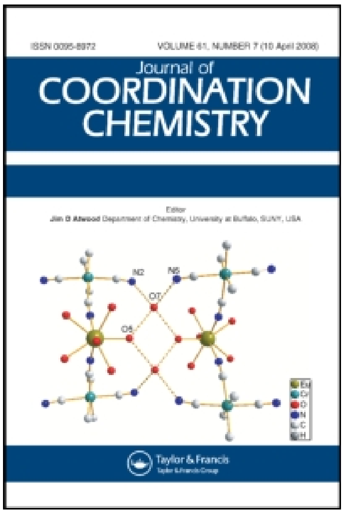

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W. Starosta[a]; H. Ptasiewicz-BĄk[a]; J. Leciejewicz[a]
[a] Institute of Nuclear Chemistry and Technology, Warszawa, Poland

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THE CRYSTAL STRUCTURE OF AN IONIC CALCIUM COMPLEX WITH PYRIDINE-3,5-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 [hexaquacalcium(μ-hydrogen pyridine-3,5-dicarboxylate-*O*,*O*′)] [triaquacalcium (hydrogen pyridine-3,5-dicarboxylate-*O*,*O*)(hydrogen pyridine-3,5-dicarboxylate-*O*)] (hydrogen pyridine-3,5-dicarboxylate) dihydrate are triclinic, space group $P\bar{1}$. They contain unipositive cations formed by two calcium(II) ions bridged by oxygen atoms belonging to two carboxylic groups of a ligand molecule forming a dimer. One calcium atom, apart from the bridging carboxylate atom, coordinates six water oxygen atoms. The second calcium atom in the dimer coordinates the bridging oxygen atoms, two oxygen atoms donated by one carboxylate group of a second ligand, one oxygen atom from a carboxylate group of a third ligand and three water oxygen atoms. The univalent anion is represented by a ligand molecule with one hydrogen atom attached to the hetero ring nitrogen atom. An extended network of hydrogen bonds is observed.

Keywords: Calcium complexes; Pyridine-3,5-dicarboxylate ligands; X-ray diffraction crystal structure analysis

INTRODUCTION

The crystal structures of two calcium(II) complexes with pyridine-3,5-dicarboxylate (dinicotinate) and water ligands have been recently reported [1,2]. Both were obtained by reacting the dinicotinic acid with calcium nitrate tetrahydrate. While testing the products of reactions of this acid with different calcium compounds we have synthesized and grown single crystals of a new complex. Its crystal structure was determined by X-ray diffraction and is described in this article.

EXPERIMENTAL

The title compound was obtained by adding 100 mL of hot aqueous solution of 1 mmol of pyridine-3,5-dicarboxylic acid (Aldrich) to 1 mmol of CaO (Aldrich). After dissolving all CaO, the solution was boiled for 1 h. Colorless single crystals in the form of elongated plates deposited in the mass of unidentified polycrystalline material

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*Corresponding author: Tel.: 48228111313. Fax: 48228111917. E-mail: jlec@orange.ichtj.waw.pl

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after evaporation to dryness at room temperature. The dimensions of the crystal selected for collection of the X-ray diffraction data are shown in Table I.

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 ($20^\circ < 2\theta < 30^\circ$). Reflections were processed using profile analysis and corrected for Lorentz factor and polarization effects. Nonhydrogen ions were located by direct methods using SHELXLS [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 nonH-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 $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$. A and B parameters are listed in Table I. Calculations were carried out using the SHELXL97 program [4]. Selected bond lengths and angles are collected in Table II. Lists of the atomic coordinates, anisotropic thermal parameters and the observed and calculated structure factors are available upon request from the authors.

TABLE I Crystal data and structure refinement details for $\{Ca_2[H(3,5\text{-}PDDC)]_3(H_2O)_9\}^{+1}\ [H(3,5\text{-}PDDC)]^{-1} \cdot 2H_2O$

Empirical formula	$C_{28}H_{37}N_4O_{27}Ca_2$
Formula weight	942.78
Temperature	293 K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 11.232(2)$ Å $b = 11.425(2)$ Å $c = 16.317(3)$ Å $\alpha = 104.17(3)^\circ$ $\beta = 102.10(3)^\circ$ $\gamma = 98.86(3)^\circ$ $V = 1937.95$ Å^3
Z	2
Calculated density	1.616 g cm^{-3}
μ (MoK_α)	0.40 mm^{-1}
$F(000)$	980.0
Crystal size	$0.1 \times 0.3 \times 0.4$ mm^3
Max 2θ for data collection	60.05°
Index range	$-15 \le h \le 0$ $-14 \le k \le 15$ $-20 \le l \le 21$
No. of measured reflections	7043
No. of reflections with $F_o > 4\sigma(F_o)$	5575
R_{int}	0.0195
Method of structure solution	Direct method
Method of structure refinement	Full-matrix least squares on F^2
No. of parameters refined	665
Goodness-of-fit on F^2	1.083
Final $R1$ [$F_o > 4\sigma(F_o)$]	0.0415
Final $wR2$ index	0.1225
Largest diff. peak and hole	0.56 and -0.44 e/Å^3
Weight parameters (A, B)	0.0876, 0.000
Mean shift/esd	0.035

TABLE II Selected bond distances (in Å) and angles (in^0) for $\{Ca_2[H(3,5\text{-}PDDC)]_3(H_2O)_9\}^{+1}$ $[H(3,5\text{-}PDDC)]^{-1} \cdot 2H_2O$

Calcium(II) atom coordination			
Cal–O11	2.299(2)	O11–Cal–O3	157.36(10)
Cal–O1	2.378(3)	O11–Cal–O5	80.77(9)
Cal–O2	2.444(3)	O5–Cal–O3	77.9(1)
Cal–O3	2.358(3)	O11–Cal–O2	124.5(1)
Cal–O4	2.382(3)	O11–Cal–O6	78.5(1)
Cal–O5	2.469(3)	O3–Cal–O2	72.0(1)
Cal–O6	2.503(3)	O3–Cal–O6	123.8(2)
Ca2–O13	2.352(2)	O13–Ca2–O9	174.04(7)
Ca2–O7	2.401(2)	O21–Ca2–O13	85.48(7)
Ca2–O8	2.390(2)	O21–Ca2–O9	88.71(8)
Ca2–O9	2.366(2)	O9–Ca2–O7	85.60(8)
Ca2–O21	2.507(2)	O9–Ca2–O8	97.8(1)
Ca2–O22	2.514(2)	O13–Ca2–O7	100.32(8)
Ca2–O31	2.316(2)	O13–Ca2–O8	84.87(9)
The PD1 ligand			
C12–C13	1.378(3)	N1–C12–C13	119.86(22)
C13–C14	1.386(3)	C12–C13–C14	118.82(22)
C14–C15	1.393(3)	C13–C14–C15	120.36(21)
C15–C16	1.384(3)	C14–C15–C16	118.49(21)
C16–N1	1.339(3)	C15–C16–N1	120.02(22)
N1–C12	1.351(3)	C16–N1–C12	122.36(21)
N1–H11	0.86(4)		
C13–C17	1.516(3)		
C17–O11	1.234(3)	O11–C17–O12	125.75(25)
C17–O12	1.245(4)		
C15–C18	1.512(3)		
C18–O13	1.250(3)	O13–C18–O14	126.43(22)
C18–O14	1.254(3)		
The PD2 ligand			
C22–C23	1.385(4)	N2–C22–C23	124.08(24)
C23–C24	1.387(3)	C22–C23–C24	117.95(22)
C24–C25	1.395(4)	C23–C24–C25	118.99(23)
C25–C26	1.392(4)	C24–C25–C26	118.44(22)
C26–N2	1.334(4)	C25–C26–N2	123.30(23)
N2–C22	1.345(4)	C26–N2–C22	117.18(23)
C23–C27	1.515(4)		
C27–O21	1.257(3)	O21–C27–O22	122.63(23)
C27–O22	1.254(3)		
C25–C28	1.502(3)		
C28–O23	1.307(3)	O23–C28–O24	123.53(24)
O23–H231	0.92(9)		
C28–O24	1.216(3)		
The PD3 ligand			
C32–C33	1.394(3)	N3–C32–C33	121.66(21)
C33–C34	1.389(3)	C32–C33–C34	118.35(20)
C34–C35	1.386(3)	C33–C34–C35	119.87(21)
C35–C36	1.394(3)	C34–C35–C36	118.32(20)
C36–N3	1.336(3)	C35–C36–N3	121.90(21)
N3–C32	1.341(3)	C36–N3–C32	119.90(20)
N3–H31	1.02(4)		
C33–C37	1.516(3)		
C37–O31	1.242(3)	O31–C37–O32	126.29(22)

(*continued*)

TABLE II Continued

The PD3 ligand			
C37–O32	1.252(3)		
C35–C38	1.518(3)		
C38–O33	1.258(3)	O33–C38–O34	126.77(22)
C38–O34	1.240(3)		
The PD4 anion			
C42–C43	1.384(3)	N4–C42–C43	119.75(22)
C43–C44	1.398(3)	C42–C43–C44	119.04(22)
C44–C45	1.393(3)	C43–C44–C45	120.21(21)
C45–C46	1.381(3)	C44–C45–C46	118.00(21)
C46–N4	1.348(3)	C45–C46–N4	120.91(21)
N4–C42	1.342(3)	C46–N4–C42	122.08(21)
N4–H41	0.86(4)		
C43–C47	1.509(3)		
C47–O41	1.217(3)	O41–C47–O42	125.22(24)
C47–O42	1.295(3)		
C45–C48	1.518(3)		
C48–O43	1.246(3)	O43–C48–O44	125.52(23)
Hydrogen bonds			
O4–H204···O32	2.737(3)		
O5–H105···O33	2.977(4)		
O1–H201···O21$^{\mathrm{II}}$	2.864(3)		
O2–H102···O12$^{\mathrm{I}}$	2.773(5)		
O3–H203···O24$^{\mathrm{VI}}$	2.789(4)		
O6–H106···O9$^{\mathrm{III}}$	2.893(5)		
O6–H206···O12$^{\mathrm{I}}$	2.677(5)		
O7–H207···O9$^{\mathrm{III}}$	2.905(3)		
O9–H109···O6$^{\mathrm{III}}$	2.893(5)		
O9–H209···O32$^{\mathrm{III}}$	2.604(3)		
O1–H101···O43$^{\mathrm{II}}$	2.748(3)		
O2–H202···O43$^{\mathrm{II}}$	3.013(4)		
O5–H205···O41$^{\mathrm{II}}$	2.799(4)		
O7–H207···O43$^{\mathrm{III}}$	2.829(3)		
O23–H123···O33$^{\mathrm{VII}}$	2.582(3)		
N1–H11···O34$^{\mathrm{VIII}}$	2.573(3)		
N4–H41···O14$^{\mathrm{IV}}$	2.658(3)		
N3–H31···O42$^{\mathrm{IX}}$	2.570(3)		
O100–H112···O8$^{\mathrm{IV}}$	3.049(6)		
O101–H113···O22$^{\mathrm{IV}}$	2.841(5)		

Symmetric code. I: $-x, -y, -z$; II: $x-1, y, z$; III: $-x+1, -y, -z$; IV: $x, y+1, z$; V: $x, y-1, z$; VI: $x-1, y+1, z$; VII: $x+1, y-1, z$; VIII: $-x+1, -y+1, -z+1$; IX: $-x+2, -y+1, -z+1$.

DISCUSSION

The crystals of the title compound contain unipositive cations composed of two calcium atoms bridged by a ligand molecule and anions represented by the univalently ionized dinicotinic acid. This assembly with the numbering of atoms is shown in Fig.1.

The cation has a remarkable structure: two calcium atoms are bridged by carboxylate oxygen atoms of a ligand molecule, each of them belonging to a different carboxylate moiety. A dimeric unit is formed in this way, however, each of the calcium atoms exhibit a different mode of coordination. Apart from the bridging carboxylate oxygen atom O11, the Ca1 atom coordinates six water oxygen atoms. It is not possible to treat the shape of its coordination polyhedron as a pentagonal bipyramid since its

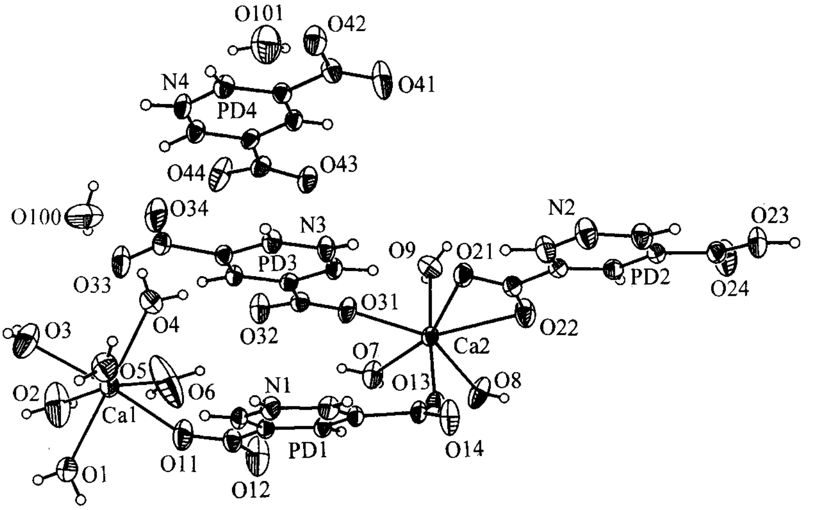

FIGURE 1 The view of the $\{Ca_2[H(3,5\text{-}PDDC)]_3(H_2O)_9\}^{+1}$ cation and the $[H(3,5\text{-}PDDC)]^{-1}$ anion with atom numbering scheme. For clarity, the coordinated ligand molecules are marked by the symbols PD1, PD2, PD3 and the anion by PD4. The nonhydrogen atoms are shown as 50% probability elipsoids.

supposed equatorial plane composed of the Ca1, O1, O2, O4, O5 and O6 atoms is strongly distorted: the maximum deviations from the least squares plane amount to +0.987 (the O2 atom) and −0.916 Å (the O6 atom). Thus, the geometry about Ca1 may only be described as nonspecific seven-coordinate. On the other hand, the Ca2 atom, apart from the bridging carboxylate oxygen atom O13, is coordinated by three water oxygen atoms (O7, O8, O9), two oxygen atoms donated by a bidentate carboxylic group of a ligand molecule (the O21 and O22 atoms) as well as by a carboxylate oxygen atom belonging to the second ligand molecule (the O31 atom). Thus, the coordination number of the Ca2 atom is also seven. Its coordination polyhedron is represented by a pentagonal bipyramid with the equatorial plane composed of the Ca2, O7, O8, O21, O22 and O31 atoms and maximum deviations from the mean plane +0.204 (the O7 atom) and −0.211 Å (the O8 atom). The pyridine rings of all three ligands attached to the calcium atoms are almost coplanar, but the carboxylate oxygen atoms deviate considerably from the respective mean planes. For example, in the bridging ligand molecule the deviations from the mean plane formed by the pyridine ring and the carboxylate carbon atoms are +0.155 Å (the O11 atom), −0.275 Å (the O12 atom), +0.402 Å (the O13 atom) and −0.330 Å (the O14 atom). For the two other ligands the deviations of carboxylate oxygen atoms are also distinct but smaller. The bond distances and angles within the ligand molecules do not deviate from those observed in the parent acid [5] and other calcium dinicotinates [1,2].

A careful inspection of the Fourier maps revealed the positions of the hydrogen atoms attached to the ligand molecules. The bridging ligand molecule as well as the third ligand molecule coordinated by the Ca2 atom appear in the zwitterionic form i.e. one hydrogen atom is bonded to the pyridine (azine) ring nitrogen atom. In the second ligand molecule coordinated to the Ca2 atom via two oxygen atoms belonging to the same carboxylate group (the O21 and O22 atoms), the hydrogen atoms remains bonded to an oxygen atom in the second carboxylate group. Therefore, the charge of the assembly composed of two Ca^{+2} ions and three ligands $[H(3,5\text{-}PDDC)]^{-1}$ is plus one.

The anion in the structure of the title compound is represented by an univalently ionized dinicotinic acid molecule appearing in the zwitterion form. Its charge is minus one. The anion is almost planar: only the O43 and O44 carboxylate oxygen atoms deviate from the mean plane by −0.136 and +0.166 Å respectively.

Figure 2, which shows cation–anion assemblies and their orientation with respect to the unit cell, reveals that the structure of the title compound can be visualized in the form of molecular ribbons, each consisting of two layers: one containing the Ca2 ion and the coordinated ligands PD2 and PD3, the other being composed of the bridging ligand PD1 and the anion PD4. Since the Ca1 ions deviate from both layers, zig-zagged atomic chains composed of the Ca ion can be distinguished. In the crystal, the ribbons are aligned approximately along the [110] direction.

An extended system of hydrogen bonds exists in the structure of the title compound. These bonds, listed in Table II, are tabulated according to their donors. The coordinated water molecules are the most active in forming bonds to the carboxylate oxygen atoms and coordinated water molecules in adjacent cations. For example, the O9 water molecule acts as a donor in two hydrogen bonds to the water oxygen atom $O6^{III}$ and the carboxylate oxygen atom $O32^{III}$, being in turn the acceptor of two hydrogen bonds donated by the coordinated water oxygen atoms O6 and O7. Another example is provided by two water oxygen atoms (O1 and O2) coordinated to the Ca1 atom and one water oxygen atom O7 bonded to Ca2 which act as donors in three hydrogen bonds to the carboxylate oxygen atom O43 of the anion (see Table II).

Intramolecular bonds between two water molecules (O4 and O5) coordinated to Ca1 and the carboxylate oxygen atoms of the ligand molecule chelated to the Ca2 atom (O32 and O33) are also observed.

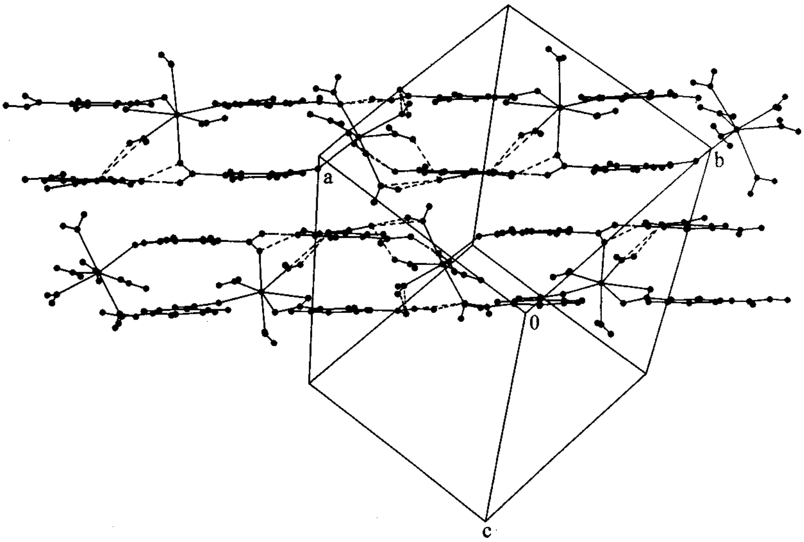

FIGURE 2 A fragment of two molecular ribbons and their alignment in respect to the unit cell in the structure of $\{Ca_2[H(3,5\text{-}PDDC)]_3(H_2O)_9\}^{+1}$ $[H(3,5\text{-}PDDC)]^{-1} \cdot 2H_2O$. For clarity, the solvation water molecules are omitted. Broken lines indicate some of the hydrogen bonds.

The hydrogen atom attached to the carboxylate oxygen atom O23 participates in a bond with the length of 2.579 Å to the carboxylate oxygen atom $O33^{VII}$ in the adjacent cation providing an additional bridging path.

The azine nitrogen atoms and the hydrogen atoms attached to them constitute the donors of three fairly short bonds to carboxylate oxygen atoms in adjacent cations and anions.

The solvation water molecules are the donors of hydrogen bonds either to the coordinated water molecules or carboxylate atoms of the ligand molecules attached to the Ca2 atom.

A distinct tendency to form dimeric molecules, composed of two calcium atoms and two ligand molecules, has been noticed in the structures of calcium complexes with pyridine dicarbxylate ligands. The Ca atoms are bridged by two bidentate oxygen atoms, each donated by one carboxylate group of the ligand molecule. The coordination around each Ca atom is completed by water oxygen atoms [1,6]. However, in two calcium complexes with pyridine-2,6-dicarboxylate ligands the coordinated water molecules bridge the dimers into a polymeric structure [7,8]. The mode of bridging Ca atoms in a dimer detected in the structure of the title compound is different: the bridging oxygen atoms are donated by both carboxylate groups of only one ligand molecule.

Calcium(II) in its complexes with carboxylate ligands exhibits large variation in coordination numbers and in geometry [10]. However, in calcium complexes with pyridine dicarboxylate ligands the coordination number is seven and a more or less distorted pentagonal bipyramid is observed. The only exception is a complex with pyridine-2,6-dicarboxylate, water and nitrate ligands in which the Ca(II) ion shows the coordination number eigth [9]. Since the geometrical shape and dimensions of the pyridine-3,5-dicarboxylate and pyridine-2,6-dicarboxylate ligand molecules are the same, it may be concluded that the stereochemical factor plays a significant role in establishing the observed coordination modes.

The other interesting feature observed in the title compound and other calcium dinicotinates [1,2] is the inactivity of the azine ring nitrogen atom in chelating the metal ion, in contrast to the mode observed in the structures of the complexes with the dipicolinate ligand in which the azine nitrogen atom and the oxygen atoms of the neighboring carboxylate groups act either as bidentate or tridentate bonding moiety [6–9]. This observation supports the conclusion that the chelating activity of the azine nitrogen atom is influenced by its position with respect to the strongly chelating carboxylate group.

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